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Flower-like microparticles and novel superparamagnetic properties of new binary $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ obtained by a rapid solid state route at ambient temperature

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ABSTRACT

A new binary $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ was synthesized by a simple, rapid and cost-effective method using $\text{CoCO}_3\text{--Fe(c--H}_3\text{PO}_4)$ system at ambient temperature. Thermal treatment of the obtained $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ at 600 °C yielded as a binary cobalt iron cyclotetraphosphate $\text{CoFeP}_4\text{O}_{12}$. The FTIR and XRD results of the synthesized $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and its final decomposed product $\text{CoFeP}_4\text{O}_{12}$ indicate the monoclinic phases with space group $P2_1/n$ and $C2/c$, respectively. The particle morphologies of both binary metal compounds appear the flower-like microparticle shapes. Room temperature magnetization results show novel superparamagnetic behaviors of the $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and its final decomposed product $\text{CoFeP}_4\text{O}_{12}$, having no hysteresis loops in the range of $\pm 10,000$ Oe with the specific magnetization values of 0.045 and 12.502 emu/g at 10 kOe, respectively. The dominant physical properties of the obtained binary metal compounds ($\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{CoFeP}_4\text{O}_{12}$) are compared with the single compounds ($\text{M}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{M}_2\text{P}_4\text{O}_{12}$; where M = Co, Fe), indicating the presence of Co ions in substitution position of Fe ions.

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1. Introduction

In recent years, a large number of inorganic natural or synthesized phosphates have the incremented use in order to supply the demands of industrial, commercial, scientific and health sectors due to valuable physical–chemical properties and reactivity [1–4]. The metal phosphate compounds are divided by block unit as PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- , $\text{P}_2\text{O}_7^{4-}$ and $\text{P}_4\text{O}_{12}^{4-}$ units, which have found widespread applications in catalysts and adsorbents, ion-exchange materials, solid electrolytes for batteries, in linear and non-linear optical components, chelating agents, tooth powder and doughs, artificial teeth and bones, corrosion-resistant coating, sewage purifying agents, glass-ceramics, refractories, fire extinguishers, cements, soap powders, biomaterials and implantates, forages for animals, superionic conductors, piezo- and ferroelectrics, gas and moisture sensors, magnets, phosphors, detergents and high-quality fertilizers [5–11]. Synthesis of these materials by solid state reaction

at ambient temperature and the morphology and architecture at microscale and nanoscale levels is a significant challenge, which attracts increased attention because of their conveniences and their strong influence on material properties.

Metal dihydrogenphosphate (H_2PO_4^-) group, one of the important metal phosphates, has found widespread applications according to above mentioned. Additionally, this metal dihydrogenphosphate group is transformed to metal cyclotetraphosphate ($\text{P}_4\text{O}_{12}^{4-}$) group by dehydration and polycondensation reactions at high temperature, which is advance material, such as ceramic pigment, catalyst and fertilizer [12–17]. Both metal dihydrogenphosphate and metal cyclotetraphosphate groups have received a great deal of attention due to simple, nontoxic and cheap synthetic routes and their friendly environment [5–11]. Consequently, in the last few years many works have been a successful attempt in the synthesis of metal (II) dihydrogenphosphate hydrates $\text{M}_{1-x}\text{A}_x(\text{H}_2\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$ (M and A = Mg, Ca, Mn, Fe, Co, Ni, Zn, or Cu; $x = 0\text{--}1$; $n = 1\text{--}4$) [12–17] and metal (II) cyclotetraphosphates $\text{M}_{2-y}\text{A}_y\text{P}_4\text{O}_{12}$ ($y = 0\text{--}2$) [15–17]. However, it is pertinent to synthesize binary metal dihydrogenphosphates, binary metal cyclotetraphosphates and their solid solutions. By varying the composition of the solid solution (within its homogeneity range), one can change its useful properties. So far, binary metal dihydrogen phosphates were synthesized from

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corresponding metal(II) carbonates (or metal oxides) and phosphoric acid at low temperature (40–80 °C) with long time periods (>48 h) [15–17]. While binary metal cyclotetraphosphate was synthesized by mix of corresponding metal cyclotetraphosphates, then melting them together on platinum dishes in an electric furnace at high temperature (>900 °C) with long time consumption (>5 h). However, binary metal cobalt iron dihydrogenphosphate and its decomposed product has not been reported in the literature.

The purpose of this work is to prepare new binary $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ by solid state reaction at ambient temperature with short time consumption (<15 min). Thermal transformation product of the synthesized sample is binary cobalt iron cyclotetraphosphate $\text{CoFeP}_4\text{O}_{12}$. The synthesized powders of $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and its thermal transformation $\text{CoFeP}_4\text{O}_{12}$ with flower-like microparticles and novel superparamagnetic properties were characterized by thermogravimetry–differential thermal analysis (TG–DTG–DTA), X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform IR (FTIR), and vibrating sample magnetometer (VSM) techniques for the first time.

2. Experimental

2.1. Preparation

All chemicals (analytical grade or chemically pure grade) were purchased from Fluka and Merck. Following procedure, 4 mL of 70% H_3PO_4 (86.4% (w/w) H_3PO_4 dissolved in DI water) was added to 1.1893 g of CoCO_3 and 0.5593 g of Fe(c) (a mole ratio corresponding to the nominal composition of Fe:Co ratio of 1.0:1.0), the resulting suspension was continuously stirred at ambient temperature until $\text{CO}_2(\text{g})$ was completely evolved and the precipitates were obtained. For this procedure, the increasing temperature of the precipitates from exothermic process was cooled to room temperature. The nearly dry sample was obtained and then 10 mL of acetone was added to allow highly crystalline product to be developed. The prepared solid was filtered by suction pump, washed with acetone and dried in air.

2.2. Characterization

Thermal property of the studied compound was investigated on a TG–DTG–DTA Pyris Diamond Perkin Elmer Instruments. The experiment was performed in dynamic air at heating rate of $10^\circ\text{C min}^{-1}$ over the temperature range from 30 to 600 °C and the flow rate of 100 mL min^{-1} . Its final decomposition product seemed to occur at temperatures above 500 °C (Fig. 1). In order to gain its final thermal transformation product, the obtained $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ was heated in the furnace at 600 °C for 3 h and the thermal transformation products was further investigated. The cobalt and iron contents were determined by dissolving in 0.0126 M hydrochloric acid using atomic absorption spectrophotometry (AAS, Perkin Elmer, Analyst100). The phosphorus content was determined by colorimetric analysis of the molybdophosphate complex. The water content was determined by TG data. The structure and crystallite size of the synthesized $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and the thermal transformation products were studied by X-ray powder diffraction using a X-ray diffractometer (Phillips PW3040, The Netherlands) with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406\text{ nm}$). The Scherrer method was used to evaluate the crystallite size [18]. The morphologies were examined with scanning electron microscope (SEM) using LEO SEM VP1450 after gold coating. The room temperature FTIR spectra were recorded in the range of 4000–370 cm^{-1} with 8 scans on a Perkin-Elmer Spectrum GX FTIR/FT-Raman spectrometer with the resolution of 4 cm^{-1} using KBr pellets (KBr, spectroscopy grade, Merck). The magnetic properties were

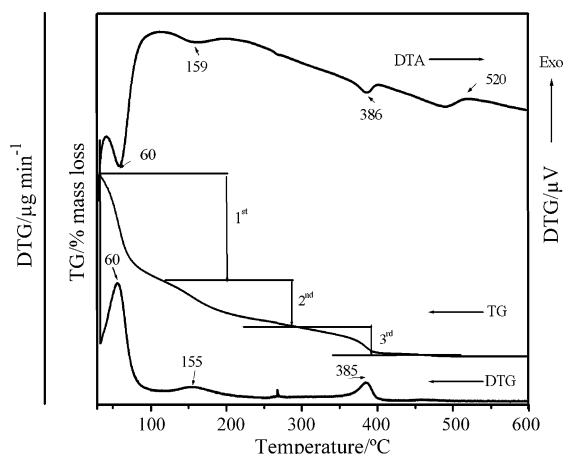


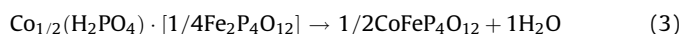
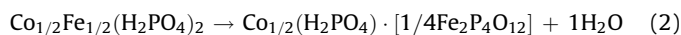
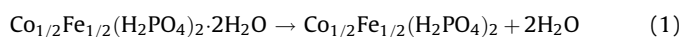
Fig. 1. TG–DTG–DTA curves of $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$.

examined at room temperature (20 °C) using a vibrating sample magnetometer (VSM 7403, Lake Shore, USA).

3. Results and discussion

3.1. Thermal analysis

The TG/DTG/DTA curves of $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ are shown in Fig. 1. The TG curve shows the mass loss between 30 and 600 °C, which is related to the elimination of water molecules in crystallization water and an intermolecular phosphate condensation. The eliminations of water were observed in three areas: 45–130, 130–300 and 300–450 °C. The mass losses in three stages are 12.80, 7.42 and 5.61%, which correspond to 2.04, 1.18 and 0.89 mol of water for $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, respectively. The DTA curve shows three endothermic effects over the temperature region at 60, 159 and 386 °C whereas the DTG curve shows three peaks at 60, 155, and 385 °C. Further, a small exothermic effect at 520 °C without appreciable mass loss is observed in the DTA curve, which can be ascribed to a transition phase from of $\text{CoFeP}_4\text{O}_{12}$. The thermal decomposition of $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ in the range of 30–600 °C involves the dehydration of the coordination water molecules (2 mol H_2O) and an intramolecular dehydration of the protonated dihydrogenphosphate groups (2 mol H_2O) as shown in Eqs. (1)–(3):



The intermediate compounds, such as acid polyphosphate $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2$ and $\text{Co}_{1/2}(\text{H}_2\text{PO}_4) \cdot [1/4\text{Fe}_2\text{P}_4\text{O}_{12}]$ and mixture of both intermediates have been registered. $\text{Co}_{1/2}(\text{H}_2\text{PO}_4) \cdot [1/4\text{Fe}_2\text{P}_4\text{O}_{12}]$ is observed in Eq. (2) due to $\text{Fe}_2\text{P}_4\text{O}_{12}$ is formed at lower temperature than $\text{Co}_2\text{P}_4\text{O}_{12}$, which related to thermal transformation of single dihydrogenphosphate dihydrate in our previous works [19,20]. The intermediates were similarly observed with single metal dihydrogen phosphate [9,10,12–15]. The binary cobalt iron cyclotetraphosphate, $\text{CoFeP}_4\text{O}_{12}$ is found to be the final product of the thermal decomposition at $T > 500^\circ\text{C}$. The total mass loss is 25.83% (4.12 mol H_2O), which is in agreement with those reported for other binary dihydrogenphosphate dihydrate in the literature ($1 < \text{mole of water} < 4$) [9,10,12–15]. The thermal stability, mechanism and phase transition temperature of the studied compound in this work are significantly different from

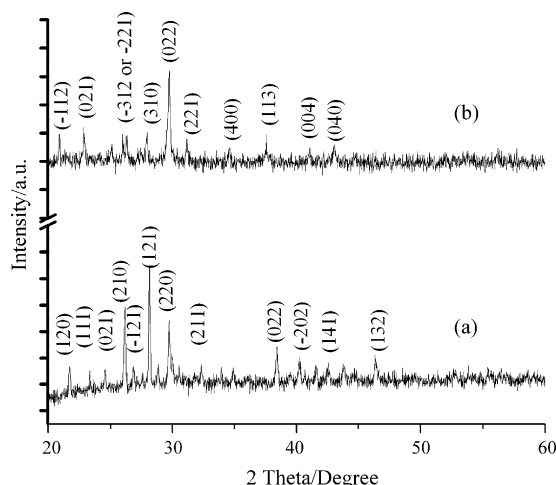


Fig. 2. XRD patterns of $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (a) and its decomposed product $\text{CoFeP}_4\text{O}_{12}$ (b).

those of the decomposition reactions of individual metal compounds ($\text{Fe}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ [19] and $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ [20]). These results indicate that the incorporation of Fe and Co metals in the skeleton has the effects of thermal behaviors, which support the formations of new binary dihydrogen phosphate $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and binary metal cyclotetraphosphate $\text{CoFeP}_4\text{O}_{12}$.

3.2. X-ray powder diffraction

The XRD patterns of $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and its decomposed product $\text{CoFeP}_4\text{O}_{12}$ are similar to those obtained from the individual $\text{M}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{M}_2\text{P}_4\text{O}_{12}$ (when $\text{M} = \text{Co}$ and Fe) but the intensities are slightly different (Fig. 2). The spectrum peaks for the systems of binary cobalt iron solid solution and single metal dihydrogen phosphate (or metal cyclotetraphosphate) are quite similar due to the electronic charges and the radii of cations are equivalent and close to each other, respectively [13–17]. According to the XRD analysis, we can draw a conclusion that the synthesized $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and its decomposed product $\text{CoFeP}_4\text{O}_{12}$ are solid solutions and not a mixture of the individual ones. In addition, the result confirmed that new binary metal ($\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{CoFeP}_4\text{O}_{12}$) are isostructural to type series of the single metal ($\text{M}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{M}_2\text{P}_4\text{O}_{12}$; where M or $\text{A} = \text{Mg}$, Mn , Co , Ni , Fe , Zn). All the reflections can be distinctly indexed as a pure monoclinic phase with space group $\text{P}2_1/\text{n}$ ($Z = 2$) for $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{C}2/\text{c}$ ($Z = 4$) for the decomposed products $\text{CoFeP}_4\text{O}_{12}$, which noted to be similar to those of standard data of $\text{M}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (PDF no 390698 for Co and PDF no 751444

for Fe) and $\text{M}_2\text{P}_4\text{O}_{12}$ (PDF no 842208 for Co and PDF no 782285 for Fe), respectively. The average crystallite sizes and lattice parameters of $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and the decomposed product $\text{CoFeP}_4\text{O}_{12}$ were calculated from XRD patterns and also tabulated in Table 1. The lattice parameters of $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and the decomposed products $\text{CoFeP}_4\text{O}_{12}$ are comparable to those of the standard data of individual ones. The average crystallite sizes of $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and the decomposed product $\text{CoFeP}_4\text{O}_{12}$ were found to be 77 ± 27 and 73 ± 18 nm, respectively. However, the crystallite sizes for the obtained compounds in this work are larger than those from the single metal compounds (Table 1) in our previous works [13,14,18,19].

3.3. FTIR spectroscopy

The FTIR spectra of $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and the decomposed products $\text{CoFeP}_4\text{O}_{12}$ are shown in Fig. 3 and they are very similar to those of $\text{M}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{M}_2\text{P}_4\text{O}_{12}$ ($\text{M} = \text{Co}$ or Fe), which confirmed their isostructural. Vibrational bands are identified in relation to the crystal structure in terms of the fundamental vibrating units namely H_2PO_4^- and H_2O for $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $[\text{P}_4\text{O}_{12}]^{4-}$ ion for $\text{CoFeP}_4\text{O}_{12}$, which are assigned according to the literature [9,10,12–15,21,22].

The FTIR spectrum of $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (Fig. 3a) is very similar to those observed by Koleva et al. [10] and Boonchom et al. [19,20]. The highest site symmetry of H_2PO_4^- ion is C_{2v} , in the crystallographic unit cell ($\text{P}2_1/\text{n}$, $Z = 2$) [10], but the four H_2PO_4^- ions are located on the set of non-equivalent site symmetry of C_1 . A pair of H_2PO_4^- ions is related to each other by a center of symmetry. The four fundamental modes of the free phosphate ion undergo factor group splitting [22]. It is known that the existence of short $\text{OH} \cdots \text{O}$ hydrogen bonds in a variety of strongly hydrogen-bonded solids is manifested by the appearance of the characteristic ABC structure of the $\nu(\text{OH})$ vibrational bands [9,10]. The problem of the origin of the ABC trio is discussed in many studies on acidic salts, but an explanation of this behaviour of strongly hydrogen-bonded systems is still to be found [9,10]. One of the most popular interpretations of the ABC trio suggests a strong Fermi resonance between the $\nu(\text{OH})$ stretching fundamentals and the overtones $[2\delta(\text{OH}) \text{ and } 2\gamma(\text{OH})]$ or combinations involving the $\delta(\text{OH})$ and $\gamma(\text{OH})$ vibrations. Usually, the ABC bands are very broad and consist of many ill-resolved components. Two bands centered at 3138 and 2427 cm^{-1} in the FTIR spectra are referred to as bands A and B, respectively. The third component (band C) is observed around 1749–1639 cm^{-1} . The intense band at about 1260 cm^{-1} is due to the in plane $\text{P}-\text{O}-\text{H}$ bending (A_2), while the out of plane bending (A_1) vibration is observed at about 816 cm^{-1} . Vibrational spectra of present hydrate are assigned by factor group analysis and derived from the same mode as in free H_2PO_4^- ion. A strong band at about

Table 1

Average crystallite sizes and lattice parameters of $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and its decomposed product $\text{CoFeP}_4\text{O}_{12}$ calculated from XRD data.

Compound	Method	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)	Average particle sizes (nm)
$\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$	PDF no 390698 Ref. [20]	7.27	9.88	5.33	94.86	26 ± 2
		7.21(3)	9.91(1)	5.29(5)	94.88(6)	
$\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$	This work	7.30(0)	9.92(0)	5.35(1)	95.01(2)	77 ± 27
$\text{Fe}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$	PDF no 751444 Ref. [19]	7.30	9.92	5.34	95.14	–
		7.25(1)	10.10(0)	5.32(0)	95.71(0)	
$\text{Co}_2\text{P}_4\text{O}_{12}$	PDF no 842208 Ref. [20]	11.8	8.297	9.923	118.72	40 ± 10
		11.83(8)	8.22(6)	9.94(0)	118.51(1)	
$\text{CoFeP}_4\text{O}_{12}$ (calcined 600 °C)	This work	11.77(3)	8.56(0)	9.63(1)	119.09(0)	73 ± 18
$\text{Fe}_2\text{P}_4\text{O}_{12}$	PDF no 782285 Ref. [19]	11.94	8.37	9.93	118.74	–
		12.80(0)	8.80(4)	10.56(0)	118.67(4)	

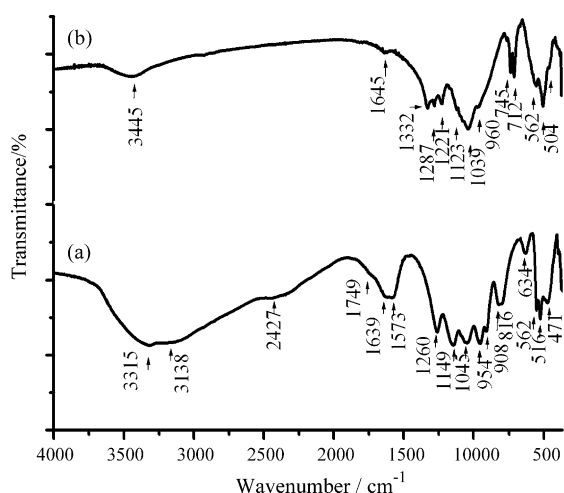


Fig. 3. FTIR spectra of $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (a) and its decomposed product $\text{CoFeP}_4\text{O}_{12}$ (b).

1149 cm^{-1} in FTIR spectra is assigned to PO_2 asymmetric stretching (B_1), while the other one at about 1045 cm^{-1} corresponds to PO_2 symmetric stretching modes (A_1). The FTIR frequency of the $\text{P}(\text{OH})_2$ asymmetric stretching (B_2) shows the strong band at about 954 cm^{-1} . The weak band at about 908 cm^{-1} is assigned to $\text{P}(\text{OH})_2$ symmetric stretching modes (A_1). The medium band at about 562 cm^{-1} is corresponding to PO_2 bending modes (B_1). Two strong bands appeared at about 516 and 471 cm^{-1} are attributed to PO_2 rocking modes as B_1 and A_2 vibrations, respectively. The bands of water vibrations are illustrated in Fig. 3a as a doublet bands (1639 and 1573 cm^{-1}) contribute both to the band C and to the water bending band. A weak band occurs in the FTIR spectra at approximately 634 cm^{-1} is assigned to rocking mode involving water librations. The ν_{OH} stretching modes of HOH in $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ appear at 3138 cm^{-1} (ν_1 or A band) and 3315 cm^{-1} (ν_3). The bands associated with the ν_{OH} stretching frequencies in H_2PO_4^- ions are observed at about 2850 and 2427 cm^{-1} .

The FTIR spectrum of the decomposed product $\text{CoFeP}_4\text{O}_{12}$ (Fig. 3b) is very similar to those obtained from the individual $\text{M}_2\text{P}_4\text{O}_{12}$ ($M = \text{Co}$ and Fe) [13,14,18,19]. The band assignment is identified in terms of the fundamental vibrating modes of $\text{P}_4\text{O}_{12}^{4-}$ ion in the frequency range of 370–1400 cm^{-1} , which are assigned according to the literature [13,14,18,19]. The anion contains the PO_2^{2-} radical and the P–O–P bridge, where are interpreted the FTIR spectra from viewpoint of the vibrations of these two groups. As the P–O bond strength in the P–O–P bridge is weaker than in the PO_2^{2-} radical, the stretching frequencies of the P–O–P bridge are expected to be lower than those in the PO_2^{2-} radical. The asymmetric and symmetric stretching frequencies of the PO_2^{2-} radical are generally observed in the areas 1325–1227 and 1151–1100 cm^{-1} , respectively. The P–O–P bridge has its asymmetric and symmetric stretching frequencies around 1000–900 and 900–700 cm^{-1} , respectively. The bending modes are expected in the area: 600–400 cm^{-1} (PO_2^{2-} radical) and 400–370 cm^{-1} (P–O–P bridge). The metal–O stretching usually appears in the bending mode region as the bending modes of the P–O–P bridge and absorption bands associated with these vibrations are usually very weak. The observation of a strong ν_{sPOP} band is known to be the most striking feature of cyclotetraphosphate spectra, along with the presence of the ν_{asOPO}^- band. From X-ray diffraction data [10], it was shown that the crystal structure is monoclinic (space group $C2/c$) with a cyclic structure of the $[\text{P}_4\text{O}_{12}]^{4-}$ anion. This has been confirmed by the FTIR measurements.

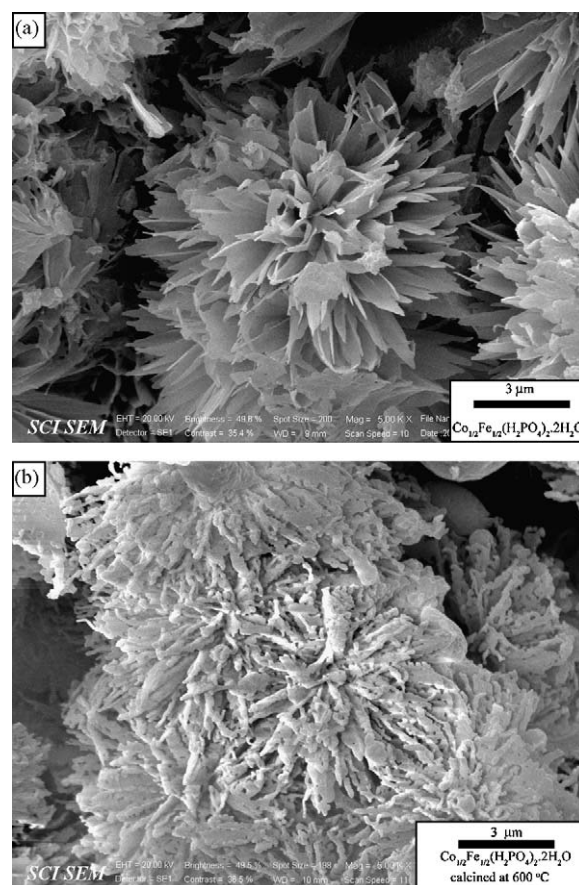


Fig. 4. SEM micrographs of $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (a) and its decomposed product $\text{CoFeP}_4\text{O}_{12}$ (b).

3.4. Scanning electron microscopy

The SEM micrographs of $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and the decomposed product $\text{CoFeP}_4\text{O}_{12}$ are shown in Fig. 4. The particle shape and size are changed throughout the whole decomposition product. The SEM micrographs of $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and the decomposed product $\text{CoFeP}_4\text{O}_{12}$ show flower-like architectures, having sizes of 15–20 μm . The morphology of $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (Fig. 4a) shows petal-bud-like microparticles, which exhibit the different features from $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Fe}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ in the our previous reports [13,14,18,19]. The morphology of the decomposed product $\text{CoFeP}_4\text{O}_{12}$ (Fig. 4b) shows filament-like structures and porosity on the filament surface, which are significant different grain from single metal cyclotetraphosphate ($\text{M}_2\text{P}_4\text{O}_{12}$; $M = \text{Mn}$ or Fe) in our previous reports [13,14,18,19]. The different morphologies between the single metal compounds ($\text{M}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{M}_2\text{P}_4\text{O}_{12}$, $M = \text{Co}$ or Fe) and the binary metal compounds confirm the formation of $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{CoFeP}_4\text{O}_{12}$, which support the presence of Co ions in substitution position of Fe ions.

3.5. VSM magnetometer

The specific magnetization curves of $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and the decomposed product $\text{CoFeP}_4\text{O}_{12}$ obtained from room temperature VSM measurements are shown in Fig. 5. All samples demonstrate typical superparamagnetic behavior with negligible coercivity and remanence, in accordance with the theory that superparamagnetic behavior is often observed at room temperature. The specific magnetization curves are typical superparamagnetic

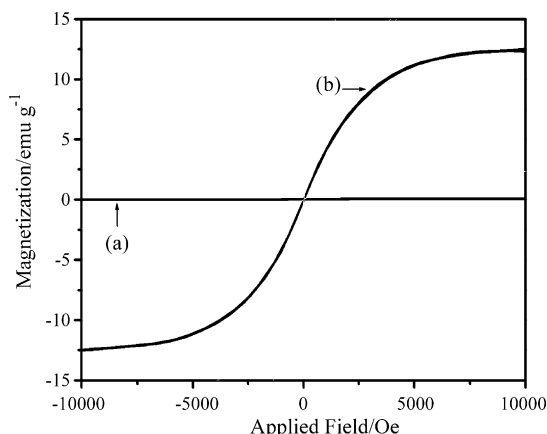


Fig. 5. The specific magnetizations of $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (a) and its decomposed product $\text{CoFeP}_4\text{O}_{12}$ (b) as a function of field, measured at 293 K.

behavior without any hysteresis in the field range of $\pm 10,000$ Oe. Specific saturated magnetization (M_s) values of $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and the decomposed product $\text{CoFeP}_4\text{O}_{12}$ are found to be 0.045 and 12.502 emu/g, respectively. It is worth nothing that these saturated magnetizations were compared with other magnetic materials (M_s of Fe_3O_4 is 10–50 emu/g) [23–25]. It is seen that magnetizations of the $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{CoFeP}_4\text{O}_{12}$ are lower than those of $\text{Fe}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (96.28 emu/g) and $\text{Fe}_2\text{P}_4\text{O}_{12}$ (85.01 emu/g) [20] but markedly distinct from the diamagnetic properties of $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Co}_2\text{P}_4\text{O}_{12}$ [19]. To our knowledge, it is worth nothing that superparamagnetic properties of the $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{CoFeP}_4\text{O}_{12}$ samples are reported for the first time in this study.

4. Conclusion

Flower-like microparticle $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ was successfully synthesized by solid state method from $\text{CoCO}_3\text{--Fe--H}_3\text{PO}_4$ system at ambient temperature with short time consumption (15 min). $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ decomposes in three steps which correspond to the loss of water of crystallization in the first step, subsequently to a continuous intermolecular polycondensation and elimination of water of constituent in anion (the second and the third steps). The thermal behaviors, flower-like morphologies, particle sizes and superparamagnetic properties of $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and the thermal transformation products $\text{CoFeP}_4\text{O}_{12}$ in this work are different from single metal compounds

in our previous reports. This work presents the simple, cost-effective and short time consuming method for the preparation of new binary metal $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{CoFeP}_4\text{O}_{12}$ compounds, which may be used in many important applications such as catalytic, superionic conductors, piezo- and ferroelectrics, magnets, electrochemical, bioceramic and environmental processes.

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Synthesis and ferromagnetic property of new binary copper iron pyrophosphate CuFeP_2O_7

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ABSTRACT

The pyrophosphate of CuFeP_2O_7 was synthesized through one step-thermal synthesis at 500 °C using the mixing of copper carbonate, iron metals and phosphoric acid. FTIR and XRD results indicate the dominant feature of pyrophosphate ($\text{P}_2\text{O}_7^{4-}$) anion and a pure monoclinic phase with space group C_{2h}^6 ($Z=4$), respectively. The crystallite size of 25 ± 9 nm for the CuFeP_2O_7 was estimated by X-ray line broadening. Room temperature magnetization result shows ferromagnetic behavior of the CuFeP_2O_7 powder, having hysteresis loop in the range of $\pm 10,000$ Oe with the specific magnetization value of 1.57 emu g^{-1} . This property is important for specific application and is presented for the first time.

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1. Introduction

Binary metal (II) pyrophosphates consisting of a homogeneous solid solution are characterized by high corrosion resistance, high tensile strengths, improved ductility and good malleability as compared with the corresponding single metals [1,2]. These materials are widely employed in various fields as catalysts, wastewater purification systems, ferroelectrics, lithium batteries, the steel and glass industries [2–4]. In the recent years, they have been proposed as the cathode in lithium batteries and lithium metal phosphates can be used as cathode or anode electrodes in lithium batteries because they are the next generation of positive-electrode materials for lithium batteries and offer additional advantages in practical applications due to their lower cost, safety, benign environmental properties, stability and low toxicity [5,6]. The binary metal $\text{M}_{2-x}\text{A}_x\text{P}_2\text{O}_7$ (M or A = Mg, Mn, Co, Cu, Ni, Fe, Zn; $0 < x < 2$) group, one of the important metal phosphates, has found widespread applications and is gaining interesting according to above mentioned [7]. Because it appears economically advantageous to substitute a portion of the divalent metal with a less costly divalent element, which influences many properties, for example, the color of pigments, the relatively stable compounds—both thermally and chemically, anticorrosion ability and luminescence [1–4]. In addition, some metals, such as copper or iron, and $(\text{P}_2\text{O}_7)^{4-}$ species are lower cost, safety, benign environmental properties and low toxicity [5,7].

Therefore, our laboratory has focused on the studies of the synthesis of new binary metal pyrophosphates [8,9], which are important for the development of new inorganic functional materials.

The present paper describes the synthesis and characterization of a new binary copper iron pyrophosphate, CuFeP_2O_7 using powder X-ray diffraction (XRD), Fourier transform infrared (FTIR) and vibrating magnetometric (VSM) techniques. The information on the synthesis and characterization of a new binary copper iron pyrophosphate, CuFeP_2O_7 are reported for the first time.

2. Experimental

All the reagents used in this study were of A.R. grade. In typical procedure, CuCO_3 and Fe (complexometric) were mixed together with mole ratio of 1.0:1.0 and then was ground for 10 min. Subsequently, 5 mL of 70 % H_3PO_4 (86.4 %w/w H_3PO_4 dissolved in DI water) was added slowly to the mixed solid with mechanically stirring at ambient temperature (10 min). Then, the mixed suspension was evaporated by heating in the furnace at 500 °C for 2 h. The obtained gray pink precursor was crushed into powder, which was washed repeatedly by DI water until no PO_4^{3-} was detected. Finally, the powder was washed again for several times with methanol and dried at room temperature. The reaction equation can be expressed as:



The copper and iron contents of CuFeP_2O_7 were determined by dissolving in 0.0126 M hydrochloric acid using atomic absorption

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spectrophotometry (AAS, Perkin Elmer, Analyst100). The phosphorus content was determined by colorimetric analysis of the molybdophosphate complex. X-ray powder diffraction (XRD) was carried out by a Phillips PW3040 X-ray diffractometer (The Netherlands) utilizing Cu K α radiation ($\lambda = 0.15406$ nm) at 40 kV/200 mA. The Scherrer method was used to evaluate the crystallite size [10]. The room temperature FTIR spectrum in the range of 4000–370 cm^{-1} was recorded by a Perkin-Elmer Spectrum GX FT-IR/FT-Raman spectrometer with 8 scans and the resolution of 4 cm^{-1} using KBr pellets. The magnetic property was examined at room temperature (20 °C) using a vibrating sample magnetometer (VSM 7403, Lake Shore, USA).

3. Results and discussion

The XRD pattern of CuFeP_2O_7 is similar to those obtained from the individual $\text{M}_2\text{P}_2\text{O}_7$ (when $\text{M} = \text{Cu}, \text{Co}, \text{Mn}$ and Fe) [1–4,11], but the intensities are slightly different (Fig. 1). The lower and higher intensities of XRD peaks indicate the differences of crystallization or amorphous phase as well as crystallite sizes of these materials. From literature, it indicates that the binary solid solutions ($\text{M}_{2-x}\text{A}_x\text{P}_2\text{O}_7$) and the single metal compounds for $\text{M}_2\text{P}_2\text{O}_7$ (M or $\text{A} = \text{Mg}, \text{Mn}, \text{Co}, \text{Cu}, \text{Ni}, \text{Fe}, \text{Zn}; 0 < x < 2$) types are isostructural [1–4,11]. In the hypothesis of isostructural, the spectrum peaks for the systems of binary copper iron pyrophosphate (solid solution) and single metal pyrophosphate ($\text{M}_2\text{P}_2\text{O}_7$, $\text{M} = \text{Cu}$ and Fe) are quite similar because of the equivalent electronic charges and the close radii of cations. In addition, no characteristic peaks of other impurities (CuCO_3 or Fe) were observed. In this respect, we can draw a conclusion that the synthesized product CuFeP_2O_7 is solid solution and not a mixture of the individual ones. Consequently, all reflections can be distinctly indexed based on a pure monoclinic phase with space group C2/c ($Z = 4$) for CuFeP_2O_7 , which noted to be similar to those of the standard XRD patterns of $\text{M}_2\text{P}_2\text{O}_7$ (PDF no. 79-2075 for Cu and PDF no. 76-1762 for Fe), respectively. The average crystallite size of product is estimated from the strongest three diffraction peaks below 40° for 2θ and found to be 25 ± 9 nm. The lattice parameters calculated from the XRD spectra are $a = 6.73$ (0), $b = 8.21$ (1), $c = 9.39$ (0) Å and $\beta = 110.65$ (4)°, which are close to those of the standard data file ($a = 6.89$ (5), $b = 8.11$ (3), $c = 9.16$ (4) Å and $\beta = 109.62$ (0)° from PDF no. 79-2075 for $\text{Cu}_2\text{P}_2\text{O}_7$ and $a = 6.65$ (0), $b = 8.48$ (4), $c = 4.49$ (0) Å and $\beta = 103.89$ (0)° from PDF no. 76-1762 for $\text{Fe}_2\text{P}_2\text{O}_7$) and the literature [11,12].

FTIR spectrum of CuFeP_2O_7 shown in Fig. 2 is very similar to those obtained from the single metal pyrophosphates $\text{M}_2\text{P}_2\text{O}_7$ ($\text{M} = \text{Mn}, \text{Ni}, \text{Co}$ and Fe) [7–9,12,14]. The vibrational modes of $\text{P}_2\text{O}_7^{4-}$ ion observed in the frequency range of 370–1400 cm^{-1} are assigned according to the literature [7–9,13,14]. The anion containing the PO_3 and the P–O–P bridge are interpreted the FTIR spectrum from viewpoint of the vibrations of these two groups. The asymmetric and symmetric

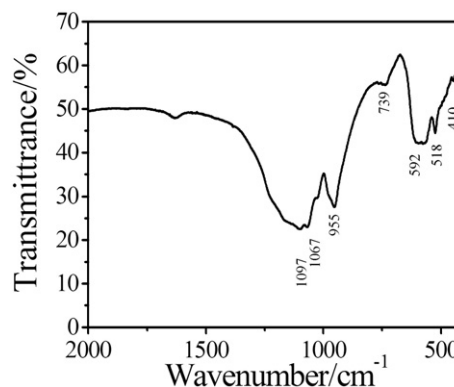


Fig. 2. FTIR spectrum of CuFeP_2O_7 .

stretching frequencies of the PO_3 are generally observed at 1097 and 1067 cm^{-1} , respectively. The bending modes of PO_3 are expected in the range of 592–518 cm^{-1} . The metal–O stretching usually appears in the bending mode region as the bending modes of the PO_3 and absorption bands associated with these vibrations are usually very weak. The bands found at 955 and 739 cm^{-1} are typical of the pyrophosphate group and correspond to the stretching and bending vibrations of the P–O–P bridge, respectively. The observation of a strong $\nu_{\text{as}}\text{POP}$ band is known to be the most striking feature of pyrophosphate spectra, along with the presence of the $\nu_{\text{as}}\text{OPO}^-$ band. The PO_3 deformation and rocking modes, the POP deformations as well as the torsional and external modes are found in the 592–410 cm^{-1} region. FTIR result is consistent with X-ray data [15], indicating that the crystal structure is monoclinic (space group C2/c) with pyrophosphate groups of the $[\text{P}_2\text{O}_7]^{4-}$ anion.

The specific magnetization curve of the CuFeP_2O_7 sample obtained from room temperature VSM measurement is shown in Fig. 3. This curve is typical for a soft magnetic material and indicates hysteresis ferromagnetism in the field range of $\sim \pm 10,000$ Oe while outside this range the specific magnetization increases with increasing field and saturates in the field range investigated (± 10 kOe). The specific saturation magnetization (M_s) value of 1.57 emu g^{-1} was observed for the CuFeP_2O_7 sample. The coercive force (H_c) obtained on the increasing and decreasing filed sides (blanket) were 67.70 (–67.70) Oe for the CuFeP_2O_7 sample. The ferromagnetic solid solution formed in CuFeP_2O_7 system is different from paramagnetic for $\text{Fe}_2\text{P}_2\text{O}_7$ and diamagnetic for $\text{Cu}_2\text{P}_2\text{O}_7$. The CuFeP_2O_7 called pyrophosphate constitutes the largest family of condensed phosphates and contains different cations (Cu^{2+} and Fe^{2+}) [15–18]. The ferromagnetic of the studied compound originates from magnetic moment of anti-parallel spins of between Cu^{2+} (non-magnetic element) at octahedral sites and Fe^{2+} (magnetic element) at distorted octahedral coordination

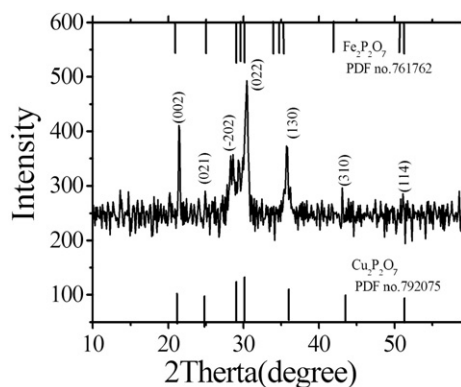


Fig. 1. XRD pattern of CuFeP_2O_7 .

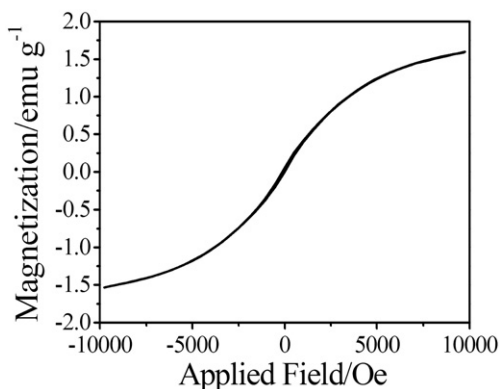


Fig. 3. The specific magnetization of CuFeP_2O_7 as a function of field, measured at 20 °C.

[17,18]. This should be necessary for the appearance of ferromagnetism [18]. Additionally, it found that the tendency of M_s to increase is consistent with the enhancement of crystallinity or particle sizes, and the saturation value of M_s for CuFeP_2O_7 is observed due to the obtained microstructure. This result has been essentially verified in a quantitative sense within the last two decades. Ferromagnetic property of the CuFeP_2O_7 sample reported for the first time is important for specific applications such as magnetic resonance imaging contrast agents, data lifetime in high density information storage, ferrofluid technology, lithium batteries and magnetocaloric refrigeration [15,16].

4. Conclusions

This research has successfully achieved a simple one-step thermal synthesis of a monoclinic phase of a new binary copper iron pyrophosphate CuFeP_2O_7 . FTIR, XRD and VSM results suggested the formation of a binary metal CuFeP_2O_7 . The FTIR and XRD data confirmed the dominant feature of pyrophosphate ($\text{P}_2\text{O}_7^{4-}$) anion indicated the formation of a binary CuFeP_2O_7 . The crystallite size of CuFeP_2O_7 shows polycrystalline having crystallite size of 25 ± 9 nm, as estimated by XRD. The synthesized CuFeP_2O_7 shows ferromagnetic property, which has hysteresis loop in the range of $-10,000 \text{ Oe} < H < 10,000 \text{ Oe}$ with the specific magnetization of 1.57 emu^{-1} at 10 kOe. This research displays that the simple, cost effective and rapid time consumption is necessary for elaboration of technology and academic scientist to produce the pyrophosphate of transition metals, which may be useful for potentially applications as inorganic ceramic pigment, catalyst, fuel cell material and corrosion-proof compositions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.matlet.2009.10.058](https://doi.org/10.1016/j.matlet.2009.10.058).

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Floral-like microarchitectures of cobalt iron cyclotetraphosphate obtained by solid state synthesis

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ABSTRACT

Floral-like microparticle of a binary cobalt iron cyclotetraphosphate CoFeP₄O₁₂ was synthesized through solid phase reaction using cobalt carbonate, iron metal and phosphoric acid with further calcinations at the temperature of 500 °C. The XRD and FTIR results indicate that the prepared CoFeP₄O₁₂ has a pure monoclinic phase without the presence of any phase impurities. The floral-like microparticle and superparamagnetic behavior of the synthesized CoFeP₄O₁₂ are important properties for specific applications, which were revealed by SEM and VSM techniques, respectively. The dominant features of the synthesized CoFeP₄O₁₂ in this work are compared with M₂P₄O₁₂ (M = Co and Fe) and CoFeP₄O₁₂ reported in our previous works.

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1. Introduction

In recent years, synthesis of the morphology and architecture of inorganic phosphates at micro-/nanoscale levels is a significant challenge, which attracts increased attention because of their strong influence on the chemical and physical properties of materials [1–3]. Morphology influences not only the intrinsic chemical, optical, and catalytic properties of micro-/nanoscale metal phosphates, but also their relevant applications in electronic, biocompatible and biodegradable in tissue [2,4]. As one of the members of phosphate material family, transition metal cyclotetraphosphate micro-/nanoparticles can be used in potential pigments, selective catalysts, phosphors, materials for corrosion-resistant coatings and biocompatible and biodegradable in tissue [5–8]. Several divalent including 3d metals, namely, Mn, Co, Fe, Zn, Cu, and Ni, are known to form the single metal cyclotetraphosphate M₂P₄O₁₂, where M(II) stands for a divalent metal. The binary metal cyclotetraphosphates M_{2–x}A_xP₄O₁₂ (M and A = Mg, Ca, Mn, Co, Ni, Zn, or Cu; x = 0–2), isostructural with the single metal cyclotetraphosphates M₂P₄O₁₂, were prepared by Trojan et al. [5–8] and Boonchom et al. [9–11]. All these compounds have similar X-ray diffraction patterns and close unit cell parameters, which crystallize in monoclinic space group C2/c (Z = 4) [12]. Various methods have been employed to synthesize binary metal cyclotetraphosphates, including two-step thermal method [5–8], hydrothermal synthesis [5] and the decompo-

sition of binary metal (II) dihydrogenphosphates (M_{1–y}A_y(H₂PO₄)₂·nH₂O; where M and A = Ca, Mg, Mn, Fe, Co, Ni, Cu or Zn; y = 0–1; n = 1–4) [9–11]. This work is of interest because it appears economically advantageous to replace partially the divalent metal cations by some cheaper divalent element which could also improve special properties as above mentioned [1–4]. However, it is relevant to synthesize binary cyclotetraphosphate and its solid solution because changing the metal ratio influences its useful properties. Consequently, it is a major challenge to synthesize binary metal cyclotetraphosphate micro-/nanoparticles with its intrinsic shape-dependent properties and resulting application. Recently, cobalt iron pyrophosphate CoFeP₂O₇ and cobalt iron cyclotetraphosphate CoFeP₄O₁₂ were prepared by mixing of CoCO₃, Fe and H₃PO₄ in water–methanol and in water–acetone, respectively [13,14]. The difference of media (solvents) in the precipitation process leads to the obtaining different phosphates, as revealed by XRD and FTIR data. Due to its solubility in water and its ability to associate with metal ions in media, solvent has been used as a binder cum gel for shaping materials (bulk, porous, micro- or nanoparticles) and a matrix for entrapment of ions to generate a gelled precursor which resulted in obtaining different material or same material with different size and morphology after heat treatment. The results obtained are also in agreement with other phosphate group reported in literature [15,16]. In this work, we report for the first time one step thermal synthesis of floral-like microarchitectures of binary cobalt iron cyclotetraphosphate CoFeP₄O₁₂ by solid state reaction from cobalt carbonate, iron metal and phosphoric acid without organic media agent (or solvent). The different preparation routes of the CoFeP₂O₇ between this work and our previous report [14] affect the differences of some physical and chemical properties such as morphology, particle size

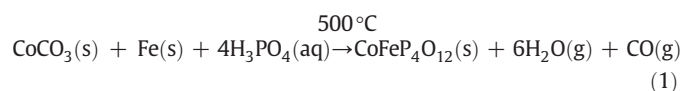
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and magnetic behavior. The synthesized sample was characterized by X-ray powder diffraction (XRD), Fourier transform infrared (FTIR), scanning electron microscope (SEM) and vibrating sample magnetometer (VSM) techniques.

2. Experimental

All the reagents used in this study were of A.R. grade. A binary cobalt iron cyclotetraphosphate $\text{CoFeP}_4\text{O}_{12}$ was prepared at laboratory temperature. In typical procedure, CoCO_3 and Fe (complexometric) were mixed together with mole ratio of 1.0:1.0 and then was ground for 10 min. Subsequently, 5 mL of 70 % H_3PO_4 (86.4 % w/w H_3PO_4 dissolved in DI water) was added slowly to the mixed solid with mechanically stirring at ambient temperature (10 min). Then, the mixed solution was evaporated by heating in the furnace at 500 °C for 2 h. The obtained gray pink precursor was crushed into powder and was washed repeatedly by DI water until no PO_4^{3-} was detected. Finally, the powder was washed again for several times with methanol and dried at room temperature. The reaction equation can be expressed as:



The cobalt and iron contents of $\text{CoFeP}_4\text{O}_{12}$ were determined by dissolving in 0.0126 M hydrochloric acid using atomic absorption spectrophotometry (AAS, Perkin Elmer, Analyst100). The phosphorus content was determined by colorimetric analysis of the molybdophosphate complex. X-ray powder diffraction (XRD) was carried out by a Phillips PW3040 X-ray diffractometer (The Netherlands) utilizing $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406$ nm) at 40 kV/200 mA. The Scherrer method was used to evaluate the crystallite size [17]. The room-temperature FTIR spectrum in the range of 4000–370 cm^{-1} was recorded by a Perkin Elmer Spectrum GX FTIR/FT-Raman spectrometer with 8 scans and the resolution of 4 cm^{-1} using KBr pellets. The morphology was examined with SEM picture by LEO SEM VP1450 scanning electron microscope. The magnetic property was examined at room temperature (20 °C) using a vibrating sample magnetometer (VSM 7403, Lake Shore, USA).

3. Results and discussion

3.1. Chemical analysis

The chemical analysis data showed that the cobalt, iron and phosphorus mass percentage were 13.58%, 12.92% and 28.75%, respectively. In other words, the molar ratio of $\text{Co}_{\text{total}}:\text{Fe}_{\text{total}}:\text{P}_{\text{total}}$ in the synthetic product is equal to 1.00:1.00:4.03, which indicates that the general formula would be $\text{CoFeP}_4\text{O}_{12}$.

3.2. X-ray powder diffraction

XRD was used to characterize the phase the crystallographic structure of the product (Fig. 1). The XRD pattern of as prepared floral-like $\text{CoFeP}_4\text{O}_{12}$ is similar to that of non-uniform particle $\text{CoFeP}_4\text{O}_{12}$ reported by our previous work [14] but the intensities are slightly different. The lower and higher intensities of XRD peaks indicate the differences of crystallization or amorphous phase as well as particle sizes of these materials. In the hypothesis of isostructural, the spectrum peaks for the systems of binary cobalt iron cyclotetraphosphate (solid solution) and single metal cyclotetraphosphate ($\text{M}_2\text{P}_4\text{O}_{12}$, $\text{M} = \text{Co}$ and Fe) are quite similar because of the equivalent electronic charges and the close radii of cations. Consequently, all the diffraction peaks in the figure are found to be in agreement with monoclinic $\text{M}_2\text{P}_4\text{O}_{12}$ (PDF no. 842208 for $\text{Co}_2\text{P}_4\text{O}_{12}$ and PDF no. 782285 for $\text{Fe}_2\text{P}_4\text{O}_{12}$), space group C2/c ($Z = 4$). No characteristic peaks of other impurities (CoCO_3 or Fe) were observed,

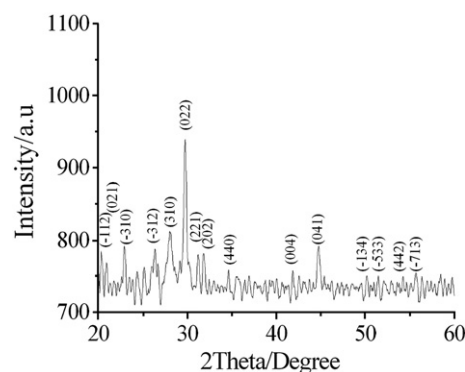


Fig. 1. XRD pattern of $\text{CoFeP}_4\text{O}_{12}$.

and all the reflections could be indexed to the pure monoclinic phase of binary cobalt iron cyclotetraphosphate $\text{CoFeP}_4\text{O}_{12}$. From XRD analysis (Fig. 1), it can conclude that the as prepared floral-like $\text{CoFeP}_4\text{O}_{12}$ is solid solution, not a mixture of the individual phases and isostructural with the single metal $\text{M}_2\text{P}_4\text{O}_{12}$ ($\text{M} = \text{Co}$ and Fe). According to the Scherrer formula: $D = K\lambda/(\beta \cos \theta)$, where D is particle diameter, $K = 0.89$ (the Scherrer constant), $\lambda = 0.15406$ (wavelength of the X-ray used), β is the width of line at the half-maximum intensity and θ is the corresponding angle. The average crystallite size of product is estimated from the strongest three diffraction peaks below 40° for 2θ and found to be 49 ± 20 nm. This crystallite size of the prepared $\text{CoFeP}_4\text{O}_{12}$ in this work is smaller than that obtained from our previous work (65 ± 24 nm) [14] but it is larger than those for the single metal compounds (40 ± 10 nm for $\text{Co}_2\text{P}_4\text{O}_{12}$ and 29 ± 6 nm for $\text{Fe}_2\text{P}_4\text{O}_{12}$) in our previous studies [9–11]. The lattice parameters calculated from the XRD spectra are $a = 11.89(0)$, $b = 8.33(0)$, $c = 10.15(0)$ Å and $\beta = 119.09(0)^\circ$, which are close to those of the standard data file (from PDF no. 842208 for $\text{Co}_2\text{P}_4\text{O}_{12}$ and PDF no. 782285 for $\text{Fe}_2\text{P}_4\text{O}_{12}$) and the literature [9–11,14].

3.3. FTIR spectroscopy

The $\text{CoFeP}_4\text{O}_{12}$ structure is characterized by a three-dimensional framework with MO_6 ($\text{M} = \text{Co}$ or Fe) polyhedral linked with P_4O_{12} rings by $\text{M}-\text{O}-\text{P}$. The basic structure unit is the centrosymmetric cyclotetraphosphate ring P_4O_{12} and therefore vibrational modes can consider it as made up of the $\text{P}_4\text{O}_{12}^{4-}$ anion. The vibrational modes of $\text{P}_4\text{O}_{12}^{4-}$ ion observed in the frequency range of 370–1400 cm^{-1} are assigned according to the literature (Fig. 2) [18–20]. The many peaks split in these regions indicate the different strength of the bond between cations ($\text{M} = \text{Co}^{2+}$ and Fe^{2+}) and anion ($\text{P}_4\text{O}_{12}^{4-}$), which confirm the inserting different cations in the skeletal as well as the formation of binary cobalt iron cyclotetraphosphate. The anion contains the PO_2^{2-} radical and the $\text{P}-\text{O}-\text{P}$ bridge which differ in their bond strength. As the $\text{P}-\text{O}$ bond strength in the PO_2^{2-} radical is stronger than in the $\text{P}-\text{O}-\text{P}$ bridge, the

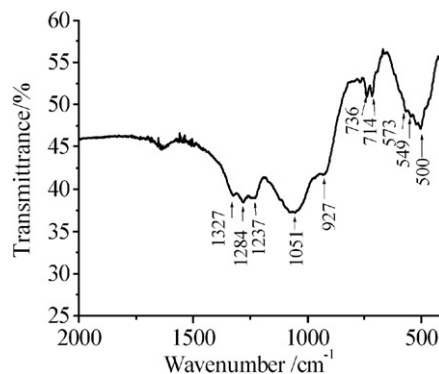


Fig. 2. FTIR spectrum of $\text{CoFeP}_4\text{O}_{12}$.

stretching frequencies of the PO_2^{2-} radical are expected to be higher than those in the P–O–P bridge. The P–O bonds in the PO_2^{2-} radical show its asymmetric and symmetric stretching frequencies around 1327–1237 and 1150–1000 cm^{-1} , respectively. The asymmetric and symmetric stretching frequencies of the P–O–P bridge are observed in the regions of 1000–900 and 800–700 cm^{-1} , respectively. The symmetric P–O–P bridge stretching modes occur at 736 and 714 cm^{-1} . These observed bands are known to be the most striking feature of cyclotetraphosphate spectra, along with the presence of the $\nu_{\text{as}}\text{OPO}^-$ band. From X-ray diffraction data [12], it was shown that the crystal structure is monoclinic (space group C2/c) with a cyclic structure of the $[\text{P}_4\text{O}_{12}]^{4-}$ anion. This has been confirmed by the FTIR measurements. The bending modes are expected in the area 600–400 cm^{-1} (PO_2^{2-} radical) and 400–370 cm^{-1} (P–O–P bridge). The metal–O stretching usually appears in the bending mode region as the bending modes of the P–O–P bridge and absorption bands associated with these vibrations are usually very weak. The weak FTIR band at 400 cm^{-1} is probably due to metal–O stretching mode.

3.4. Scanning electron microscopy

SEM micrograph of $\text{CoFeP}_4\text{O}_{12}$ sample is shown in Fig. 3. It can be seen that the sample is composed of floral-like structures. There is soft agglomeration phenomenon among the particles of $\text{CoFeP}_4\text{O}_{12}$, which is attributed that the strong absorption of each other exists among particles with the layered structure compound. The floral-like morphology consists of similar petal-like flakes growing radially from the centre as can be observed under a higher magnification (inset). The different morphologies between the single metal compounds ($\text{M}_2\text{P}_4\text{O}_{12}$, $\text{M} = \text{Co}$ or Fe) and the binary $\text{CoFeP}_4\text{O}_{12}$ indicate the presence of Co ions in substitution position of Fe ions, which confirms the formation of binary cobalt iron cyclotetraphosphate $\text{CoFeP}_4\text{O}_{12}$. The result of SEM experiment indicates that the grain sizes of $\text{CoFeP}_4\text{O}_{12}$ are not consistent with the crystallite sizes in the XRD analysis indicating the influence of media agents on particle nucleation and growth mechanisms. In addition, the floral-like morphology of the prepared $\text{CoFeP}_4\text{O}_{12}$ in this work is different from the non-uniform particles of $\text{CoFeP}_4\text{O}_{12}$ reported in our previous work [14]. These results indicate that the medium reagents for precipitation have the strong effect on the morphology of binary metal cyclotetraphosphate and are also in agreement with other reported other phosphate groups [12–15].

3.5. VSM magnetometer

The room-temperature magnetization curves of the floral-like microparticle $\text{CoFeP}_4\text{O}_{12}$ displays typical superparamagnetic behavior (Fig. 4). This curve is typical superparamagnetic behavior without any

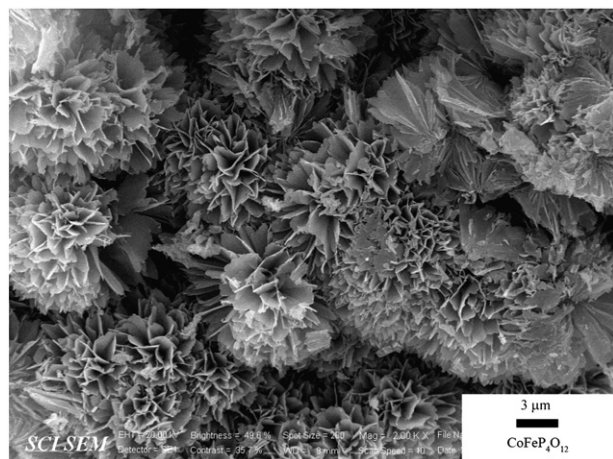


Fig. 3. SEM micrograph of $\text{CoFeP}_4\text{O}_{12}$.

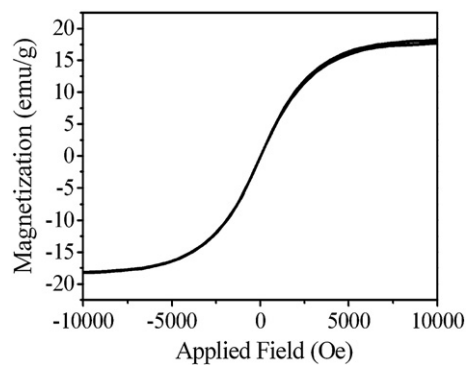


Fig. 4. The specific magnetization of $\text{CoFeP}_4\text{O}_{12}$ as a function of field, measured at 20 °C.

hysteresis in the field range of $\pm 10,000$ Oe. Specific saturated magnetization (M_s) value of the floral-like microparticle $\text{CoFeP}_4\text{O}_{12}$ (18.202 emu/g) in this work is higher than that of non-uniform microparticle $\text{CoFeP}_4\text{O}_{12}$ (14.243 emu/g) reported in our previous work [14] because of their small size. The result is lower than the saturated magnetization for Fe_3O_4 nanoparticles (in a range of 30–50 emu/g) [21,22]. It is seen that magnetization of the prepared $\text{CoFeP}_4\text{O}_{12}$ is lower than that of $\text{Fe}_2\text{P}_4\text{O}_{12}$ (85.01 emu/g) but markedly distinct from the diamagnetic properties of $\text{Co}_2\text{P}_4\text{O}_{12}$ [9,10]. This result indicates that the presence of Co ions in substitution position of Fe ions has the strong effect on the magnetic behavior of $\text{CoFeP}_4\text{O}_{12}$. This study demonstrates that the floral-like microparticle $\text{CoFeP}_4\text{O}_{12}$ is truly superparamagnetic, which is a unique feature of magnetic materials. This material may be used in modern technologies including magnetic resonance imaging contrast agents, data lifetime in high density information storage, ferrofluid technology, and magnetocaloric refrigeration [21–25].

4. Conclusions

Floral-like microparticle $\text{CoFeP}_4\text{O}_{12}$ was successfully synthesized by solid state route from cobalt carbonate, iron metal and phosphoric acid at 500 °C. The floral-like morphology and higher magnetization value of $\text{CoFeP}_4\text{O}_{12}$ in this work are different from those obtained from other works indicating that this may be caused by the media agents. The morphology of $\text{CoFeP}_4\text{O}_{12}$ shows floral-like crystals, as revealed by SEM data. The synthesized powder is polycrystalline, having crystallite size of 49 ± 20 nm for $\text{CoFeP}_4\text{O}_{12}$, as estimated by XRD. The synthesized $\text{CoFeP}_4\text{O}_{12}$ is superparamagnetic, having no hysteresis loop in the range of $-10,000 \text{ Oe} < H < 10,000 \text{ Oe}$ with the specific magnetization of 18.202 emu/g at 10 kOe. The results obtained are necessary for elaboration of technology to produce the cyclotetraphosphate of transition metals, which may be useful for potentially applications as catalytic, ceramic and the biomedical materials etc.

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Dielectric properties and phase transition behaviors in $(1-x)\text{PbZrO}_3-x\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ ceramics

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The solid solution of lead zirconate [PbZrO_3 (PZ)] and lead magnesium tungstate [$\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ (PMW)] has been synthesized by the wolframite precursor method. The crystal structure, phase transformations, dielectric and thermal properties of $(1-x)\text{PZ}-x\text{PMW}$, where $x=0.00-0.10$, were investigated. The crystal structure of sintered ceramics was analyzed by x-ray diffraction. Phase-pure perovskite was obtained for all compositions. Furthermore, a change from orthorhombic to rhombohedral symmetry was observed as the mole fraction of increased PMW. As a result, it was found that $\text{PbZrO}_3-\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ undergoes successive transitions from the antiferroelectric phase to the ferroelectric phase to the paraelectric state. The coexistence of orthorhombic and rhombohedral phases in this binary system is located near the composition $x=0.1$. © 2009 American Institute of Physics. [doi:10.1063/1.3212991]

I. INTRODUCTION

Antiferroelectric (AFE) materials are widely used for various devices: high charge storage capacitors, large strain actuators, and microelectromechanical systems.^{1,2} The basic physics for these applications is due to the behaviors of electric-field-induced AFE to ferroelectric (FE) phase transformation. Lead zirconate [PbZrO_3 (PZ)] has been considered as the prototype AFE since its discovery by Sawaguchi *et al.* in 1951.³ At room temperature, PZ has an orthorhombic structure with the lattice parameters $a=5.884$ Å, $b=11.768$ Å, and $c=8.22$ Å.⁴ The orthorhombic unit cell consists of eight formula units and eight primitive cells with a tetragonal structure.³ AFE PZ has spontaneous polarization, with adjacent rows of dipoles oriented antiparallel to each other, and no net spontaneous polarization at the equilibrium. AFE PZ has a phase transition to the paraelectric (PE) state, which occurs at approximately 236 °C. However, transition from the orthorhombic AFE to a rhombohedral FE structure, at a few degrees below the PE transition temperature, has been reported by several authors.^{5,6} It is well known that the AFE to FE phase transformation in PZ ceramic requires a very strong electric field; otherwise, dielectric breakdown occurs.³ Consequently, most commercial AFE ceramics are chemically modified by adding Ti^{4+} , Nb^{5+} , Sn^{4+} , or La^{3+} to reduce the critical field and optimize the physical and electrical properties.^{7,8}

Lead magnesium tungstate [$\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ (PMW)] is a complex perovskite compound with Mg^{2+} and W^{6+} ordered on the *B*-site of the ABO_3 perovskite structure.⁹ PMW-

based ceramics have been known as dielectric materials possessing low dielectric loss and low sintering temperature.¹⁰ Therefore, these materials can be used to fabricate multilayer capacitors with inner electrodes that melt in low temperature. At room temperature, PMW has an AFE phase, which has an orthorhombic structure. It undergoes a first order phase transition from an orthorhombic AFE phase to the cubic phase ($Fm\bar{3}m$) at 38 °C.⁹ The room temperature x-ray diffraction (XRD) pattern of PMW shows the presence of superlattice reflections due to the *B*-site ordering.⁹

Most studies of FE solid solutions have focused on relaxor-PT systems, such as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-\text{PbTiO}_3$,¹¹ $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-\text{PbTiO}_3$,^{11,12} and $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3-\text{PbTiO}_3$,¹³ and AFE-PT systems, for example, $\text{PbZrO}_3-\text{PbTiO}_3$.^{14,15} A small number of studies have focused on AFE-AFE systems. Furthermore, the structure-property relationship between solid solution and an AFE-AFE system is still unclear.

Since PZ is an AFE with a sharp dielectric peak near $T_c \sim 236$ °C, and PMW is a *B*-site ordered AFE with a sharp maximum permittivity at $T_c \sim 38$ °C, the Curie temperature in the PZ-PMW system can be engineered over a wide range of temperatures by controlling the amount of PMW in the system. This study deals with the binary compound of PZ-PMW because, to the author's knowledge, there has been no detailed report on the structure and electrical properties of this entire system. In order to obtain more information about the combination of AFE and ordered AFE materials and recognize the properties of PZMW ceramics, this paper attempted to carry out synthesis of the quasibinary solid solu-

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tion, $\text{Pb}[\text{Zr}_{(1-x)}(\text{Mg}_{1/2}\text{W}_{1/2})_x]\text{O}_3$ with $x=0.0-0.1$, using the wolframite precursor method. This paper also reported some properties of the ceramics obtained.

II. EXPERIMENTAL PROCEDURE

Samples of $\text{Pb}[\text{Zr}_{(1-x)}(\text{Mg}_{1/2}\text{W}_{1/2})_x]\text{O}_3$, $x=0.00, 0.02, 0.04, 0.06, 0.08$, and 0.10 , were synthesized from high-purity ($>99\%$) oxides via a modified wolframite-type route. The wolframite (MgWO_4) was initially prepared by mixing starting magnesium oxide (MgO) and tungsten (VI) oxide (WO_3). Single phase formation of MgWO_4 was confirmed by XRD. The wolframite precursor was then mixed and ball milled with predetermined amounts of PbO (with 2 at. % excess) and ZrO_2 powders. The mixture was calcined in an alumina crucible at 900°C for 2 h to form phase-pure perovskite powders. The calcined powders were milled for 6 h to reduce the particle size. After grinding and sieving, the calcined powder was mixed with a 5 wt % polyvinyl alcohol binder and uniaxially pressed into a pellet. The binder burn-out occurred by slowly heating the pellets to 500°C and holding them at that temperature for 2 h. Sintering occurred between 1100 and 1250°C with a dwell time of 4 h depending on the composition. To mitigate the effects of lead loss during sintering, the pellets were sintered in a closed alumina crucible containing PbZrO_3 powder. The density of the sintered PZ-PMW pellets was measured by the Archimedes water immersion method. The relative density of all the sintered pellets was approximately 96%–97% of the theoretical density. The crystal structure of the sintered ceramics was analyzed by XRD (Bruker D8 Advance diffractometer). To determine the dielectric and FE properties, the maximum density of each composition sample was lapped on their major faces, and silver electrodes were made from a low-temperature silver paste by firing at 550°C for 30 min to enable recording of electrical measurements. The relative permittivity (ϵ_r) (calculated from the capacitance using the sample dimensions and sample thickness) and dissipation factor ($\tan \delta$) of stress-free samples were measured using a precision LCR meter (HP-4284A, Hewlett-Packard, Palo Alto, CA). The capacitance and dissipation factors of the samples were measured at 100 Hz–1 MHz, the temperature varied between 25 and 300°C , and a heating rate of $2^\circ\text{C}/\text{min}$ was used while measurements were being taken. The phase transitions were also measured by a differential scanning calorimeter (DSC 2920, TA Instrument) between ambient temperature and 350°C at a rate of $10^\circ\text{C}/\text{min}$. The FE polarization versus electric field (P - E) measurements were made using an RT66A standard FE test system with a frequency of about 4 Hz. The peak field was maintained at 30 kV/cm during measurement.

III. RESULTS AND DISCUSSION

A. Crystal structure

XRD patterns for the $(1-x)\text{PZ}$ - $x\text{PMW}$, $x=0.0-0.1$, are presented in Fig. 1. The complete crystalline solutions of a perovskite structure were formed throughout the whole composition range. Evidence of the pyrochlore or other second

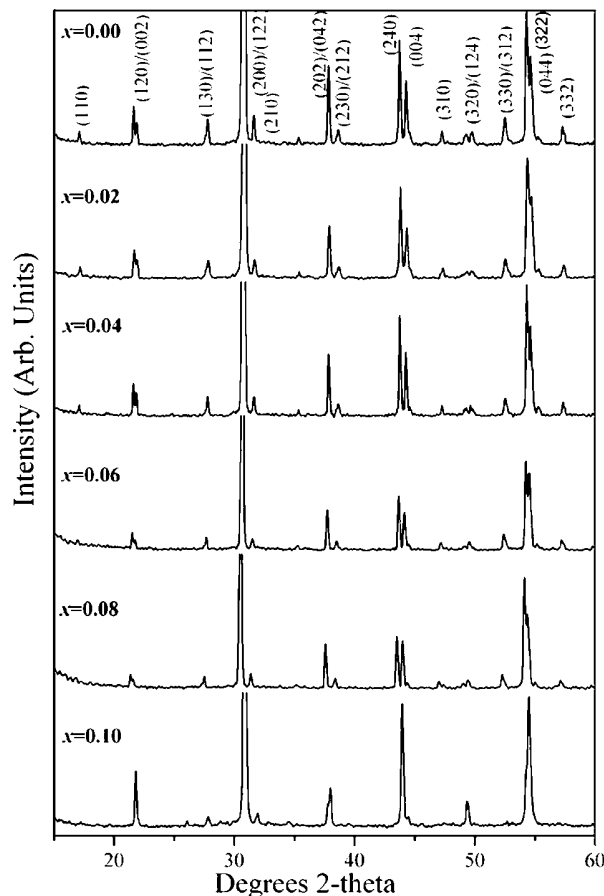


FIG. 1. XRD profiles for $(1-x)\text{PZ}$ - $x\text{PMW}$ obtained at optimum sintering temperature.

phases was not detected in the patterns. It is believed that Mg^{2+} and W^{6+} ions diffuse into PZ lattices to form a solid solution. In general, XRD patterns of pure PZ ceramic exhibit $\frac{1}{4}(hkl)$ superlattice reflections arising from the antiparallel displacements of Pb^{2+} ions. Meanwhile, XRD patterns of perovskite PMW display $\frac{1}{2}(hkl)$ superlattice reflections, resulting from the ordering of B -site ions in an ABO_3 structure. Figure 1 shows that the $\frac{1}{4}(hkl)$ superlattice reflections were clearly presented in all compositions. Unfortunately, the $\frac{1}{2}(hkl)$ superlattice reflections were not detected, indicating that the long range Mg/W/Zr cation order was not developed. Furthermore, the intensity of $\frac{1}{4}(hkl)$ superlattice reflections decreased with increased $\text{Mg}^{2+}/\text{W}^{6+}$ content. This result indicates that the replacement of the Zr^{4+} ions by $\text{Mg}^{2+}/\text{W}^{6+}$ ions decreases the driving force for an antiparallel shift of Pb^{2+} ions.

Figure 2 shows enlarged profiles of the (111) , (240) , and $\frac{1}{4}(hkl)$ superlattice reflections for determining the crystal structure of the as-sintered ceramics. Based on the careful XRD spectra study of the $\frac{1}{4}(hkl)$ superlattice reflection, (111) and (240) reflections in Fig. 2, a phase transformation from the orthorhombic to the rhombohedral structure was found to occur with increasing PMW content. The XRD data show that the $\frac{1}{4}(hkl)$ superlattice reflection peak (*) and splitting of (240) peaks are clearly observed in the composition $x=0.0-0.08$, indicating that the major

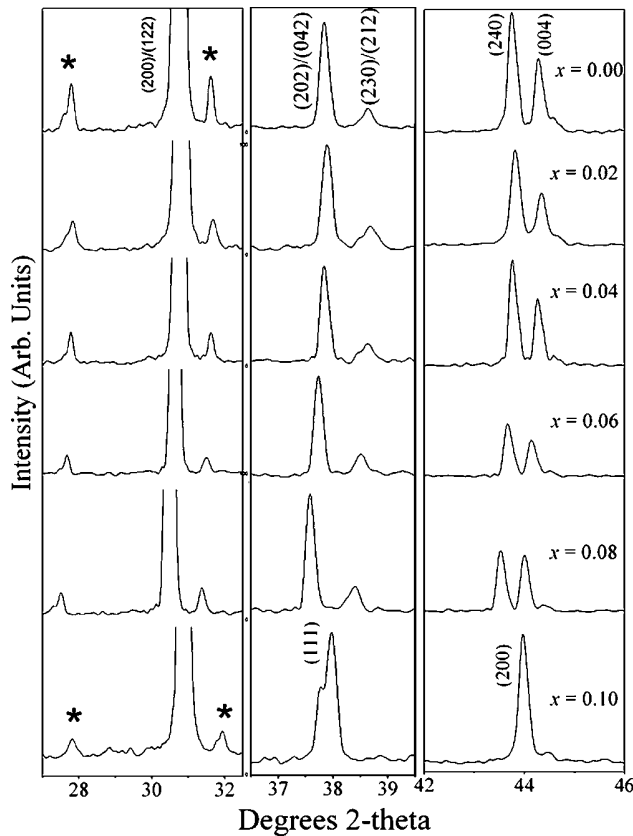


FIG. 2. XRD profiles for the $\frac{1}{4}(h k l)$ superlattice reflection (*) and (200) peaks of $(1-x)\text{PZ}-x\text{PMW}$, $x=0.00-0.10$, ceramics.

phase in those compositions had an orthorhombic symmetry. At $x=0.1$ composition, the split (2 4 0) peaks from an orthorhombic symmetry were rapidly combined into a single peak, and the (1 1 1) diffraction peaks began to split, indicating that the crystal transformed into a rhombohedral symmetry. However, the $\frac{1}{4}(h k l)$ superlattice reflections still remained. This indicates that both orthorhombic and rhombohedral phases coexist in this composition. Nevertheless, hysteresis loop results indicated that the $x=0.1$ composition shows an AFE phase at room temperature. We believe that this composition is within the orthorhombic-rich side of the coexistent phase. It is interesting to note that the phase evolution sequence in the present PZ-PMW system is very similar to that in the $\text{Pb}_{(1-x)}\text{Ba}_x\text{ZrO}_3$,¹⁶ $\text{PbZrO}_3-\text{Pb}(\text{Co}_{1/3}\text{Nb}_{2/3})\text{O}_3$,¹⁷ $\text{PbZrO}_3-\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$,¹⁸⁻²⁰ and $\text{PbZrO}_3-\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ^{21,22} systems.

B. Dielectric properties

The temperature dependencies of the relative permittivity and dielectric losses during as-sintered ceramic heating are shown in Fig. 3. A pure PZ ceramic shows the first order phase transition. The temperature dependence of relative permittivity shows discontinuities at the transitions, and the maximum relative permittivity is 3600. Above the Curie temperature, the relative permittivity follows the Curie-Weiss law, $\epsilon_r = C/(T-T_0)$, with the Curie constant $C \sim 1.59 \times 10^{-5} \text{ K}$ and Curie-Weiss temperature $T_0 \sim 191^\circ\text{C}$. The fact that the Curie-Weiss temperature T_0 is lower than the transition temperature ($T_c = 231^\circ\text{C}$) confirms the first order type of the phase transition in PbZrO_3 . The measured Curie

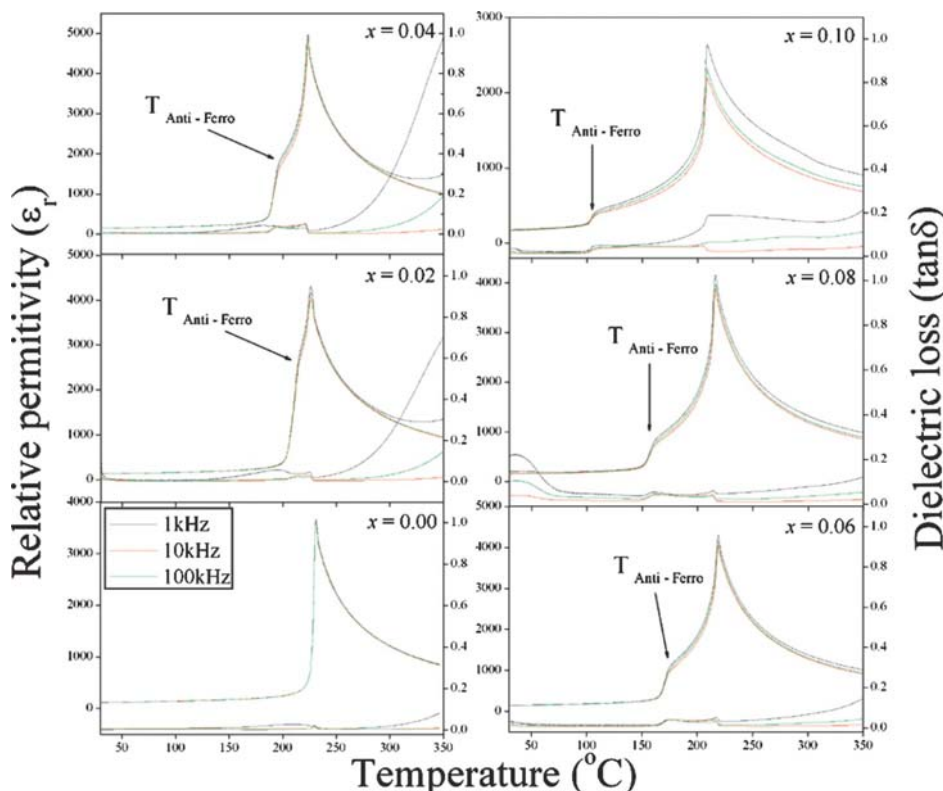


FIG. 3. (Color online) Relative permittivity (ϵ_r) and dielectric loss ($\tan \delta$) as a temperature function of $(1-x)\text{PZ}-x\text{PMW}$, $x=0.00-0.10$, ceramics.

TABLE I. Dielectric properties of $(1-x)\text{PZ}-x\text{PMW}$, $x=0.00-0.10$, ceramics.

Compositions	Crystal structure	$\epsilon_{r,\text{room}}$	$\epsilon_{r,\text{max}}$	$T_{\text{AFE-FE}}$ (°C)	$T_{\text{FE-PE}}$ (°C)
$x=0.00$	O	116	3670	...	231
$x=0.02$	O	140	4318	214	226
$x=0.04$	O	150	4836	195	222
$x=0.06$	O	155	4057	174	219
$x=0.08$	O	200	4160	160	216
$x=0.10$	O+R	180	2643	105	206

O is the orthorhombic phase and R is the rhombohedral phase.

constant and Curie–Weiss temperature are in close agreement with that reported by Sawaguchi.^{18,19} For the composition $x=0.02$, there were two distinct changes in both dielectric peak and loss. The first one occurred at around 214 °C, where both relative permittivity and dielectric loss increased by one order of magnitude. This anomaly is due to the transformation from the AFE to the FE intermediate phase. Later FE data descriptions supported this assumption.

The dielectric anomaly corresponding to the AFE-FE transition was also observed at 195, 174, and 160 °C, and at 105 °C for compositions $x=0.04$, 0.06, 0.08, and 0.1. The value of relative permittivity at the AFE-FE phase transition temperature decreases with increasing PMW content from 2700 for $x=0.02$ to 400 for $x=0.1$. Crystal structure, dielectric data, and transition temperature are summarized in Table I. The temperature range width of the FE phase increases progressively with PMW content. It is interesting to note that all compositions show the AFE-FE phase transition temperature higher than room temperature, and an AFE state is expected to be observed in all compositions at room temperature.

The second abrupt change occurred at the dielectric maximum ($\epsilon_{r,\text{max}}$). This anomaly is linked to the transition of the FE into the cubic PE phase. Dielectric results have shown a significant difference in $\epsilon_{r,\text{max}}$ across the composition range. This may be due to the ionic size difference between Zr^{4+} and $\text{Mg}^{2+}/\text{W}^{6+}$. However, the transition temperature is well dispersed over the compositions. The FE-PE transition temperature ($T_{\text{FE-PE}}$) decreases nearly linearly at the rate of 2.28 °C/mol % of PMW when compared with its value for pure PZ. It is noticeable that this rate is much less than PZ-PNN (2.81 °C/mol %).^{18,19}

C. FE properties

To clarify the dielectric behavior of the FE intermediate phases further in the PZ-PMW system, electrical polarization hysteresis loop measurements were performed under a peak field of 30 kV. At 30 °C, no FE hysteresis loop was observed in the composition $0.0 \leq x \leq 0.1$. The linear polarization was observed, as a function of electric fields, in a range of up to 30 kV/cm. This could indicate that ceramics with the composition $x \leq 0.1$ have an AFE behavior at room temperature. For AFE ceramics, the net remanent polarization (P_r) is zero due to the existence of the antiparallel dipole moments. To induce an AFE-FE phase transition, an intense electric field needs to be applied to the ceramics. However, it is well

known that the electric field required for inducing the AFE-FE transition at room temperature in PZ ceramics is usually higher than the breakdown strength of the ceramics. FE data support the assumption of an existing AFE stage at room temperature in dielectric results.

Figures 4(a)–4(d) show the changes in the hysteresis loop with rising temperature for the 0.9PZ-0.1PMW ceramic. The FE hysteresis loop was recorded after the temperature was stabilized for at least 5 min. As shown in Fig. 4(a), very small polarizations can be induced by the electric field applied in the ceramic at room temperature. This is typical of an AFE ceramic subjected to electric fields that are not sufficient enough to induce the AFE to FE phase transition. Such linear behavior with minimum polarization remains at temperatures of up to 100 °C [Fig. 4(b)].

When the temperature was raised to 150 °C, a regular hysteresis loop exhibiting ferroelectricity was clearly demonstrated, corresponding to the intermediate phase between 105 °C and $T_{\text{FE-PE}}$ [Fig. 4(c)]. At 150 °C, the $P_r = 19.2 \mu\text{C}/\text{cm}^2$ and $E_c = 7.9 \text{ kV}/\text{cm}$ were observed. Above $T_{\text{FE-PE}}$, a linear curve was also seen as an indication of the cubic PE phase [Fig. 4(d)].

D. Thermal properties

The DSC technique was used as the secondary tool to investigate and confirm the phase transition of PZ-PMW ceramics with increasing PMW concentration. The phase transition temperature in PZ-PMW ceramics, clearly confirmed by DSC measurement, is presented in Fig. 5, which shows that two distinct endothermic peaks were observed for PZ-PMW samples with $0.0 \leq x \leq 0.10$. The lower temperature corresponds to the transition temperature of the AFE→FE phase transition, while the higher temperature corresponds to the FE→PE phase transition. AFE→FE phase transition, FE→PE phase transition, ΔH , ΔS , and $\Delta S/T_i$ are summarized in Table II. The AFE→FE phase transition was found in the composition $0.0 \leq x \leq 0.10$. The peaks shifted to lower temperatures with higher compositions of x . In Table II, the temperature range width of progressive FE phase continuously increases with PMW content. The temperature range widths of the FE phase are around 7.5, 25, 40, 52.6, 67.5, and 80 °C for compositions $x=0.00$, 0.02, 0.04, 0.06, 0.08, and 0.10, respectively. The peak value of heat capacity became weaker, and the heat capacity anomaly gradually broader, with increasing PMW concentration. These results

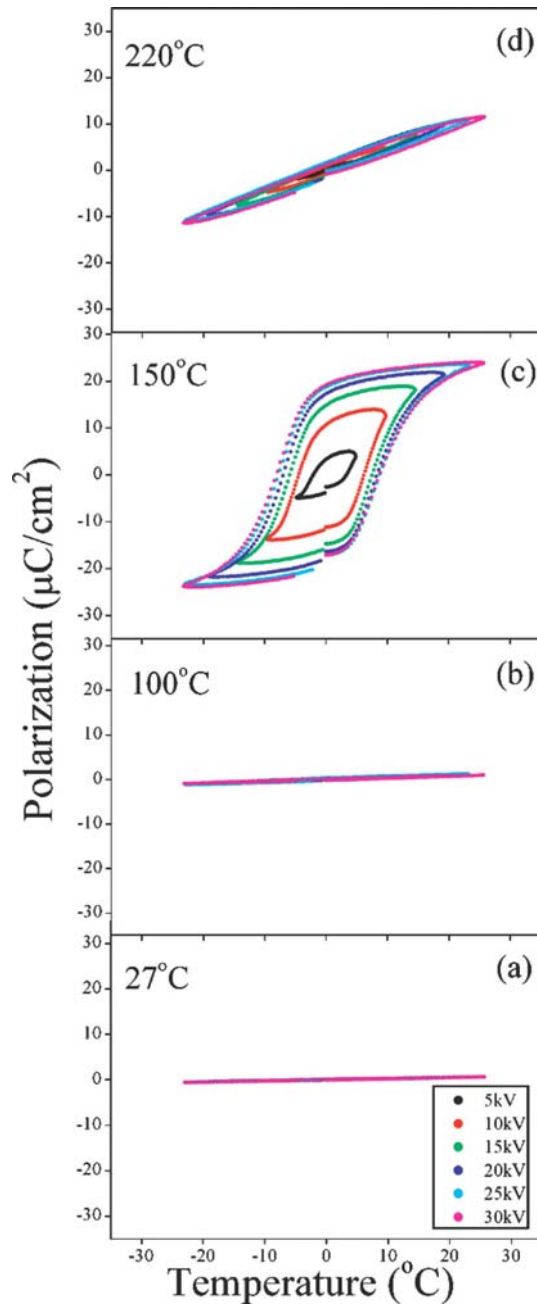


FIG. 4. (Color online) Polarization hysteresis loops recorded from 0.9PZ-0.1PMW at 4 Hz during heating at (a) 25 °C, (b) 100 °C, (c) 150 °C, and (d) 200 °C.

indicated that the phase transition deviates gradually from the first order type. Stenger and Burggraaf²³ observed that the change in entropy (ΔS) and $\Delta S/T_i$ correlates with the fluctuation probability in conjunction with a small spontaneous lattice deformation and polarization. They explained that large values of the ratio, $\Delta S/T_i$, give sharp transition and lower values, which lead to diffuse behavior. Table II shows small ΔS and $\Delta S/T_i$ values for the PMW doped sample when compared to the pure PZ sample, indicating existence of diffuseness in the phase transition behavior that increases with increased PMW content, which coincides well with the dielectric results in the composition range investigated.

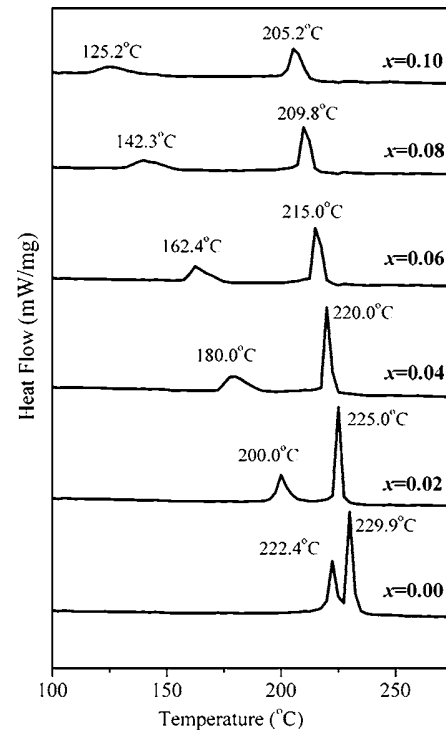


FIG. 5. Typical DSC curves for $(1-x)\text{PZ}-x\text{PMW}$, $x=0.0-0.1$, ceramics.

E. FE phase diagram

After accumulating all these data, a FE phase diagram for the $(1-x)\text{PZ}-x\text{PMW}$, $x=0.0-0.1$, was finally determined and is shown in Fig. 6. The phase diagram consists of three distinct crystallographic phases in this system: high-temperature PE cubic, FE rhombohedral, and AFE orthorhombic. At room temperature, the composition $0.0 \leq x \leq 0.08$ has an AFE orthorhombic phase. With increasing temperature, an AFE orthorhombic to a FE rhombohedral phase was observed in the samples with $0.02 \leq x \leq 0.10$. The temperature range width of the FE rhombohedral phase increases progressively with PMW content. At room temperature, the phase boundary between the AFE orthorhombic and FE rhombohedral phases was observed near $x=0.10$.

IV. CONCLUSIONS

In this work, the phase transition and dielectric properties of the solid solution between AFE PZ and AFE PMW have been investigated. AFE PMW has been found to strongly influence the phase development and physical property responses of PZ ceramics. The crystal structure data obtained from XRD indicate that the solid solution, $(1-x)\text{PZ}-x\text{PMW}$, where $x=0.0-0.1$, successively transforms from orthorhombic to rhombohedral phase with an increase in PMW concentration. The coexistence of orthorhombic and rhombohedral phases in this binary system is located near the composition $x=0.1$.

ACKNOWLEDGMENTS

This work was supported by the Thailand Research Fund (TRF), National Research Council of Thailand (NRCT), and

TABLE II. Thermal properties of $(1-x)\text{PZ}-x\text{PMW}$, $x=0.00-0.10$, ceramics.

Compositions	$T_{\text{AFE-FE}}$ (°C)	$T_{\text{FE-PE}}$ (°C)	ΔH (J g ⁻¹)	$\Delta S \times 10^3$ (J g ⁻¹ K ⁻¹)	$(\Delta S/T_l) \times 10^6$ (J g ⁻¹ K ⁻²)
$x=0.00$	222	230	2.227	9.682	42.096
$x=0.02$	200	224	2.148	9.568	42.169
$x=0.04$	180	220	2.354	10.676	48.416
$x=0.06$	163	216	2.325	10.764	49.830
$x=0.08$	140	211	1.956	9.270	43.934
$x=0.10$	123	205	1.855	9.049	44.141

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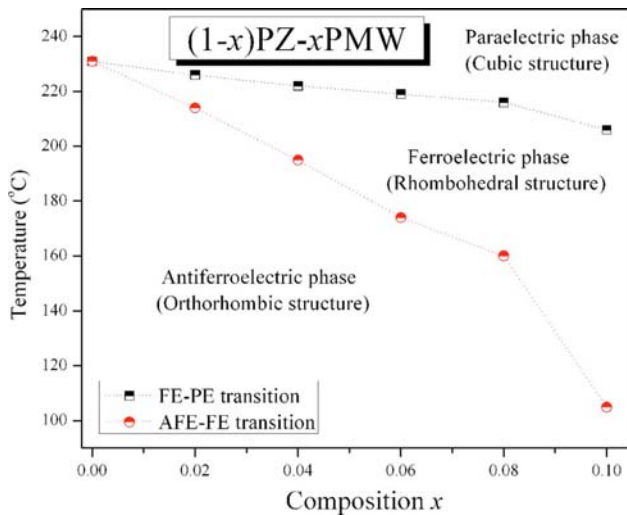


FIG. 6. (Color online) FE phase diagram of $(1-x)\text{PZ}-x\text{PMW}$, $x=0.0-0.1$, system.

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Antiferroelectric–ferroelectric phase transition in lead zinc niobate modified lead zirconate ceramics: crystal studies, microstructure, thermal and electrical properties

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Abstract The combination of antiferroelectric PbZrO_3 (PZ) and relaxor ferroelectric $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ was prepared via the columbite precursor method. The basic characterizations were performed using X-ray diffraction (XRD), scanning electron microscopy (SEM), linear thermal expansion, differential scanning calorimetry (DSC) techniques, dielectric spectroscopy, and hysteresis measurement. The XRD result indicated that the solid solubility limit of the $(1-x)\text{PZ}-x\text{PZN}$ system was about $x = 0.40$. The crystal structure of $(1-x)\text{PZ}-x\text{PZN}$ transformed from orthorhombic to rhombohedral symmetry when the concentration of PZN was increased. A ferroelectric intermediate phase began to appear between the paraelectric and antiferroelectric phases of pure PZ, with increasing PZN content. In addition,

the temperature range of the ferroelectric phase increased with increasing PZN concentration. The morphotropic phase boundary (MPB) in this system was located close to the composition, $x = 0.20$.

1 Introduction

Ferroelectric materials are extensively used for many different electronic devices, such as actuators, transducers, and multilayer capacitors [1–3]. Study over several decades has focused mainly on the development of physical and electrical properties of ferroelectric materials [2, 3]. Many ferroelectric ceramics have been developed from binary systems containing a combination of antiferroelectric and normal ferroelectric ceramics such as $(1-x)\text{PbZrO}_3-x\text{PbTiO}_3$ (PZ–PT, PZT) [3, 4], and $(1-x)\text{SrTiO}_3-x\text{PbZrO}_3$ [4, 5]. Among them, PZT is a very famous ferroelectric ceramic, due to its exhibition of high piezoelectric coefficient and electromechanical coupling factor around the morphotropic phase boundary (MPB) [3, 4]. The combination of normal ferroelectric and relaxor ferroelectric ceramics also shows excellent piezoelectric and dielectric properties such as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--PbTiO}_3$ (PMN–PT) [5], $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--PbTiO}_3$ (PZN–PT) [6, 7], $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--Pb}(\text{Zr}_{1/2}\text{Ti}_{1/2})\text{O}_3$ (PZN–PZT) [8], and $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--Pb}(\text{Zr}_{1/2}\text{Ti}_{1/2})\text{O}_3$ (PNN–PZT) [9]. Furthermore, PZN–PZT, PNN–PZT, and $\text{Pb}(\text{Zr}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{--Pb}(\text{Co}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PZT–PCN) [8–10] ceramics show high, relative permittivity.

Metal oxide Lead zirconate (PbZrO_3 , PZ) is a prototype of antiferroelectric ceramics. The PZ phase changes from the orthorhombic antiferroelectric phase (AFE) to cubic paraelectric phase (PE) at 236°C , and a ferroelectric phase (FE) exists over a very narrow temperature range

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(230–233°C) [11]. Stability of the ferroelectric phase can be altered by substitutions such as Ba^{2+} ions or La^{3+} ions at the A-site of the perovskite structure (ABO_3) [12–14]. Besides, PZ-based thin films are also particularly interesting because of the characteristic hysteresis loop resulting from the electric field-induced antiferroelectric-to-ferroelectric phase switching [14, 15]. Our recent work reported that the combination of antiferroelectric PZ and relaxor ferroelectric (RFE), $\text{Pb}(\text{Co}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PCoN), or $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PNN) can also induce the ferroelectric phase of PZ [16, 17]. Nevertheless, due to PCoN and PNN having a low transition temperature ($T_m \sim -90^\circ\text{C}$ and $\sim -120^\circ\text{C}$ for PCoN and PNN, respectively), the transition temperature of PZ–PCoN and PZ–PNN systems was dramatically decreased [17, 18].

Complex metal oxide lead zinc niobate ($\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$, PZN) is an RFE material with a rhombohedral perovskite structure at room temperature. A diffuse phase transition from paraelectric to ferroelectric polar state occurs at the high temperature of 140°C [6, 7]. There has been extensive research carried out on single PZN crystals because of their high relative permittivity ($\epsilon_{r,10\text{kHz}}$ reaching 50,000), pyroelectric constant ($P_{20^\circ\text{C}} = 7 \times 10^{-12} \text{ C/m}^2 \text{ K}$) [6], high piezoelectric coefficient ($d_{33} \approx 1100 \text{ pC/N}$), and high electromechanical coupling factors ($k_{33} \approx 92\%$) [7]. Single crystals of PZN can be prepared by the flux-growth method, but pure perovskite PZN ceramics are difficult to synthesize via the conventional mixed-oxide method under atmospheric pressure [19, 20]. It is well known that forming solid solutions with other perovskites such as $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$, BaTiO_3 , and SrTiO_3 [20, 21] is considered an effective way to stabilize the perovskite PZN ceramic.

As both PZ and PZN have a perovskite structure, it has been suggested that PZN can be alloyed with PZ in order to stabilize the perovskite structure and find a suitable composition across the MPB. To the best of the author's knowledge, there has been no detailed report on the structure, solubility limit, dielectric properties, thermal properties, or phase transition in this system. Additionally, as PZN is a relaxor ferroelectric with broad dielectric peak near $T_m \sim 140^\circ\text{C}$, and PZ is an antiferroelectric with sharp maximum permittivity at $T_c \sim 230^\circ\text{C}$, the Curie temperature in the PZ–PZN system can be engineered over a wide range of temperatures via control of the PZN amount in the system. With a complementary characteristic, it is expected that excellent properties can be obtained from PZ–PZN ceramics. The relationship between the phase evolution and the properties was emphasized.

2 Experiment

The composition series of $(1-x)\text{PbZrO}_3-x\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ceramics, where $x = 0.00, 0.02, 0.04, 0.06, 0.08, 0.10,$

0.20, 0.30, 0.40, and 0.50 were fabricated via a columbite precursor. The reagent-grade oxide powders of PbO (99.9%, Aldrich, Milwaukee, WI, USA), ZnO (99.9%), Nb_2O_5 (99.5%), and ZrO_2 (99.6%) were used as starting raw materials. Prior to reaction with other raw materials, ZnO was reacted with Nb_2O_5 at 975°C for 4 h to form ZnNb_2O_6 . The precursors, ZnNb_2O_6 , ZrO_2 , and PbO (with 2 mol% excess PbO), were weighed and mixed well by ball-milling in a polyethylene bottle together with methyl alcohol and partially stabilized zirconia balls. Methyl alcohol was removed by heating at 80°C for appropriate durations, and then the mixture was dried at 150°C for 24 h. After drying, the mixed powders were calcined at $750\text{--}850^\circ\text{C}$ for 4 h in a covered Al_2O_3 crucible. After that, all compositions of $(1-x)\text{PZ}-x\text{PZN}$ were ball-milled again for 18 h. The calcined powders were sieved and uniaxially cold-pressed at 300 MPa. The disks were sintered at $1,200\text{--}1,250^\circ\text{C}$ for 4 h depending on the composition. To compensate PbO volatilization; the PbO atmosphere for the sintering was maintained using PbZrO_3 as the spacer powder.

The crystal structure and phase transition of the sintered pellets were characterized using an X-ray diffractometer (XRD; Bruker-AXS D8, $\text{CuK}\alpha$ radiation). The density of PZ–PZN ceramics was measured via Archimedes water immersion method. Scanning electron microscopy (SEM; Hitachi, s4007) was employed to investigate the microstructure of sintered pellets. The phase transition of samples was investigated using a differential scanning calorimeter (DSC 2920, TA Instrument) between room temperature and 300°C at a heating rate of $10^\circ\text{C}/\text{min}$. To confirm the phase transition of samples, the sintered pellets were measured by a dilatometer (DIL 402 PC, Netzsch) between $25\text{--}300^\circ\text{C}$ at a rate of $1^\circ\text{C}/\text{min}$. For the measurement of electrical properties, both sides of the maximum density of each composition sample were polished and electroded with silver paste (C1000, Heraeus). An LCR meter (HP4284A, Hewlett-Packard, Palo Alto, CA) was used to measure the dielectric properties, and the temperature varied between $25\text{--}350^\circ\text{C}$ with a heating rate of $2^\circ\text{C}/\text{min}$. The polarization–electric field (P – E) hysteresis loops were obtained at room temperature using a standardized ferroelectric tester system (RT-66A, Radiant Technologies, Albuquerque, NM) at a frequency of 4 Hz.

3 Results and discussion

3.1 Crystal structure

The XRD patterns of the sintered $(1-x)\text{PZ}-x\text{PZN}$ ceramics for $0.00 \leq x \leq 0.50$ are shown in Fig. 1. At the composition, $0.00 \leq x \leq 0.40$, ceramic samples had a pure perovskite structure. Evidence for the secondary phases was

not observed in the patterns, indicating homogeneous solid solution of PZ–PZN. However, increasing the amount of PZN further to 50 mol%, gave rise to formation of the pyrochlore phase, $\text{Pb}_{1.88}\text{Zn}_{0.3}\text{Nb}_{1.25}\text{O}_{5.305}$, which could be matched with JCPDS No. 25-0446. This result could explain the larger ionic size of Zn^{2+} ($0.88 \text{ \AA}$) [22], as compared to

the sixfold lattice sites formed by the oxygen octahedra. Then, Zn^{2+} cannot enter the B-site of the perovskite structure as a replacement for Zr^{4+} ($0.86 \text{ \AA}$) ions [22]. This result indicated that the solubility limit of the $(1-x)\text{PZ}-x\text{PZN}$ system was found at $x = 0.40$. Furthermore, the $1/4(hkl)$ -type superlattice reflection peaks, identified with “*”, arise from antiparallel displacement of Pb^{2+} cations, and this was clearly seen in all compositions. The relative intensity of $1/4(hkl)$ -type superlattice reflection peaks decreased with increasing PZN, which indicated that the substitution of Zr^{4+} ions by $\text{Zn}^{2+}/\text{Nb}^{5+}$ ions decreased the driving force for an antiparallel shift of Pb^{2+} ions.

Figure 2 shows enlarged profiles of the $1/4(hkl)$ -type superlattice reflections (*): $(1\ 1\ 1)$, $(2\ 0\ 0)$, and $(2\ 2\ 0)$ reflections. At the composition, $0.00 \leq x \leq 0.10$, the XRD data exhibit the superlattice reflections and splitting of $(2\ 4\ 0)$ peak at roughly 43° , indicating that the crystal structure of samples at the composition, $0.00 \leq x \leq 0.10$, are orthorhombic perovskite. Furthermore, the compositions, $0.20 \leq x \leq 0.50$, showed a split $(1\ 1\ 1)$ and $(2\ 2\ 0)$ reflection, and single $(2\ 0\ 0)$ reflection, indicating that the crystal structure transformed into a rhombohedral structure. Moreover, the XRD patterns of $0.20 \leq x \leq 0.50$ compositions also showed $1/4(hkl)$ -type superlattice reflections. Therefore, it could be assumed that the orthorhombic and rhombohedral phase coexist in these compositions. Consequently, the composition, $x = 0.20$, is expected to be close to the MPB, whereas the $0.30 \leq x \leq 0.50$ compositions are in the rhombohedral-rich region of the coexistent phase. Elu-

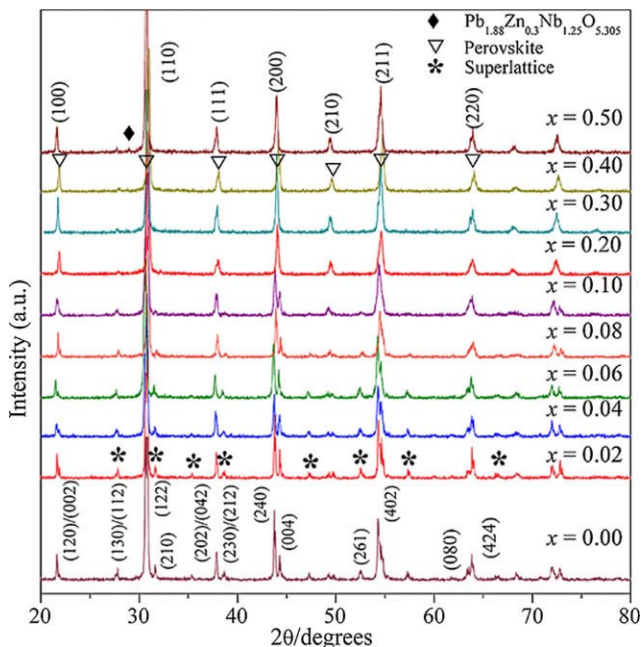


Fig. 1 XRD patterns of sintered ceramics for various compositions of $(1-x)\text{PbZrO}_3-x\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$, where $x = 0.0-0.5$

Fig. 2 XRD patterns of the $1/4(hkl)$ -type superlattice reflections, and the $(1\ 1\ 1)$, $(2\ 0\ 0)$ and $(2\ 2\ 0)$ peaks of $(1-x)\text{PZ}-x\text{PZN}$ ceramics with $x = 0.0-0.5$

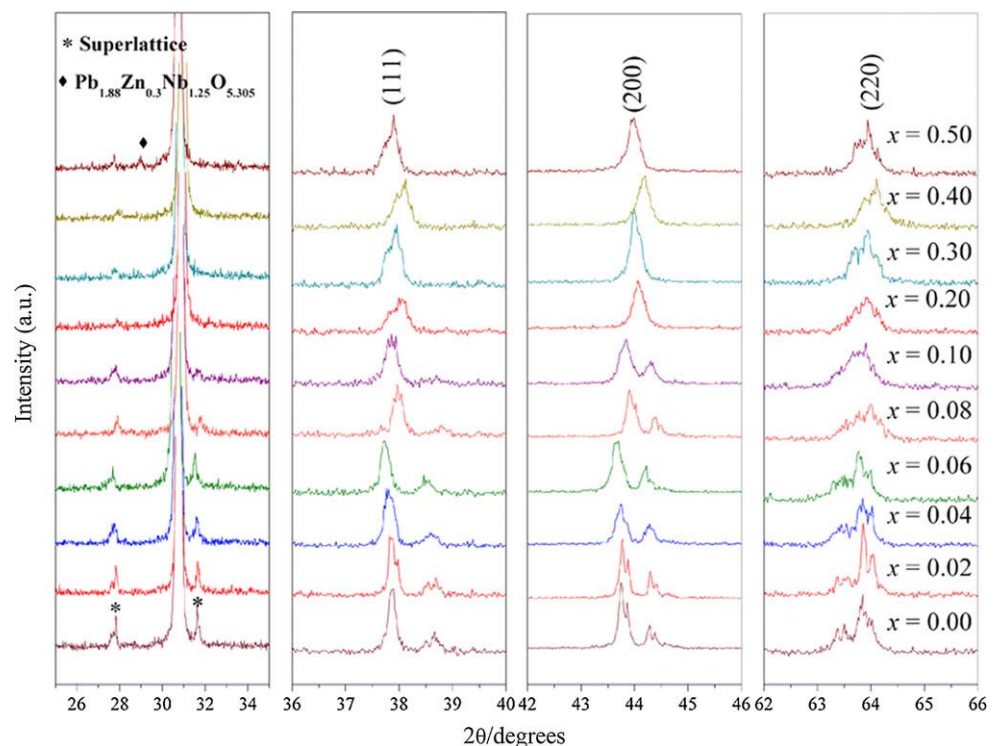
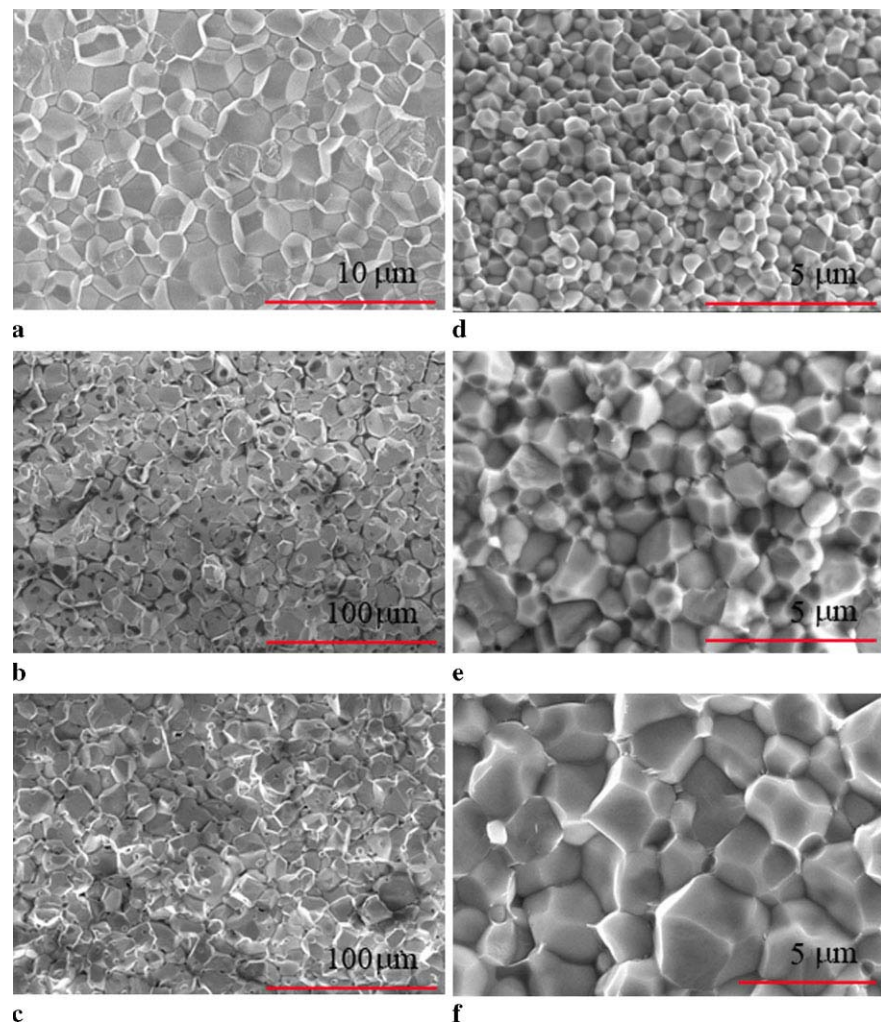


Fig. 3 SEM micrographs of the fractured surfaces of $(1-x)\text{PbZrO}_3-x\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ with various compositions (**a**) $x = 0.00$, (**b**) $x = 0.02$, (**c**) $x = 0.04$, (**d**) $x = 0.10$, (**e**) $x = 0.30$, and (**f**) $x = 0.50$



culated electrical property data later confirmed this assumption. It is interesting to note that the influence of additional $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ on phase transition of the PbZrO_3 system was similar to that of PZ–PMW and PZ–PCoN systems [17, 23].

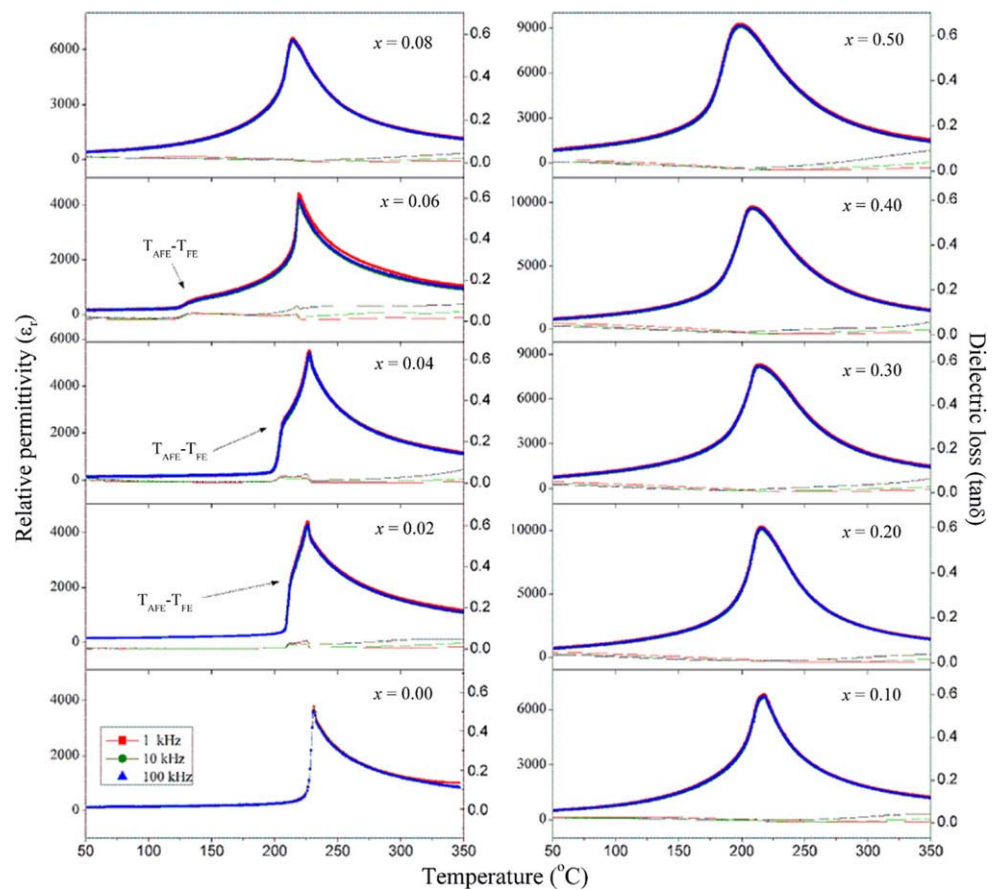
3.2 Microstructure

The effects of PZN amount on the microstructure of $(1-x)\text{PZ}-x\text{PZN}$, where $x = 0.00, 0.02, 0.04, 0.10, 0.30$, and 0.50 ceramics, are shown in Fig. 3. From these micrographs, specimens show the absence of pyrochlore formation. It is interesting to note that at the composition, $x = 0.50$, the pyrochlore phase was detected by XRD but not observed from the SEM micrograph in Fig. 3(f). As the pyrochlore phase was probably located at the surface, and the scale was too small, it did not appear in the SEM micrograph of the fractured surface. This result was similar to that in the PMN system [24]. The ceramics displayed a dense microstructure, and most of the grains were fractured in an intergranular manner. The grain boundaries could be clearly observed,

and then the average grain size was calculated directly by the linear interception method [25]. Physical properties of the sintered $(1-x)\text{PZ}-x\text{PZN}$ ceramics are listed in Table 1. The SEM images in Fig. 3 reveal that the addition of PZN resulted in significant changes in the microstructure of the ceramics. All ceramics exhibited high density with an average grain size range of about 0.54 ± 0.09 to $17.02 \pm 0.19 \mu\text{m}$. The relative densities were obtained in the range of 90–97% of theoretical density. Additionally, shrinkage of about 11–17% of $(1-x)\text{PZ}-x\text{PZN}$ ceramics could be achieved in this study. This value is consistent with other lead-based systems [26]. The average grain size dramatically increased from $\sim 1.80 \mu\text{m}$ in the composition, $x = 0.0$, to approximately $17.02 \mu\text{m}$ in the composition, $x = 0.06$. Conversely, in concentrations of PZN increasing to $x = 0.08$, the grain size significantly decreased with increasing PZN. From these results, it can be assumed that a small amount of PZN substitution improves the sinterability of the ceramic. While excessive PZN substitution was segregated at the grain boundary, which acts as impuri-

Table 1 Physical properties of $(1-x)\text{PbZrO}_3-x\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ceramics (R, Rhombohedral; O, Orthorhombic; Pyr, Pyrochlore)

Composition (x)	Crystal structure	Average grain size (μm)	Shrinkage (%)	Relative density (%)
0.00	O	1.80 ± 0.31	15.0 ± 0.02	97.2 ± 0.11
0.02	O	11.96 ± 0.21	11.0 ± 0.01	89.8 ± 0.21
0.04	O	12.22 ± 0.17	12.7 ± 0.03	93.3 ± 0.33
0.06	O	17.02 ± 0.19	13.5 ± 0.03	92.5 ± 0.30
0.08	O	1.20 ± 0.15	12.9 ± 0.02	91.1 ± 0.13
0.10	O	0.54 ± 0.09	13.9 ± 0.01	94.3 ± 0.09
0.20	O + R	0.77 ± 0.26	13.9 ± 0.02	93.0 ± 0.16
0.30	R-rich	0.95 ± 0.16	15.6 ± 0.01	93.8 ± 0.14
0.40	R-rich	1.59 ± 0.31	17.1 ± 0.01	95.1 ± 0.18
0.50	R-rich + Pyr	1.96 ± 0.48	17.3 ± 0.01	94.4 ± 0.39

Fig. 4 Temperature dependence of dielectric properties of $(1-x)\text{PbZrO}_3-x\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ceramics

ties, the grain growth was inhibited. This phenomenon was similar to those in other solid solution systems [27].

3.3 Dielectric properties

The relative permittivity of $(1-x)\text{PZ}-x\text{PZN}$ ceramics, as a function of temperature at differently applied frequencies between 1 and 100 kHz, are given in Fig. 4. At the compo-

sition, $0.00 < x \leq 0.06$, two distinct dielectric peaks were observed. The phase transitions at lower temperatures were due to transformation from the orthorhombic antiferroelectric phase to rhombohedral ferroelectric phase [16], while the maximum dielectric was linked with the transformation of the rhombohedral ferroelectric phase into the cubic paraelectric phase [17, 23]. Later descriptions in ferroelectric data supported this finding.

Table 2 Phase transition temperatures and enthalpy of $(1-x)\text{PbZrO}_3-x\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ceramics

Composition (<i>x</i>)	Phase transition temperature (°C)						ΔH (J g ^{−1})	$\Delta S \times 10^3$ (J g ^{−1} K ^{−1})	$\Delta S/T_i \times 10^6$ (J g ^{−1} K ^{−2})
	Dielectric constant		Thermal expansion		DSC				
	$T_{\text{AFE-PE}}$	$T_{\text{FE-PE}}$	$T_{\text{AFE-PE}}$	$T_{\text{FE-PE}}$	$T_{\text{AFE-PE}}$	$T_{\text{FE-PE}}$			
<i>x</i> = 0.00	–	233	212	220	208.4	225.6	2.6	11.6	51.7
<i>x</i> = 0.02	212	226	192	213	193.1	224.9	3.3	14.6	64.8
<i>x</i> = 0.04	207	227	181	215	184.7	223.2	3.3	14.7	65.8
<i>x</i> = 0.06	130	219	110	205	137.4	222.1	3.6	16.2	72.8
<i>x</i> = 0.08	–	214	–	200	94.7	219.5	3.3	15.1	68.9
<i>x</i> = 0.10	–	217	–	–	59.0	217.3	2.6	11.8	54.2
<i>x</i> = 0.20	–	216	–	–	–	211.2	1.5	7.1	33.8
<i>x</i> = 0.30	–	213	–	–	–	209.4	0.8	4.0	19.4
<i>x</i> = 0.40	–	210	–	–	–	188.5	0.6	3.4	18.0
<i>x</i> = 0.50	–	200	–	–	–	–	–	–	–

Phase transition temperature of $(1-x)\text{PZ}-x\text{PZN}$ ceramics is summarized in Table 2. The transition temperatures of the AFE to FE phase became lower, and the temperature range width of the FE phase also increased continuously with increasing PZN. For the composition, $x \geq 0.08$, transition of the orthorhombic antiferroelectric phase to rhombohedral ferroelectric phase was not observed. As PZN concentration increased, the diffuse phase transition (DPT) behavior, with broad maximum and frequency dispersion, became more self-evident. The FE to PE transition decreased nearly linearly at the rate of $0.48^{\circ}\text{C}/\text{mol}\%$ of PZN, when compared with its value for pure PZ. Noticeably, this rate was much lower than that of PZ-PCoN ($2.20^{\circ}\text{C}/\text{mol}\%$) [17] and PZ-PNN ($2.81^{\circ}\text{C}/\text{mol}\%$) [18]. The maximum relative permittivity for all compositions is listed in Table 3. The composition, $x = 0.20$, showed the highest value of relative permittivity, and existence of the MPB near this composition was expected. This result is consistent with the X-ray diffraction finding that both orthorhombic and rhombohedral phases coexist in this composition. It was found that the addition of PZN also shifts the transition temperature (T_m) value of PZ-PZN ceramics down from 243°C (T_c for PZ) in the composition, $x = 0.0$, to 199°C in the composition, $x = 0.5$. A similar trend has also been found in the PZ-PNN [18] and PZ-PCoN system [17].

It is well known that the relative permittivity of a normal ferroelectric, which is above the maximum relative permittivity temperatures, can be described by the Curie–Weiss law [4]:

$$\frac{1}{\varepsilon_r} = \frac{T - T_0}{C}, \quad (1)$$

where T_0 is the Curie–Weiss temperature, and C the Curie constant. Above the Curie temperature, the relative permittivity of pure PZ obeys the Curie–Weiss law, with the Curie

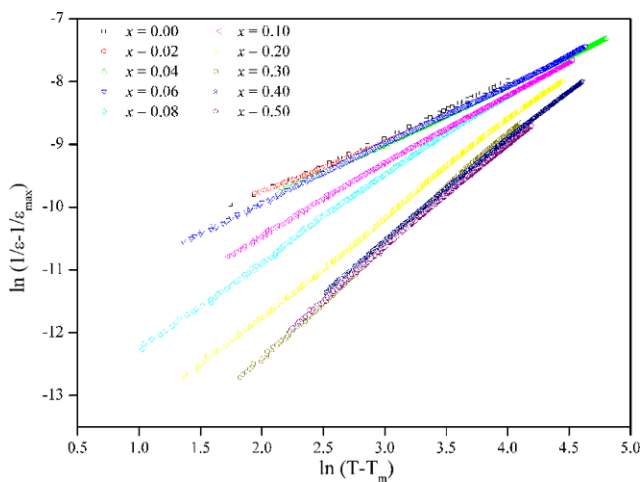
constant $C \sim 1.70 \times 10^5^{\circ}\text{C}$ and Curie–Weiss temperature $T_0 \sim 179^{\circ}\text{C}$. However, a broad relative permittivity of relaxor ferroelectric can be described by a simple quadratic law. The relative permittivity of relaxor ferroelectric above the maximum relative permittivity temperatures can be derived via the following expression [28]:

$$\frac{\varepsilon'_m}{\varepsilon'(f, T)} = 1 + \frac{(T - T_m(f))^{\gamma}}{2\delta_{\gamma}^2} \quad (1 \leq \gamma \leq 2), \quad (2)$$

where ε'_m is the maximum value of the permittivity at $T = T_m(f)$. The value of γ expresses the degree of dielectric relaxation in the relaxor ferroelectric material, when $\gamma = 1$ (2) expresses Curie–Weiss behavior, while $\gamma = 2$ in this equation is identical to the quadratic relationship. Many relaxor ferroelectric materials can fit (2) with $\gamma = 2$ at temperatures above T_{max} . The parameter δ_{γ} can be used to measure the degree of diffuseness of the phase transition in mixed relaxor antiferroelectric materials. The values γ and δ_{γ} are both material constants depending on the structure and composition of the material. The δ_{γ} value can be determined from the slope of $\varepsilon'_m/\varepsilon'$ versus $(T - T_m)^2$, which should be linear. By plotting $\ln(1/\varepsilon - 1/\varepsilon_{\text{max}})$ versus $\ln(T - T_m)$, γ can be determined directly from the gradient. According to (2), the values of $\ln(1/\varepsilon - 1/\varepsilon_{\text{max}})$ for the sintered ceramics measured at 100 kHz are plotted against $\ln(T - T_m)$ in Fig. 5. As shown in the figure, the plotted lines for all samples demonstrate significantly good linearity within the measured temperature range. The intercept and gradient of lines in Fig. 5 are used to calculate and demonstrate γ and δ_{γ} for each sample in Table 3. The value of γ presented in Table 3 varies between 1.02 and 1.81. The δ_{γ} values are increased also from 11.5 to 15.6 with increasing PZN content, thus confirming that a diffuse phase transition occurs in the PZ-PZN system. Nevertheless, a minor swing of γ values

Table 3 Dielectric and ferroelectric properties of $(1-x)\text{PbZrO}_3-x\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ceramics

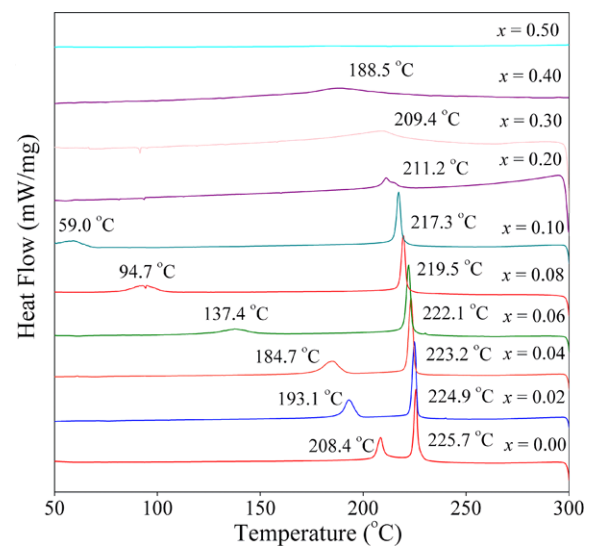
Composition (x)	T_m (°C)	$\epsilon_r \text{ max}$	δ_γ	γ	P_r ($\mu\text{C}/\text{cm}^2$)	P_s ($\mu\text{C}/\text{cm}^2$)	E_c (kV/cm)
0.00	233	2850	11.5	1.02	—	—	—
0.02	226	4400	11.6	1.02	—	—	—
0.04	227	5500	11.8	1.04	—	—	—
0.06	219	4400	11.8	1.08	—	—	—
0.08	214	6600	13.5	1.33	20.20	22.86	17.88
0.10	217	6800	12.6	1.09	22.69	25.69	19.59
0.20	216	10300	14.8	1.55	26.90	31.45	15.52
0.30	213	8300	16.0	1.81	18.59	25.66	13.34
0.4	209	9700	15.3	1.59	20.73	27.48	13.04
0.5	199	9300	15.6	1.65	19.65	26.18	14.80

**Fig. 5** The $\ln(1/\epsilon - 1/\epsilon_{\text{max}})$ vs. $\ln(T - T_m)$ plots for $(1-x)\text{PZ}-x\text{PZN}$ ceramics with $x = 0.00-0.50$

as a function of composition was found in some compositions. For ferroelectric ceramics, it has been established that the degree of dielectric relaxation could also be caused by the decrease of grain size [29], and the observed difference of γ value could be a result of grain size variation. A similar propensity also has been detected in several prior investigations [29, 30].

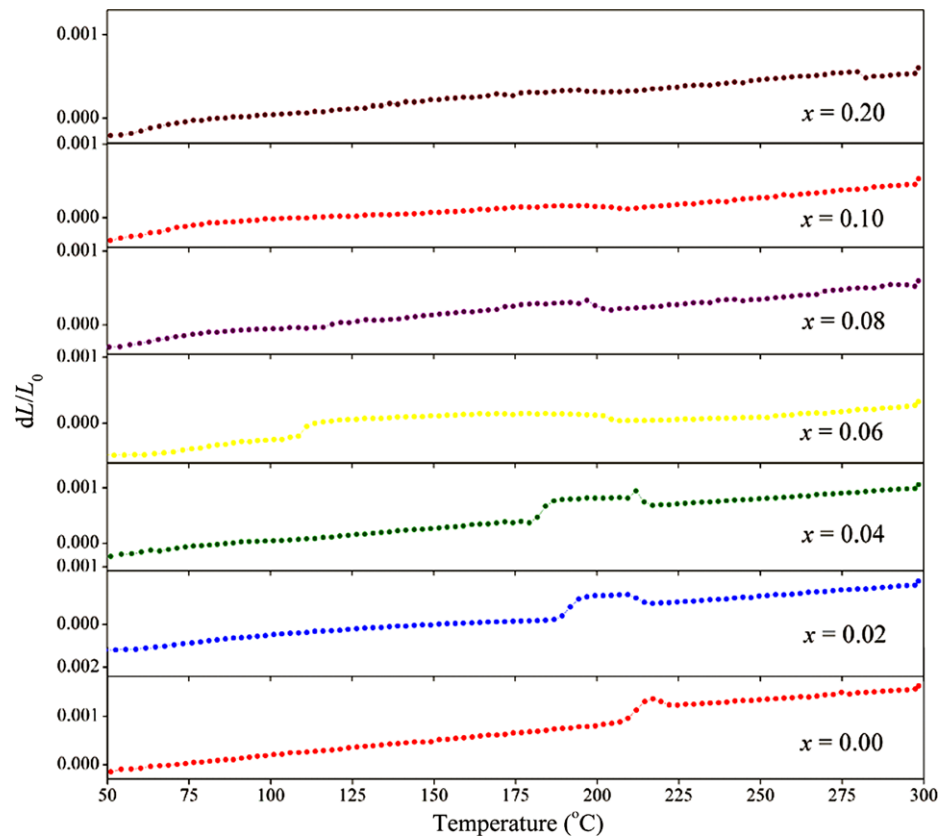
3.4 Thermal properties

The DSC technique was used as a primary tool to confirm the phase transition of the PZ–PZN system. DSC analysis results of the PZ–PZN ceramics are presented in Fig. 6, in which two distinct endothermic peaks for the composition, $0.0 \leq x \leq 0.10$, are observed. The lower temperature corresponds to the transition temperature of the AFE→FE phase transition, while the higher temperature corresponds to the FE→PE phase transition. The AFE→FE peaks shift to lower temperatures, with a higher composition of x . This

**Fig. 6** Typical differential scanning calorimetry (DSC) curves for $(1-x)\text{PZ}-x\text{PZN}$ ceramics with $x = 0.00-0.50$

result corresponds to a decreasing AFE phase, and the temperature range width of the FE phase increases, with increasing amounts of PZN content. Moreover, the endothermic peaks become progressively broader, while the areas under these peaks (ΔH) decrease with increasing PZN content. These results indicate that phase transition diverges from the first-order type. Burggraaf et al. [31] reported that the change in entropy (ΔS) and $\Delta S/T_i$ related to fluctuation in conjunction with a small spontaneous lattice deformation and polarization. They also reported that large values of the $\Delta S/T_i$ ratio give sharp phase transition, whereas the lower values lead to diffusing phase transition. Transition temperatures and the values of ΔH , ΔS , and $\Delta S/T_i$ for all compositions are calculated and summarized in Table 2. Notably, the values of $\Delta S/T_i$ gradually reduce, which indicates that the diffuse phase transition behavior of PZ–PZN increases with increased PZN.

Fig. 7 Thermal expansion curves of $(1-x)\text{PbZrO}_3-x\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ceramics in heating



It is well known that in phase transition from AFE to FE or FE to PE the volume of material yields abrupt changes. Therefore, the thermal expansion measurement was employed as a secondary tool to confirm the phase transition sequence. Figure 7 shows thermal expansion curves for the PZ–PZN system. In the expansion curves of $0.00 < x \leq 0.06$, with rising temperature, the volume expansion that resulted from the transformation of AFE to FE, and the small volume contraction of FE to PE transition, were observed. The thermal expansion curves exhibited FE to PE phase transition only when the amount of PZN increased to $x = 0.08$; however, the transition temperature tended to decrease continuously with increasing PZN. There was no clear anomaly in the thermal expansion at transition temperature for the composition, $x \geq 0.10$, because these compositions showed the second-order phase transition, which is the behavior of relaxor-like FE [16]. This occurrence was similar to those in other researches on different solid solution systems [32]. In demonstrating phase transition of PZ–PZN ceramics by relative permittivity, DSC, and thermal expansion measurements, it is noteworthy that all compositions showed the difference of transition temperature in each technique, as listed in Table 2. This result attributed to the different heating rates used during the measurements.

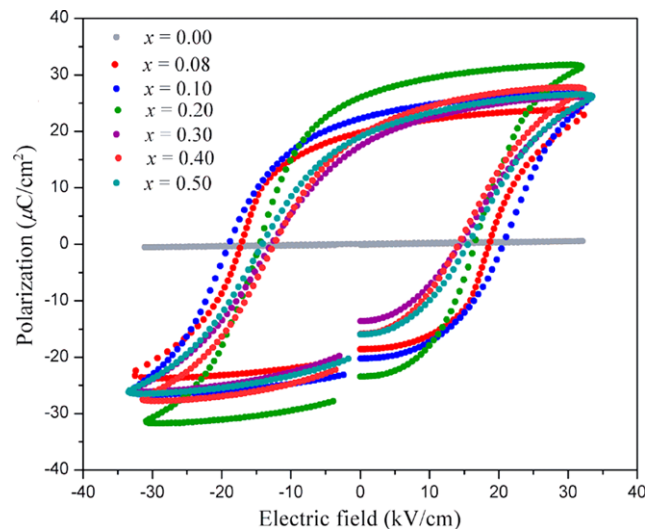


Fig. 8 Polarization–electric field hysteresis loops of $(1-x)\text{PbZrO}_3-x\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ceramics

3.5 Ferroelectric properties

The ferroelectric measurement was used to clarify further dielectric behavior of the FE phase in the PZ–PZN system. The P–E hysteresis loops for all composition ceramics at room temperature are shown in Fig. 8. At the composition, $0.00 \leq x \leq 0.06$, a near-linear relationship of P–E

loop is observed, due to electric fields being insufficient to switch any ferroelectric domains. It is well known that in PZ ceramics, the electric field required for inducing the AFE to FE phase transition at room temperature is higher than the breakdown strength of the ceramics [11, 33]. This result indicated that the AFE phase of pure PZ persisted in the PZ–PZN system for $x < 0.08$ at room temperature, which corresponded to the dielectric and thermal expansion results. For $0.08 \leq x \leq 0.50$, at the 35 kV/cm electric field strength, fully and symmetrical hysteresis loops were detected. The driving force for an antiparallel shift of Pb^{2+} ions was decreased, due to the replacement of the Zr^{4+} ion by $\text{Zn}^{2+}/\text{Nb}^{5+}$ ions, which interrupted the translational symmetry. Then, the ferroelectric phase appeared when the amount of PZN was more than 6 mol%. Moreover, the hysteresis loop of ceramics at $0.08 \leq x \leq 0.50$ showed normal-like ferroelectric behavior with the square loop. The remanent polarization (P_r) and coercive field (E_c) value of ceramics at $0.08 \leq x \leq 0.50$ did not change significantly. However, the highest P_r value of this system was found in the composition, $x = 0.20$, where $P_r = 26.90 \mu\text{C}/\text{cm}^2$ and $E_c = 15.52 \text{ kV}/\text{cm}$. The ferroelectric properties, together with the basis of XRD and dielectric measurements, led to the conclusion that the MPB of the $(1-x)\text{PZ}-x\text{PZN}$ system exists at $x = 0.20$. Interestingly, the MPB of the $(1-x)\text{PZ}-x\text{PZN}$ system shows higher remanent polarization and coercive field when compared to that of the PZT system [34, 35]. It is well known that the MPB and grain size effect are important parameters that strongly influence electrical properties of lead-based piezoelectric ceramics. However, this study showed that the MPB in the PZ–PZN system is more influential to electrical properties than the grain size effect. For the composition, $x = 0.50$, the value of P_r decreased to $19.65 \mu\text{C}/\text{cm}^2$, due to the coexistence of a pyrochlore phase, as observed by the XRD technique.

4 Conclusion

The solid solubility limit of the $(1-x)\text{PbZrO}_3-x\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ system, which was prepared via the columbite method, was about $x = 0.40$. Relaxor ferroelectric PZN was found to strongly influence crystal structure, and electrical and thermal properties of PZ ceramics. The XRD results indicate that the crystal structure of solid solution $(1-x)\text{PZ}-x\text{PZN}$, where $x = 0.00-0.50$, successively transforms from orthorhombic to rhombohedral symmetry, with increased PZN concentration. The AFE→FE phase transition shifts to lower temperatures with higher compositions of x . The temperature range width of the FE phase increases with the amount of PZN increase. The dielectric properties of PZ–PZN exhibited significant improvement with PZN loading. The MPB of the $(1-x)\text{PZ}-x\text{PZN}$ system exists close to the composition, $x = 0.20$.

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Grass blade-like microparticle $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ prepared by a simple precipitation at room temperature

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ABSTRACT

Grass blade-like microparticle $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ was synthesized by a simple precipitation at room temperature using a mixture of manganese sulphate monohydrate, phosphoric acid and water at $\text{pH} = 7$. The thermogravimetric study indicates that the synthesized compound is stable below 500°C and its final decomposed product is $\text{Mn}_2\text{P}_2\text{O}_7$. The pure monoclinic phases of the synthesized $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ and its final decomposed product $\text{Mn}_2\text{P}_2\text{O}_7$ are verified by XRD data. FTIR spectra indicate the presences of the PO_4^{3-} ion and water molecules in the $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ structure and the $\text{P}_2\text{O}_7^{4-}$ ion in the $\text{Mn}_2\text{P}_2\text{O}_7$ structure. The thermal stability, crystallite size, and grass blade-like microparticle of $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ in this work are different from previous reports, which may be caused by the starting reagents and reaction condition for the precipitation.

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1. Introduction

In the recent years, a large number of inorganic natural and synthesized metal phosphates have the incremented use in order to supply the demands of industrial, commercial, agricultural, scientific and health sectors because of their valuable physical–chemical properties and reactivity [1,2]. The metal phosphate compounds are divided by phosphate block unit as PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- , $\text{P}_2\text{O}_7^{4-}$ and $\text{P}_4\text{O}_{10}^{6-}$ units [3], which have found widespread applications in laser host [4], ceramic [5], dielectric [6], electric [7], magnetic [8], fertilizer [9], and catalytic [10] processes. Synthesis of these phosphate materials by precipitation reaction at room temperature with short time consumption and the morphology and architecture at micro-/nanoscale levels have attracted the interest of many researchers due to their conveniences and their strong influence on material properties [4–10]. Compared with hydrothermal method, solid state method, and sol–gel method, the remarkable advantages of precipitation reaction are its flexibility of operation, simple and rapid route, and environmental benign and cost-effective technique [7,11–13].

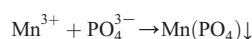
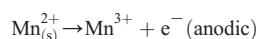
Manganese phosphate monohydrate ($\text{MnPO}_4 \cdot \text{XH}_2\text{O}$, $x = 1.0$ – 1.7 mol), non-toxic foundational compound, has been applied widely in catalysis, fertilizer, and electrical fields, was synthesized by various methods (hydrothermal method, sol–gel method, solid state route or high-temperature method) and was also found in nature [14,15]. Christensen [16] reported for the first time the synthesis of $\text{MnPO}_4 \cdot \text{XH}_2\text{O}$ by manganese(II) nitrate–phosphoric acid system in the presence of nitric acid, which was used for the oxidation of manganese(II) nitrate. The another preparation method involved the oxidation of manganese(II) carbonate by nitric acid in the presence of phosphoric acid [17–19]. Recently, our group reported the synthesis of $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ by soft solution route using manganese (II) nitrate–phosphoric acid–methanol system at 40°C [20]. To improve its functional properties and enlarge its application, many attempts have been conducted during the last two decades, one of which is to control shaping powder material (bulk, porous, micro- or nanoparticles) [11–13,21]. So far, there have been structural and spectroscopic reports on $\text{MnPO}_4 \cdot \text{XH}_2\text{O}$ ($x = 1.0$ – 1.7 mol), to our knowledge, little are the morphology and architecture data available.

In this present, $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ powder was prepared by simple precipitation at room temperature using manganese sulphate monohydrate, phosphoric acid and water at $\text{pH} = 7$. This method is simple, rapid, cost-effective and has non-toxic routes to synthesize grass blade-like microparticle $\text{MnPO}_4 \cdot \text{H}_2\text{O}$. The precipitates were characterized by TG/DTG, DSC, XRD, SEM and FTIR techniques. The data obtained will be important for further studies of the compound.

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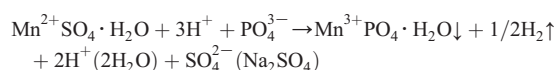
2. Experimental

MnPO₄·H₂O crystalline powder was prepared by a solution precipitation method using MnSO₄·H₂O (>99% purity, Fluka) and phosphoric acid (86.4% w/w H₃PO₄, Merck) as starting materials. Following procedure, 1.70 g of MnSO₄·H₂O was dissolved in 18 mL of 1 M H₃PO₄. The pH of the manganese- and phosphate-containing solution was adjusted to 7 by the addition of NaOH, and MnPO₄·H₂O was precipitated at room temperature. The powder was obtained, then isolated by filtration, washed with deionized water and dried in air. This process can be explained by the following reaction:



Therefore, the overall reaction can be rewritten by:

NaOH pH = 7 at room temperature



Thermal property of the studied compound was investigated on a TG-DTG (Thermogravimetry, TG; Derivative Thermogravimetry, DTG) Pyris One Perkin-Elmer instrument and a DSC (Differential Scanning Calorimetry) 204 F1 Phoenix Perkin-Elmer apparatus with α -Al₂O₃ powder as the reference material. On the basis of TG data, its final decomposed product seemed to occur at a temperature above 500 °C and the water content was determined. In order to gain the thermal decomposition phase, the synthesized MnPO₄·H₂O was heated in a box furnace at 500 °C for 2 h. The manganese contents of the synthesized MnPO₄·H₂O and its decomposed product Mn₂P₂O₇ were determined by dissolving in 0.0126 M hydrochloric acid using atomic absorption spectrophotometry (AAS, Perkin-Elmer, Analyst100). The phosphorus contents were analyzed by colorimetric method of the molybdophosphate complex [22]. The structure and crystallite sizes of the prepared powder and its decomposed product were studied by X-ray powder diffraction using a D8 Advanced powder diffractometer (Bruker AXS, Karlsruhe, Germany) with Cu K α radiation (λ = 0.1546 nm). The Scherrer method was used to evaluate the crystalline size [23]. The room temperature FTIR spectra were recorded in the range of 4000–400 cm^{−1} with 8 scans on a Perkin-Elmer Spectrum GX spectrometer with the resolution of 4 cm^{−1}. The morphology was examined by SEM using Hitachi S4700 after gold coating.

3. Results and discussion

The TG/DTG curves of MnPO₄·H₂O are shown in Fig. 1. The TG curve shows the weight loss between 50 and 600 °C, which is related to the elimination of crystallization water and oxygen. The first weight loss in the range of 50–320 °C was 10.80%, which corresponds to the elimination of one molecule of crystallization water. The second weight loss in the range of 320–500 °C was 5.20%, which corresponds to the consequent release of oxygen due to the reduction of manganese (III) to manganese(II) [17,18]. Total weight loss of 16.00% is close to the reported values by previous works [17–20]. The mass retained of about 84% is comparable with the value expected for the formation of Mn₂P₂O₇, which is verified by XRD and FTIR measurements. In the DTG curve, the corresponding peaks at 120, 190, 260 and 330 °C are observed. The overall reaction formally could be presented as:

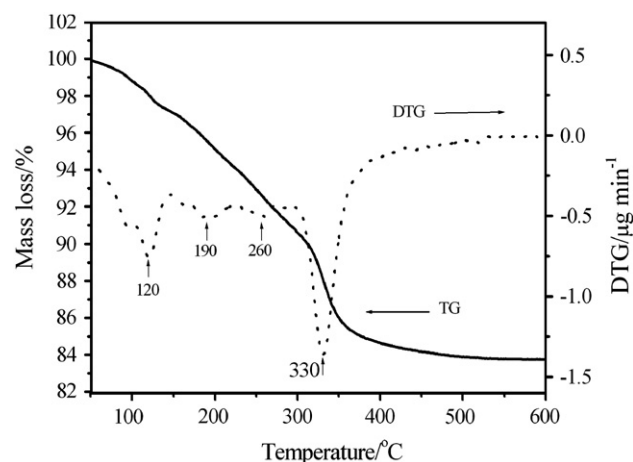


Fig. 1. TG/DTG curves of the synthesized MnPO₄·H₂O at the heating range of 10 °C min^{−1}.

The temperature at which theoretical mass loss is achieved can be also determined from TG trace and considered to be the minimum temperature needed for the calcinations process. Thus, the MnPO₄·H₂O powder was calcined at 500 °C for 2 h in a box furnace, which is lower temperature comparable with this phosphate reported by previous works [17–20]. The thermal behavior of the prepared MnPO₄·H₂O powder in this work is significantly different from that of the decomposition reactions of MnPO₄·H₂O reported in the literature [17–20]. The result indicates that starting reagent and reaction condition for the precipitation have the effects on the thermal transformation of MnPO₄·H₂O.

The DSC curve of MnPO₄·H₂O in N₂ is shown in Fig. 2. The DSC trace shows three endothermic peaks and one exothermic peak at 130, 268, 324, and 475 °C (onset peak at 117, 250, 300, and 450 °C) which are due to two dehydration, reduction and phase transformation reactions of this compound, respectively. According to the DSC curve, the heat of two dehydration, reduction and phase transformation reactions can be calculated and were found to be 20.70, 19.65, 140.88 and −17.18 J g^{−1}, respectively. The reduction step exhibits higher heat energy in comparison with other ones. This result indicates that it occurs harder than the dehydration and phase transformation reactions.

The XRD patterns of MnPO₄·H₂O and its decomposed product Mn₂P₂O₇ are shown in Fig. 3. The five strong peaks (2 θ data) were observed at 27.898(021), 30.988(−202), 34.003(−221), 41.1204(−311), and 55.961(042) for the MnPO₄·H₂O and 28.837(111),

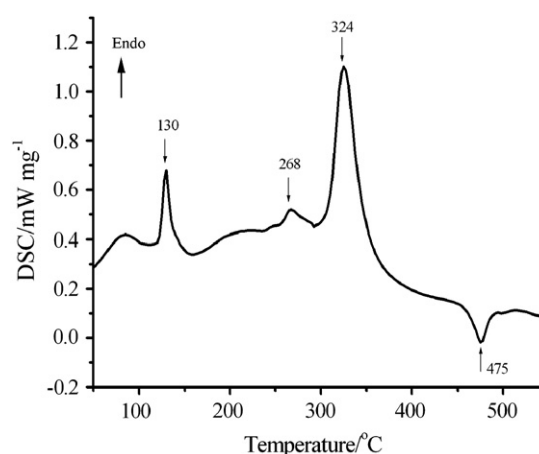


Fig. 2. DSC curve of the synthesized MnPO₄·H₂O at the heating range of 10 °C min^{−1}.

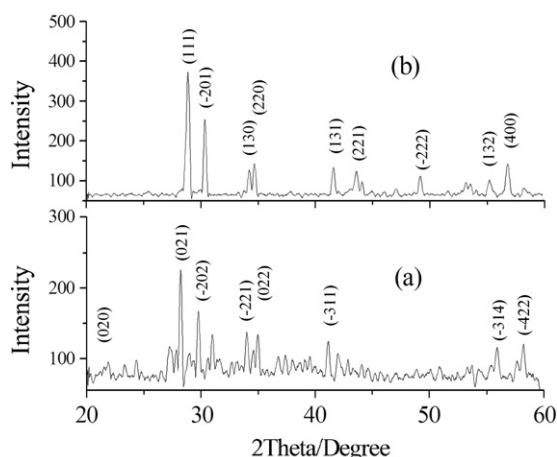


Fig. 3. XRD patterns of the synthesized $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ (a) and its decomposed product $\text{Mn}_2\text{P}_2\text{O}_7$ (b).

30.317(−201), 34.206(130), 34.661(220), and 41.657(131) for $\text{Mn}_2\text{P}_2\text{O}_7$, respectively (indices are given in parentheses). The patterns match the standard XRD data for the $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ of PDF no. 511548 and for $\text{Mn}_2\text{P}_2\text{O}_7$ of PDF no. 771243. These results indicated that both crystal structures are monoclinic systems with space group C2/c ($Z=4$) for $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ and C2/m ($Z=2$) for $\text{Mn}_2\text{P}_2\text{O}_7$. The average crystallite sizes and lattice parameters of the $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ and the decomposed product $\text{Mn}_2\text{P}_2\text{O}_7$ were calculated from XRD patterns and also tabulated in Table 1. The lattice parameters of $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ and $\text{Mn}_2\text{P}_2\text{O}_7$ are close to those of the standard data PDF no. 511548 and PDF no. 771243, respectively. However, the problem here is that the XRD patterns are very weak, so the lattice parameters obtained from these data are different from the value presented by other researchers. The result is caused by the different synthetic methods, which are in agreement with the results reported in the literature [11,12,19,20]. The average crystallite size of 41 ± 13 nm for $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ sample and 38 ± 11 nm for $\text{Mn}_2\text{P}_2\text{O}_7$ in this work are smaller than those prepared from $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} - \text{H}_3\text{PO}_4 - \text{CH}_3\text{OH}$ system reported by Boonchom et al. (66 ± 28 nm for $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ and 54 ± 18 nm for $\text{Mn}_2\text{P}_2\text{O}_7$) [20]. The crystallite size of $\text{Mn}_2\text{P}_2\text{O}_7$ in this work is close to that from $\text{Mn}_2\text{P}_2\text{O}_7$ prepared at 800°C (31 ± 13 nm) in our previous study [24], although the $\text{Mn}_2\text{P}_2\text{O}_7$ in this work was obtained from the lower temperature (500°C). These results confirmed that the different crystallite sizes of the synthesized $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ and $\text{Mn}_2\text{P}_2\text{O}_7$ depend on the starting reagent and reaction condition for the precipitations, which is consistent with the literature [25–27].

The FTIR spectrum of the synthesized $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ powder (Fig. 4a) reflects characteristic vibrations of PO_4^{3-} ion and H_2O molecules. Water bonding at 1639 cm^{-1} and O–H stretching broad

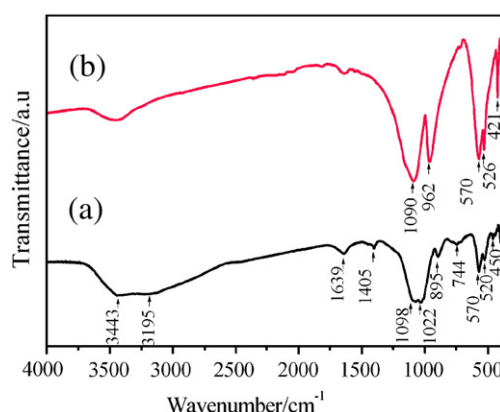


Fig. 4. FTIR spectra of the synthesized $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ (a) and its decomposed product $\text{Mn}_2\text{P}_2\text{O}_7$ (b).

band center at 3443 cm^{-1} can be observed, implying the presence of crystalline hydrate. Spectra involving phosphate vibrations center on four regions because of the idealized T_d symmetry of the phosphate ion. Vibrational bands of PO_4^{3-} ion are observed in the regions of 990–950, 1100–1020, 480–400 and $650\text{--}500\text{ cm}^{-1}$, which are assigned to the symmetric stretching region (ν_1), the antisymmetric stretching region (ν_3), the symmetric bending region (ν_2), and the antisymmetric bending region (ν_4), respectively [28,29]. The several strong and sharp bands in the ranges of 1100–890 and $600\text{--}500\text{ cm}^{-1}$, which split into several peaks, report complexes of stretching and bending of PO_4^{3-} group, respectively. Antisymmetric stretching and bending vibrations are found at higher wavenumbers than symmetric stretching and bending vibrations, are more intense in infrared spectroscopy and weaker in Raman spectroscopy. Hence most absorptions in the $1000\text{--}1100\text{ cm}^{-1}$ region are attributable to antisymmetric (ν_3) vibrations. For the synthesized $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ powder strong band was observed at 1098 and 1022 cm^{-1} . Another strong band observed at 895 cm^{-1} was attributed to the symmetric stretching mode of PO_4^{3-} . Antisymmetric bending (ν_2) vibrations are observed at 570 and 520 cm^{-1} . These phosphate band positions are in excellent agreement with published data [28,29]. The weak bands at 1639 and 1405 cm^{-1} are the H–O–H bending broad. The last band is assigned to the very low bending of water molecule, which is in excellent agreement with the literature [28,29]. The middle intense bands at 3443 and 3195 cm^{-1} are assigned to the antisymmetric and symmetric stretchings of water molecule, respectively. In addition, a weak band observed at 744 cm^{-1} is assigned to water libration (rocking mode) [28,29]. These results show that only the tribasic form of PO_4^{3-} was present and some crystalline water existed in the title compound.

Table 1
Average crystallite sizes and lattice parameters of $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ and $\text{Mn}_2\text{P}_2\text{O}_7$ calculated from XRD data.

Lattice parameters	$\text{MnPO}_4 \cdot \text{H}_2\text{O}$			$\text{Mn}_2\text{P}_2\text{O}_7$		
	This work	PDF #511548	DIF (This work-PDF)	This work	PDF #771243	DIF (This work-PDF)
<i>a</i> (Å)	7.009(0)	6.913	+0.096	6.845(0)	6.633	+0.212
<i>b</i> (Å)	7.666(0)	7.474	+0.192	8.651(4)	8.584	+0.067
<i>c</i> (Å)	7.234(0)	7.363	−0.129	4.657(0)	4.646	+0.011
β (°)	113.27(0)	112.30	+0.97	102.17(0)	102.67	−0.50
Average crystallite size (nm)	41 ± 13	–	–	38 ± 11	–	–

FTIR spectrum of the calcined $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ powder at 500°C (Fig. 4b) exhibits the same characteristic as that of $\text{Mn}_2\text{P}_2\text{O}_7$. FTIR bands are assigned according to the literature [24,30] based on the fundamental vibrating unit $\text{P}_2\text{O}_7^{4-}$ anion. One of the most noteworthy features of the spectrum is the presence of the strong bands at 1090, 962, 570, 526, and 421 cm^{-1} . These bands can be assigned to $\nu_{\text{as}}(\text{PO}_3)$, $\nu_{\text{as}}(\text{POP})$, $\delta(\text{PO}_3)$, $\delta(\text{PO}_3)$, and $\rho(\text{PO}_3)$, respectively. The symmetric and asymmetric vibrations of the POP bridge ($\nu_{\text{as}}\text{ POP}$ and $\nu_{\text{s}}\text{ POP}$) observed in the range $700\text{--}970\text{ cm}^{-1}$ [24,30], which indicate the presence of the $\text{P}_2\text{O}_7^{4-}$ anions with a bent POP angles in this salt.

The morphologies of $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ and its decomposed product $\text{Mn}_2\text{P}_2\text{O}_7$ powders are shown in Fig. 5a and b. The $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ shapes in this work show well-defined grass blade-like microparticles, which are not similar to those of $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ reported in previous works [18–20]. The grass blade-like morphology consists of similar leaf-like flakes growing radially from the inside. Its decomposed product $\text{Mn}_2\text{P}_2\text{O}_7$ shows high agglomerate of non-uniform polyhedral particles, which is possibly caused by the dehydration and reduction processes. The morphology of $\text{Mn}_2\text{P}_2\text{O}_7$ indicates further nucleation/growth of the nanocrystals inside the powder. This phenomenon is still not clear. The morphologies of the synthesized $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ and its decomposed product $\text{Mn}_2\text{P}_2\text{O}_7$ in this work are significantly different from those of our previous reports [20,24,25]. The results indicate that the starting reagent and reaction condition of the

precipitation have the strong effect in the morphologies of the studied compounds.

4. Conclusion

Grass blade-like microparticle $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ was successfully synthesized by simple precipitation at room temperature using the mixture of manganese sulphate monohydrate, phosphoric acid and water at $\text{pH} = 7$. The $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ decomposes in more complex steps which correspond to the loss of crystallization water in the first step, subsequently to the reduction of manganese(III) to manganese(II) and the consequent release of oxygen (last step). The XRD and FTIR results confirmed the formation of $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ and its decomposed product $\text{Mn}_2\text{P}_2\text{O}_7$. The thermal behaviors, grass blade-like shapes, particle size and crystallite sizes of the synthesized $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ and $\text{Mn}_2\text{P}_2\text{O}_7$ are different from previous reports. This is possibly due to the effects of the starting reagents and reaction condition for the precipitation. The results obtained are necessary for theoretical study, application development, and industrial production to produce the $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ and $\text{Mn}_2\text{P}_2\text{O}_7$, which play potential applications as catalytic, ceramic and the biomedical materials etc.

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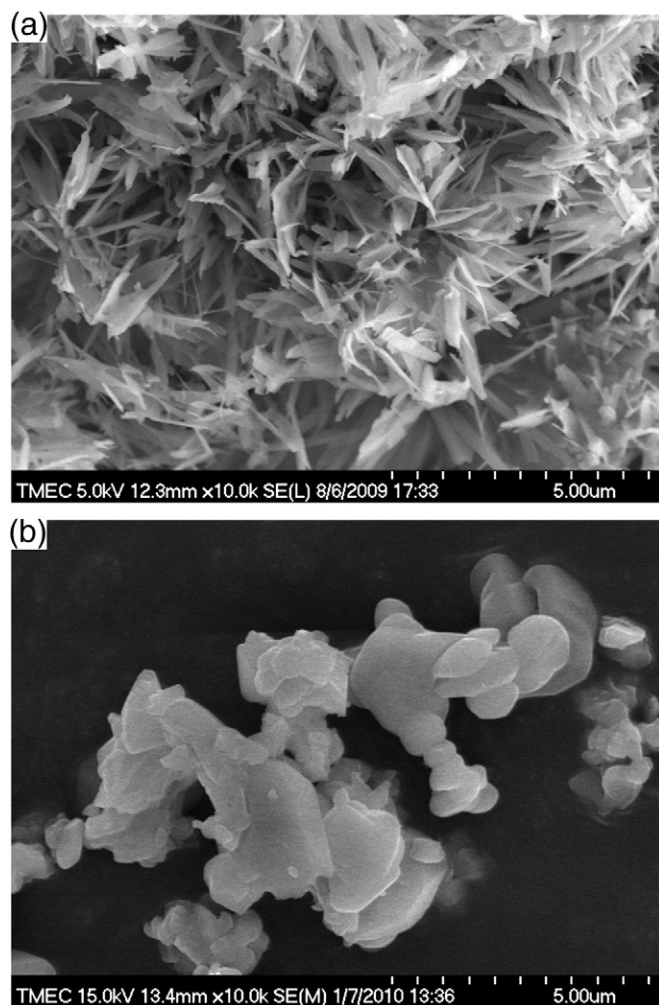


Fig. 5. SEM micrographs of the synthesized $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ (a) and its decomposed product $\text{Mn}_2\text{P}_2\text{O}_7$ (b).

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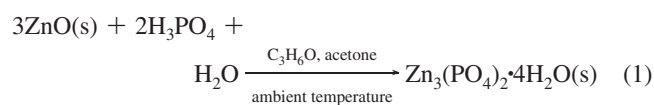
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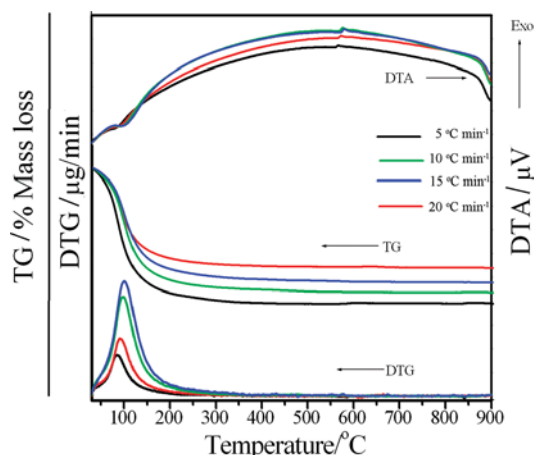


Figure 1. TG-DTG-DTA curves of $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4 \cdot 2.5\text{H}_2\text{O}$ in dry air at heating rates of (5, 10, 15, and 20) $^{\circ}\text{C} \cdot \text{min}^{-1}$.

reaches pH 3.80. The precipitates were filtered by suction, washed by hot deionized water, and dried in air. The resultant solid was kept in a desiccator for further investigation.

2.2. Sample Characterization. Thermal analysis measurements of about (8.0 ± 0.3) mg sample mass were carried out by a Pyris1 Perkin-Elmer apparatus with an alumina crucible at heating rates of (5, 10, 15, and 20) $^{\circ}\text{C} \cdot \text{min}^{-1}$ in dynamic air in the range of (30 to 900) $^{\circ}\text{C}$. DSC was carried out for samples ((5 to 10) mg) in aluminum crucibles, over the temperature range of (50 to 500) $^{\circ}\text{C}$ using DSC, a Perkin-Elmer DSC 204 F1 Phoenix apparatus. The heating rate employed was $10^{\circ}\text{C} \cdot \text{min}^{-1}$. The structures of the prepared sample and its decomposed product were studied by X-ray powder diffraction using a D8 Advanced powder diffractometer (Bruker AXS, Karlsruhe, Germany) with Cu $K\alpha$ radiation ($\lambda = 0.1546$ nm). The room temperature Fourier transform infrared (FTIR) spectra were recorded in the range of (4000 to 400) cm^{-1} with eight scans on a Perkin-Elmer Spectrum GX spectrometer with a resolution of 4 cm^{-1} . The morphology was examined by scanning electron microscopy (SEM) using Hitachi S4700 after gold coating.

3. Results and Discussion

3.1. Thermal Analysis. Figure 1 shows the TG-DTG-DTA curves of the thermal decomposition of $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4 \cdot 2.5\text{H}_2\text{O}$ at four heating rates. TG curves of $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4 \cdot 2.5\text{H}_2\text{O}$ show a single well-defined dehydration in the range of (30 to 300) $^{\circ}\text{C}$. The water eliminated below 100 $^{\circ}\text{C}$ is related to the physical adsorbed water, whereas water eliminated at 100 $^{\circ}\text{C}$ and above (200 $^{\circ}\text{C}$) can be considered as crystal water and coordinated water. The dehydration temperature obtained in this work suggest that the water in hydrated binary aluminum iron phosphate can be considered as physical adsorbed water and crystal water.^{8,9,17,18} The peaks in the DTG and DTA curves closely correspond to the mass loss observed on the TG traces. All TG-DTG-DTA curves are approximately the same shape. However, the dehydration stage was shifted toward higher temperatures when the heating rates increase, which indicate that the mass loss is dependent on the heating rate. The average observed mass losses of four TG curves are 26.22 % by mass, which correspond to 2.51 mol of water, which is close to the theoretical value for $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4 \cdot 2.5\text{H}_2\text{O}$ (26.11 %, $2.50 \text{ H}_2\text{O}$). An endothermic effect in the DTA curves is observed at about 100 $^{\circ}\text{C}$ that agrees with the respective DTG peak. Further, an exothermic effect at 572 $^{\circ}\text{C}$ without appreciable weight loss is observed in the DTA curve, which can be ascribed to a transition phase from an amorphous to crystalline form of $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4$.¹¹

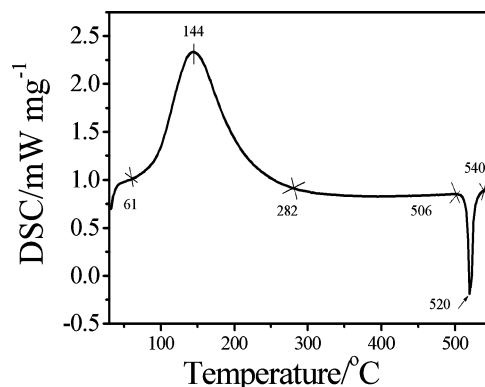


Figure 2. DSC curve of $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4 \cdot 2.5\text{H}_2\text{O}$ at the heating rate of $10 \text{ K} \cdot \text{min}^{-1}$ in a N_2 atmosphere.

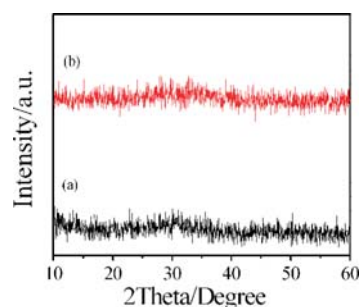
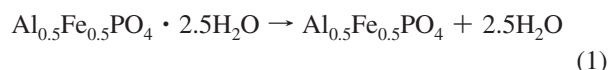


Figure 3. XRD patterns of $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4 \cdot 2.5\text{H}_2\text{O}$ (a) and its decomposed product $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ (b).

The retained mass of about 73.78 % is compatible with the value expected for the formation of $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4$. The overall reaction is:



The binary iron aluminum phosphate, $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4$, is found to be the final product of the thermal decomposition at $T > 300^{\circ}\text{C}$. The thermal stability, mechanism, and phase transition temperature of the synthesized $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4 \cdot 2.5\text{H}_2\text{O}$ are lower than those of the dehydration reactions of individual metal phosphates ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ ¹⁷ and $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ ¹⁸). On the basis of these results, we can conclude that the different thermal properties are caused by the incorporation of Fe and Al metals in the skeleton.

The DSC curve of $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4 \cdot 2.5\text{H}_2\text{O}$ (Figure 2) shows an endothermic peak at 144 $^{\circ}\text{C}$ (onset peak at 61 $^{\circ}\text{C}$) and an exothermic peak at 520 $^{\circ}\text{C}$ (onset peak at 506 $^{\circ}\text{C}$) due to the dehydration and the transition phase from an amorphous to crystalline form of this compound, respectively. The temperatures of the DSC peaks are well in accordance with that of the DTG and DTA peaks (Figure 1), so results of the TG/DTG/DTA and DSC methods are credible.

3.2. XRD Analysis. The XRD studies of $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4 \cdot 2.5\text{H}_2\text{O}$ and its dehydrated product $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ revealed that the structures remained in the amorphous or poor crystallization phases as well as nanoparticles of these compounds (Figure 3). The problem here is that the XRD data show poorly crystalline patterns, which are no indication of $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4 \cdot 2.5\text{H}_2\text{O}$ and $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ as separated phases. The studied compounds synthesized by the precipitation route in this work were poor crystalline phases, which differ from crystallization phases of those synthesized by a hydrothermal method.^{5–10} These results are in agreement with the results reported in the literature.^{5–10}

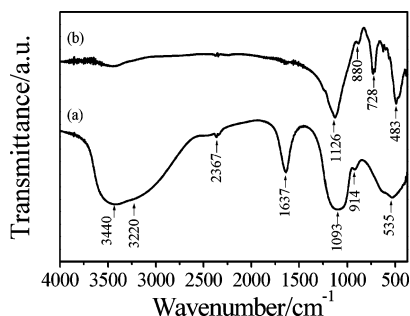


Figure 4. FTIR spectra of $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4 \cdot 2.5\text{H}_2\text{O}$ (a) and its decomposed product $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ (b).

3.3. FTIR Analysis. Figure 4 shows FTIR spectra of $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4 \cdot 2.5\text{H}_2\text{O}$ and its dehydrated product $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4$. The vibrational motions of $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4 \cdot 2.5\text{H}_2\text{O}$ are divided into two block units of the water molecule H_2O and phosphate anion PO_4^{3-} , whereas $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ is divided into a block unit of the only phosphate anion PO_4^{3-} . It is worth mentioning that the antisymmetric stretching (ν_{OH}), the symmetric stretching (ν_{OH}), and the bending (δ_{OH}) vibrations of water molecules are solely observed at (3440, 3220, and 1637) cm^{-1} , respectively. These bands disappear in the FTIR spectrum of $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ (Figure 4b), implying the presence of anhydrous crystal. For the intramolecular vibrations of the PO_4^{3-} anion, we identify the symmetric stretching mode at $\nu_1 = 990 \text{ cm}^{-1}$, the doublet at $\nu_2 = (447 \text{ to } 485) \text{ cm}^{-1}$, the triplets ν_3 at (1000 to 1085) cm^{-1} , and the triplet ν_4 in the region (570 to 640) cm^{-1} . For condensed phosphates, the intensity of the P–O stretching IR bands near 1000 cm^{-1} are always greater than those near 880 cm^{-1} , assigned to the stretching vibration $\nu_{\text{P–O–P}}$ of P–O–P bridges. These phosphate band positions of $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4 \cdot 2.5\text{H}_2\text{O}$ and $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ are in excellent agreement with published data.^{19,20}

3.4. SEM Analysis. The scanning electron micrographs of $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4 \cdot 2.5\text{H}_2\text{O}$ (Figure 5a) and $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ (Figure 5b) powders showed different uniform morphological features due to the loss of crystallization waters. It can be seen that the $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ powders were clearly coarser than the $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4 \cdot 2.5\text{H}_2\text{O}$ powders. The $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ powders consisted of round particles near 100 nm in size along with a narrow size distribution. Additionally, the SEM photographs show that both crystals have grown through a combination of surface deposition and agglomeration.

3.5. Kinetics Analysis. In the rate equation for the isothermal decomposition of a solid-state process,²¹ $\text{A (solid)} \rightarrow \text{B (solid)} + \text{C (gas)}$ is often written from:

$$d\alpha/dt = A \exp(-E_a/RT) f(\alpha) \quad (2)$$

In most thermal analysis experiments, the heating rate $\beta = dT/dt$ is a constant value, so eq 2 may also lead to the corresponding equations of Ozawa²² and Kissinger–Akahira–Sunose (KAS)²³ methods after integration.

$$\text{Ozawa equation: } \ln \beta = \ln \left(\frac{A E_a}{R g(\alpha)} \right) - 5.3305 - 1.0516 \left(\frac{E_a}{RT} \right) \quad (3)$$

$$\text{KAS equation: } \ln \left(\frac{\beta}{T^2} \right) = \ln \left(\frac{A E_a}{R g(\alpha)} \right) - \left(\frac{E_a}{RT} \right) \quad (4)$$

where A (the pre-exponential factor) and E_a (the activation energy) are the Arrhenius parameters and R is the gas constant.

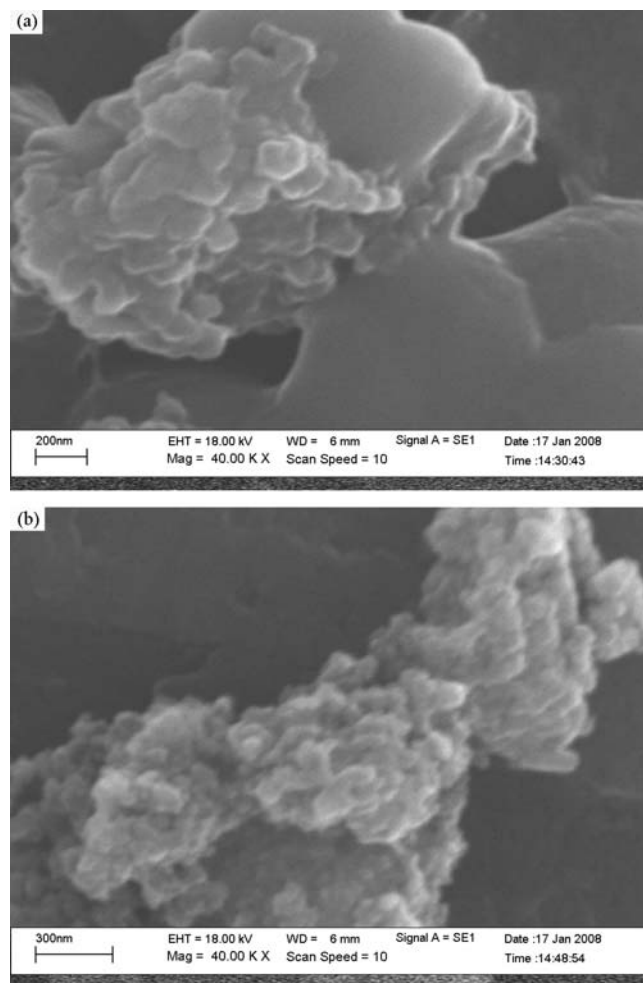


Figure 5. SEM photographs of $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4 \cdot 2.5\text{H}_2\text{O}$ (a) and its decomposed product $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ (b).

The $g(\alpha) = \int_0^\alpha (d\alpha/f(\alpha))$ is the integral form of $f(\alpha)$, which is the reaction model that depends on the reaction mechanism. The reaction can be expressed through the temperatures corresponding to fixed values of the extent of conversion ($\alpha = (m_i - m_a)/(m_i - m_f)$), where m_i , m_a , and m_f are the initial, actual, and final sample mass at time t from experiments at different heating rates (β).

Hence, the dependences of $\ln \beta$ and $\ln \beta/T^2$ on $1000/T$, calculated for the same α values (0.10 to 0.90) at different heating rates β ((5, 10, 15, and 20) $^\circ\text{C} \cdot \text{min}^{-1}$) can be used to calculate the activation energy, so we can obtain the activation energies through the experimental data for the dehydration of $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4 \cdot 2.5\text{H}_2\text{O}$ as shown in Table 1. The activation energies E_a can be calculated from the slopes of the straight lines with a good coefficient of determination ($R^2 > 0.99$). The activation energies worked out through the Ozawa and the KAS methods vary slightly, so the results are credible. If E_a values are independent of α , the decomposition may be a simple reaction, while the dependence of E_a on α should be interpreted in terms of multistep reaction mechanisms.^{24,25} From Table 1 it can be seen that the activation energies decrease first and increase at α higher than 0.6. A decreasing dependence of E_a on α is found for consecutive reactions, while an increasing dependence of E_a on α is found for competitive reactions. According to the decreasing E_a at $\alpha < 0.6$, the kinetics scheme of which corresponds to a reversible reaction followed by an irreversible one. In addition, the increasing E_a at $\alpha > 0.6$ corresponds to a two-pathway competitive reaction model.^{24,25}

Table 1. Activation Energies (E_a) Versus the Coefficient of Detemination (R^2) Calculated by Ozawa and KAS Methods for the Dehydration of $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4 \cdot 2.5\text{H}_2\text{O}$

α	Ozawa method		KAS method	
	$E_a/\text{kJ} \cdot \text{mol}^{-1}$	R^2	$E_a/\text{kJ} \cdot \text{mol}^{-1}$	R^2
0.1	231.14	0.9985	237.50	0.9985
0.2	158.58	0.9937	160.99	0.9933
0.3	136.83	0.9968	137.98	0.9965
0.4	129.85	0.9984	130.54	0.9983
0.5	126.05	0.9972	126.44	0.9970
0.6	125.90	0.9970	126.16	0.9966
0.7	136.37	0.9976	137.02	0.9974
0.8	167.18	0.9989	169.21	0.9988
0.9	275.09	0.9959	323.93	0.9957

So it is concluded that there is a fourth reaction for the dehydration reaction. Additionally, the obtained activation energy values of the dehydration reaction of the studied compound are higher than those of individual metal phosphates ($69.68 \pm 7 \text{ kJ} \cdot \text{mol}^{-1}$ (Kissinger method) for $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ ¹⁷ and $68.48 \pm 1 \text{ kJ} \cdot \text{mol}^{-1}$ (Flynn–Wall–Ozawa method) and $65.55 \pm 1 \text{ kJ} \cdot \text{mol}^{-1}$ (KAS method) for $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ ¹⁸ reported in our previous works. As can be clearly seen, there is a direct relationship between the cation radius of Al(III) and Fe(III) and its thermal stability and activation energy of the dehydration reaction. A common conclusion is that the reason for this is the different interaction of iron and aluminum with water molecules in the structure, which supports the incorporation of Fe and Al metals in the skeleton and forms the $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4 \cdot 2.5\text{H}_2\text{O}$ solid solution.

The Avrami exponent, n , can be evaluated by the Ozawa equation. First, the volume fraction of phase transition x , at the same temperature, T , from four crystallization steps under different heating rates is calculated by the ratio of partial area at T to the total area of crystallization. After plotting $\ln[-\ln(1-x)]_T$ versus $\ln(\beta)$ and if the data can be fitted to the linear function, then the slope of the function is $-n$,²⁶ which is really the combined process of nucleation and growth. The most common approach used to describe the overall nonisothermal crystallization is given below:

$$-n = \frac{d \ln[-\ln(1-x)]}{d \ln(\beta)} \quad (5)$$

The volumetric function of the growth mechanism directly affects the transformation rate, and the dimensionality of the transformation is reflected in the value of the Avrami exponent.^{26,27} Higher dimensionality leads to a higher value of the exponent. Therefore, determination of the Avrami exponent allows one to determine which geometric model of the phase transformation is the best fit: one-, two-, or three-dimensional growth. For the dehydration step of $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4 \cdot 2.5\text{H}_2\text{O}$, the Avrami exponent, n , has a value of 1.11 ($R^2 = 0.991$), indicating a one-dimensional growth mechanism. The Avrami exponent, in addition to giving information regarding the dimensionality of the growth, can also yield insight into the rate-determining step (phase boundary control or diffusion control). An analysis of the Avrami exponent suggests a phase boundary mechanism.

3.6. Thermodynamic Analysis. Thermodynamic parameters, that is, enthalpy change ($\Delta H^*/\text{J} \cdot \text{mol}^{-1}$), heat capacity ($C_p/\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), entropy change ($\Delta S^*/\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), and Gibbs energy change ($\Delta G^*/\text{J} \cdot \text{mol}^{-1}$) were calculated from the DSC experiment. The enthalpy change was calculated directly from the amount of heat change involved in each step per unit mass of the test sample. ΔH^* , ΔS^* , and ΔG^* were calculated using the following equations:^{15,16}

$$C_p = \frac{\Delta H}{\Delta T} \quad (6)$$

$$\Delta S^* = 2.303 C_p \log \frac{T_2}{T_1} \quad (7)$$

$$\Delta G^* = \Delta H^* - T_p \Delta S^* \quad (8)$$

where $\Delta T = T_2 - T_1$, T_1 is the temperature at which the DSC peak begins to depart the baseline, and T_2 is the temperature at which the peak lands. T_p is the DSC peak temperature at the corresponding stage.

The values of ΔH^* , ΔS^* , C_p , and ΔG^* were calculated and found to be $104.64 \text{ kJ} \cdot \text{mol}^{-1}$, $72.40 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, $290.75 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, and $744.57 \text{ kJ} \cdot \text{mol}^{-1}$ for the dehydration reaction and $-852.61 \text{ kJ} \cdot \text{mol}^{-1}$, $-10.74 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, $-968.21 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, and $5.77 \text{ J} \cdot \text{mol}^{-1}$ for a transition form, respectively. The transition phase can be considered as the transformation of an amorphous to a crystalline form of this compound.^{7,8} It is well-known that ΔS^* can be less than, equal to, or higher than zero. In the case when $\Delta S^* < 0$, the reactions are classified as “slow” and when $\Delta S^* > 0$ as “fast”.^{28–30} The positive value of ΔS^* indicates a malleable activated complex that leads to a large number of degrees of freedom of rotation and vibration, whereas the negative value of ΔS^* indicates a highly ordered activated complex, and the degrees of freedom of rotation as well as of vibration are less than they are in the nonactivated complex. Therefore, the dehydration reaction and a transition form of $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4 \cdot 2.5\text{H}_2\text{O}$ may be interpreted as “fast” and “slow” stages, respectively.^{28–30} The positive and negative values of the enthalpy ΔH^* for the dehydration reaction and a transition form are in good agreement with an endothermic and an exothermic effect in DTA and DSC data, respectively. The positive and negative values of ΔG^* indicate that nonspontaneous and spontaneous processes for dehydration and a transition form stages, respectively. The thermodynamic parameters obtained indicate that the dehydration reaction is softer than the transition phase reaction. The results obtained in this work are different from those of the individual metal phosphates ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ ¹⁷ and $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$)¹⁸ reported in our previous work.

4. Conclusions

The results obtained in this study show that the dehydration behavior of an $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4 \cdot 2.5\text{H}_2\text{O}$ solid solution varies with the function of their cations (Al(III) and Fe(III)). The feature of great interest here is that $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4 \cdot 2.5\text{H}_2\text{O}$ decomposes at a relatively low temperature ($< 300 \text{ }^\circ\text{C}$). A fluctuating value of E for different α can be assigned to a complex multistep reaction process, which corresponds to the different interactions of iron and aluminum with water molecules in the skeleton. The thermal behavior and kinetic and thermodynamic parameters of the dehydration reaction of $\text{Al}_{0.5}\text{Fe}_{0.5}\text{PO}_4 \cdot 2.5\text{H}_2\text{O}$ are different from those of individual metal phosphates ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$), which result from the perturbation of the molecular orbitals of the anion and cations occurring during the formation of the studied compound. The kinetic and thermodynamic data obtained from such studies can be directly applied in material science for the synthesis of various composite compounds.

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The phase evolution with temperature in $0.94\text{PbZrO}_3\text{--}0.06\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ antiferroelectric ceramic

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ABSTRACT

The perovskite structure of the lead zirconate–lead magnesium tungstate ceramic, $0.94\text{PbZrO}_3\text{--}0.06\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ (0.94PZ–0.06PMW), was prepared by the wolframite precursor method. The phase evolution with temperature in the 0.94PZ–0.06PMW ceramic was investigated, with dielectric permittivity, differential scanning calorimetry and polarization measurements. The ceramic was in the antiferroelectric phase when below 177°C , based on dielectric measurement, and an intermediate phase was detected between 177 and 219°C . Evidence from ferroelectric data was found to suggest that this intermediate phase is ferroelectric.

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1. Introduction

Active studies of antiferroelectric (AFE) materials have been recently enhanced for next-generation electronic systems, for example, microelectromechanical systems consisting of sensors and actuators and high performance energy storage devices [1,2]. The phase transition from AFE to the field-forced ferroelectric (FE) state, induced by an electric field [3,4], is characterized by typical double P–E hysteresis loops. These materials are suitable for nonlinear charge storage capacitors because a field-forced ferroelectric state releases all polarized charges and can therefore supply very high instantaneous currents at the ferroelectric to antiferroelectric reverse phase transition. Recently, AFE materials, including $\text{Pb}(\text{Zr,Ti})\text{O}_3$, $(\text{Pb,Ba})\text{ZrO}_3$, $(\text{Pb,Sr})\text{TiO}_3$, $(\text{Pb,Lu})(\text{Zr,Ti})\text{O}_3$, NaNbO_3 , and $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ systems, have attracted increasing scientific attention [3–9]. Among them, lead zirconate (PbZrO_3 ; PZ) and PbZrO_3 -based are the most attractive AFE materials, due to their high longitudinal strain response, and the latter is a proto-type of AFE ceramics that belongs to an ABO_3 -type perovskite family of oxides [10,11]. At temperatures below the Curie temperature (230°C), PZ displays an orthorhombic perovskite structure with

lattice parameters of $a = 5.87 \text{ \AA}$, $b = 11.74 \text{ \AA}$ and $c = 8.20 \text{ \AA}$ [12]. This structure possesses an antiparallel shift of Pb ions along the $[110]$, resulting in antiferroelectricity [13]. At temperatures above 230°C , PbZrO_3 is in the paraelectric phase, with cubic $m3m$ symmetry [13,14]. An intermediate phase, characterized by $1/2\{110\}_c$ -type superlattice diffractions, is in between the AFE and paraelectric phase, within a narrow temperature range of $225\text{--}230^\circ\text{C}$ [13,14]. It is well known that the AFE to FE phase transformation in PZ ceramic requires a very strong electric field; otherwise, dielectric breakdown occurs. Consequently, most commercial AFE ceramics are chemically modified by adding Ba^{2+} , Sr^{2+} , Ti^{4+} or Sn^{4+} to reduce the critical field and optimize the physical and electrical properties [3–9]. Sawaguchi [15] studied the effect of Ti^{4+} substitution in PZ on temperature variation of the P–E hysteresis loop and established the ferroelectric intermediate phase between the AFE and PE phase. Shirane [16] investigated the phase transition behavior of Ba^{2+} doping in PZ and reported that the ferroelectric intermediate phase between the AFE and PE phase for Ba^{2+} concentrations was lower than $x = 0.175$. Pokharel and Pandey [17,18] reported that relaxor ferroelectric behavior for Ba^{2+} concentrations was higher than $x = 0.25$. Recently, it was reported that antiferroelectric $(\text{Pb}_{1-x}\text{Ba}_x)\text{ZrO}_3$ (PBZ) films, with a higher barium content of more than 45 mol%, were in paraelectric state at room temperature and possessed excellent dielectric properties comparable to $(\text{Ba,Sr})\text{TiO}_3$ [6]. On the contrary, a ferroelectric intermediate phase was not observed in lanthanum doping in PZ. Otherwise, lanthanum

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doping in PZ would be found to increase the stability range of the antiferroelectric phase [19,20]. Furthermore, Tan et al. [20] studied the doping effect of various metal oxide elements on field-induced polarization in PZ ceramics and found that addition of Bi^{3+} and K^{+} substantially increased stability of the antiferroelectric phase. Chen et al. [21] observed antiferroelectric-like or double hysteresis loops behavior in $(\text{Pb,Sr})\text{TiO}_3$. However, the antiferroelectric nature is different from PZ ceramics. Rubia et al. [22] investigated the effect of Hf^{4+} substitution in PZ on phase transition, when the intermediate phase was found to increase with increasing Hf^{4+} concentrations. Up to now, scientific information about the effect of metal oxide substitution in PZ and nature of the intermediate phase is still unclear. Recently, our research work reported that the intermediate phase can also be introduced by partial replacement of Zr^{4+} ions with complex B-site ions such as $\text{Ni}^{2+}/\text{Nb}^{5+}$ [23,24], $\text{Zn}^{2+}/\text{Nb}^{5+}$ [25], or $\text{Co}^{2+}/\text{Nb}^{5+}$ [26]. Furthermore, our previous study found that by adding minor amounts (2–10 mol%) of antiferroelectric $\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ (PMW) into antiferroelectric PZ, the temperature range expanded to an intermediate phase, which was characterized by evident frequency dispersion in dielectric permittivity [27]. As a consequence, a series of outstanding phase transitions were revealed by the dielectric measurement [27]. Nevertheless, the nature of the intermediate phase is still open for debate. The 0.94PbZrO_3 – $0.06\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ ceramic was selected in this study for further investigation of phase transformation sequence, while heating to 250°C with ferroelectric measurement.

2. Experimental procedures

The perovskite structure of the lead zirconate–lead magnesium tungstate ceramic, 0.94PbZrO_3 – $0.06\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ (0.94PZ–0.06PMW), was prepared by the wolframite precursor method via the ball-milling technique. The wolframite structure (MgWO_4) was synthesized first before stoichiometric amounts of the precursor (MgO and WO_3) were mixed and milled in ethyl alcohol for 18 h. The mixture was then dried and calcined at 1100°C for 4 h, and MgWO_4 and ZrO_2 were subsequently mixed with PbO . After re-milling and drying, the mixtures were calcined at 900°C for 4 h in a closed alumina crucible. Pellets measuring 15 mm in diameter were pressed using 5% PVA, the binder was burned out slowly by heating to 500°C over 2 h, and the samples were sintered at 1150°C for 4 h. Phase formation of 0.94PZ–0.06PMW was investigated by X-ray diffraction (XRD). Scanning electron microscopy (SEM; Hitachi, s4007) was employed to investigate the microstructure of the sintered pellets. The major faces of the samples were lapped to determine their dielectric and ferroelectric properties, and silver electrodes were made from a low-temperature silver paste by firing at 550°C for 30 min to enable electrical measurements to be taken. The relative permittivity (ϵ_r) and dissipation factor ($\tan \delta$) were measured using an HP-4284A LCR meter. The capacitance and dissipation factors of the sample were measured at 1–100 kHz, and the temperature varied between 25 and 350°C . A heating rate of $2^\circ\text{C}/\text{min}$ was used during measurement, and the phase transitions also were measured by differential scanning calorimeter (DSC 2920, TA Instrument) between ambient temperature and 350°C at a rate of $10^\circ\text{C}/\text{min}$. The electrical polarization versus field hysteresis loops was recorded at a series of temperatures by a standardized ferroelectric test system (RT-66A, Radiant Technologies). The peak field was maintained at 30 kV/cm during measurement, and the ferroelectric hysteresis loop was recorded after the temperature was stabilized for at least 5 min.

3. Results and discussion

The XRD pattern of 0.94PZ–0.06PMW ceramic is presented in Fig. 1. The 0.94PZ–0.06PMW ceramic was identified from the patterns as a single-phase material with a perovskite structure having orthorhombic symmetry. Evidence of the pyrochlore or other second phases was not detected in the pattern, but the $1/4(hkl)$ superstructure lines were present in the 0.94PZ–0.06PMW ceramic, indicating that the Pb^{2+} ions suffer antiparallel displacements with respect to their original position in the cubic perovskite lattice. The indexed pattern with the least number of refinement squares gave a cell with dimensions of $a = 5.85(1) \text{ \AA}$, $b = 11.67(3) \text{ \AA}$ and $c = 8.16(8) \text{ \AA}$. The cell parameters of 0.94PZ–0.06PMW were close to those of the standard data: PDF#751607 [$a = 5.88(4)$, $b = 11.76(0)$ and $c = 8.22(0)$]. A 97.8% relative density of the ceramic was measured

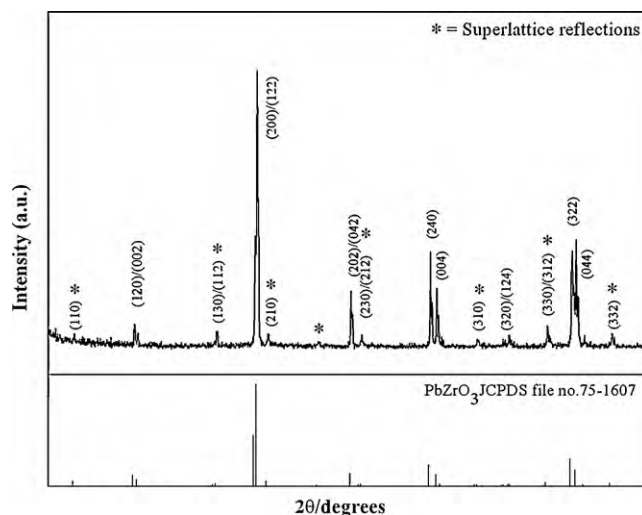


Fig. 1. XRD pattern of 0.94PZ–0.06PMW ceramic.

using the Archimedes method, and the grain size was examined by scanning electron microscopy (SEM). The fresh surface of the 0.94PZ–0.06PMW ceramic was almost free of pores, with a grain size in the range of 10–14 μm , as shown in Fig. 2.

The temperature dependence of relative permittivity and dielectric loss was measured at frequencies of 1, 10 and 100 kHz, while heating from 25 to 350°C , and the results are displayed in Fig. 3. There were clearly two abrupt changes in both relative permittivity and dielectric loss in the 0.94PZ–0.06PMW ceramic. The first one occurred at around 177°C , where both relative permittivity and dielectric loss increased by one order of magnitude. The other one took place at the Curie temperature of 219°C , where significant suppression of dielectric loss was seen. Therefore, the dielectric response in the 0.94PZ–0.06PMW ceramic can be divided into three stages. At temperatures below 177°C , both the relative permittivity and the dielectric loss have low values and show negligible increases with increasing temperatures. At temperatures above 219°C , the relative permittivity begins to decrease following the Curie–Weiss law [3,4]. In the intermediate temperature range (177 – 219°C), the relative permittivity increases dramatically, while the dielectric loss remains high at around 0.08.

To elucidate further on the dielectric behavior of different phases in the 0.94PZ–0.06PMW ceramic, electrically polarized hysteresis loop measurements were performed at a series of tem-

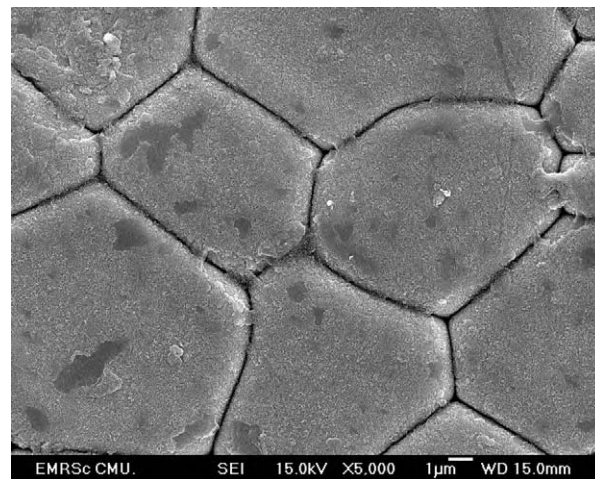


Fig. 2. SEM image of 0.94PZ–0.06PMW ceramic surfaces.

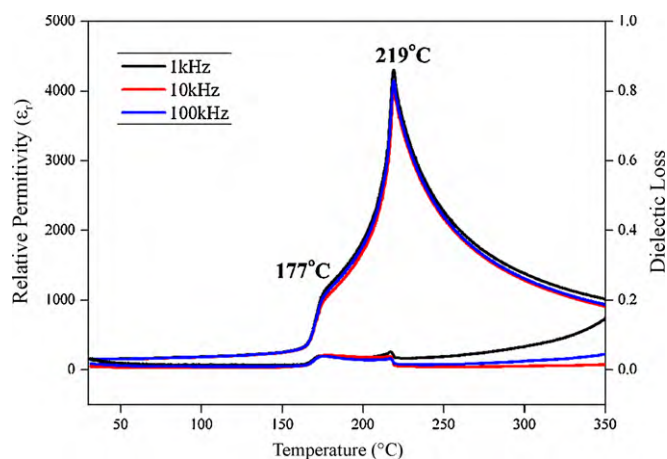


Fig. 3. Dielectric properties during heating at 1, 10 and 100 kHz in a bulk 0.94PZ–0.06PMW ceramic.

peratures under a peak field of 30 kV/cm. A circular disk specimen, with a diameter of about 10 mm and thickness of around 800 μm , was used. The loop was recorded after the temperature had been stabilized for at least 5 min. Linear polarization was displayed as a function of electric field between room temperature and 155°C, as shown in Fig. 4(a)–(d). This could indicate that the 0.94PZ–0.06PMW ceramic has AFE behavior between room temperature and less than 150°C [Fig. 4(a)]. Regarding bulk AFE ceramic specimens, the net remnant polarization (P_r) was zero, due to the existence of antiparallel dipole moments. To induce an AFE–FE phase transition, an intense electric field needs to be applied to the ceramics.

Hysteretic behavior starts to develop when the temperature increases to 155°C, and a regular hysteresis loop has a coercive E_C field of 8.29 kV/cm, as shown in Fig. 4(b). However, the hystere-

sis loop observed does not indicate the presence of a ferroelectric phase. As seen in Fig. 4(b), close examination of the hysteresis loop at 155°C reveals that slight distortions, which are marked by two circles, occurred at ~ 10 kV/cm. Similar distortions were found on the hysteresis loop in 0.98PbZrO₃–0.02Pb(Ni_{1/3}Nb_{2/3})O₃ and Pb_{0.99}Nb_{0.02}[Zr_{0.57}Sn_{0.43}]_{1-x}Ti_xO₃ ceramics, and these have been attributed to the onset of electric field-induced AFE to FE transition [28,29]. Therefore, the 0.94PZ–0.06PMW ceramic is still in the AFE phase at this temperature and it should be noted that the distortions marked at 155°C in Fig. 4(b) indicate the AFE–FE phase transition. A regular hysteresis loop, exhibiting ferroelectricity, clearly demonstrated the intermediate phase between the AFE and PE phase when the temperature was raised to 190°C [Fig. 4(c)]. Moreover, hysteretic behavior transition from the FE to PE phase occurred when the temperature increased to over 220°C [Fig. 4(d)]. It is well known that the occurrence of antiferroelectricity in pure PZ is due to an antiparallel shift of Pb ions along the [1 1 0] direction and it also results in a superstructure line in the XRD pattern. It is apparent that replacement of the Zr⁴⁺ ion by Mg²⁺/W⁶⁺ ions decreases the driving force for the antiparallel shift of Pb²⁺ ions, because they interrupt the translational symmetry. This interruption causes the appearance of an intermediate ferroelectric phase and similar behavior has been found in PZ–PNN ceramics [28]. The DSC technique was used as the third tool to confirm the phase transition of PZ–PMW ceramics. Fig. 5 shows the temperature dependence of the heat flow (DSC curves) obtained when heating the 0.94PZ–0.06PMW sample at a rate of 10°C/min. Two phase transitions in the 0.94PZ–0.06PMW ceramic were obtained with dielectric measurement and clearly confirmed by DSC measurement. The lower temperature of 163°C corresponded to the transition temperature of the AFE→FE phase transition, while the higher one (215°C) corresponded to the FE→PE phase transition. It is interesting to note that the difference in values of AFE–FE and FE–PE transition temperature in dielectric, ferroelectric and DSC measurement techniques is due to that in heating

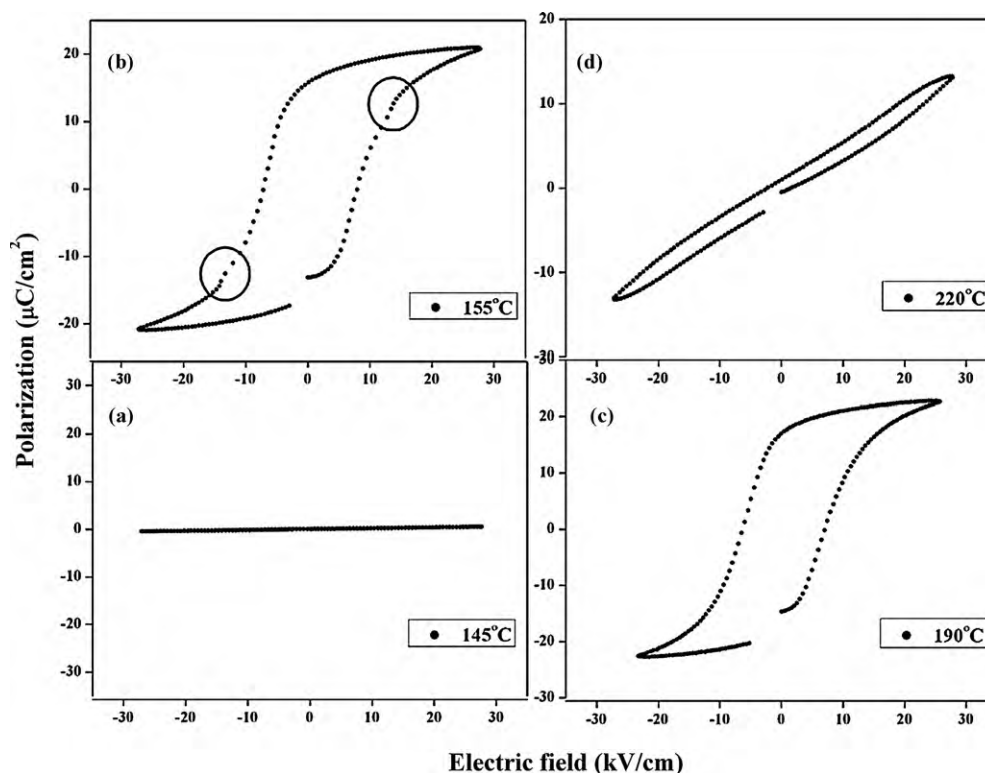


Fig. 4. Hysteresis loops of 0.94PZ–0.06PMW ceramic from temperatures of 145–220°C.

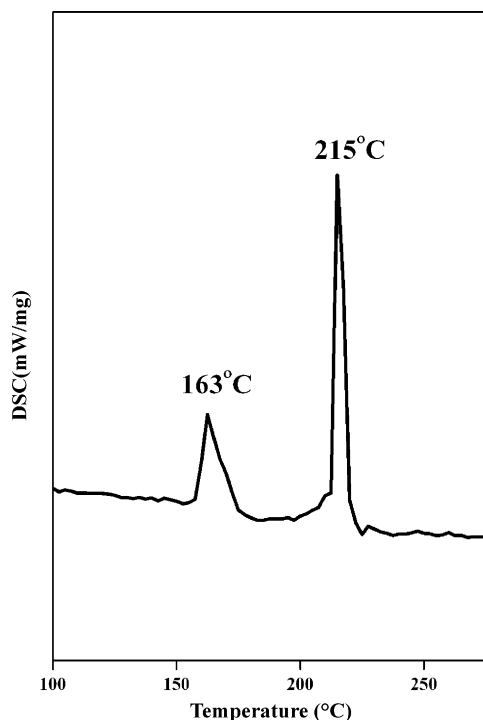


Fig. 5. DSC curves of 0.94PZ–0.06PMW ceramic.

rate and dwell time measurement. Thermodynamic parameter, enthalpy ($\Delta H^*/J\ g^{-1}$), heat capacity ($C_p/J\ g^{-1}\ K^{-1}$), entropy change ($\Delta S^*/J\ g^{-1}\ K^{-1}$), and Gibbs energy change ($\Delta G^*/J\ g^{-1}$) were calculated from the DSC results. The enthalpy change was calculated directly from the amount of heat change involved in each step per unit mass of the sample. The ΔH^* was thus determined and implemented to calculate the specific heat capacity (C_p) using the following equation [30,31]:

$$C_p = 2.303C_p \log(T_2/T_1) \quad (1)$$

where $\Delta T = T_2 - T_1$, T_1 is the temperature at which the DSC peak begins to depart from the baseline, and T_2 is the temperature at which the peak lands. Consequently, the changes of entropy (ΔS^*) and Gibbs energy (ΔG^*) were calculated using the following equations [30,31]:

$$\Delta S^* = 2.303C_p \log(T_2/T_1) \quad (2)$$

$$\Delta H^* = \Delta G^* - T_p \Delta S^* \quad (3)$$

On the basis of DSC data, the value of ΔH^* , ΔS^* , C_p and ΔG^* for the phase transition can be calculated according to Eqs. (1)–(3), which are presented in Table 1. In terms of the activated complex theory (transition theory), the higher value of ΔS^* for the AFE to FE phase transition indicates a lower ordered activated complex. Also, the degree of rotation freedom as well as vibration is higher than that in non-activated complex antiferroelectric and paraelectric phases, which corresponds well with the formation of a non-stability phase. This means that the rate of AFE to FE phase transition is higher than that of the FE to PE phase transition

Table 1
Values of thermodynamic parameters for phase transition of 0.94PZ–0.06PMW ceramics calculated from DSC data.

Temperature ranges/K	T_p/K	$\Delta H^*/J\ g^{-1}$	$C_p/J\ g^{-1}\ K^{-1}$	$\Delta S^*/J\ g^{-1}\ K^{-1}$	$\Delta G^*/J\ g^{-1}$
431–441	436	1.207	2.768×10^{-3}	6.350×10^{-5}	1.179
487–491	488	2.325	4.764×10^{-3}	3.858×10^{-5}	2.308

of thermal transformation. Therefore, the FE to PE transformation step occurs harder than the AFE to FE transformation step. On the other hand, the thermodynamic parameter, ΔH^* and ΔG^* , was calculated according to Eqs. (1)–(3) and gave the positive values for both steps, thus indicating that the AFE to FE to PE phase transitions are connected to the introduction of heat, and phase transitions are non-spontaneous processes.

4. Conclusions

The investigation of 0.94PZ–0.06PMW ceramics using XRD, dielectric behavior, differential scanning calorimetry and ferroelectric measurements has clearly shown a series of phase transitions that occur above room temperature. When the ceramic is in an antiferroelectric nature below 177 °C, both the dielectric property and the loss tangent are low and stable against temperature change. One order of magnitude increase in dielectric property occurs at around 177 °C, and loss tangent results within a narrow temperature range. The ceramic is in an intermediate phase at a temperature range of 177–219 °C, when it is believed to be ferroelectric. When the ceramic is above 219 °C, it is in the cubic paraelectric phase, with relative permittivity following the Curie–Weiss law. A thermodynamic parameter indicated that the AFE to FE to PE phase transitions are connected to the introduction of heat, and phase transitions are non-spontaneous processes.

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Soft Synthesis Route and Characterization of Superparamagnetic $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and Its Decomposed Product

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ABSTRACT: The superparamagnetic $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ was synthesized by a soft synthesis method using a $\text{Mn}(\text{c})\text{--Fe}(\text{c})\text{--H}_3\text{PO}_4$ system in water–acetone medium at ambient temperature. The synthesized $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ decomposed through the dehydration and the phosphate condensation reactions at high temperature and yielded binary manganese iron cyclotetraphosphate $\text{MnFeP}_4\text{O}_{12}$. The XRD and FTIR results of the synthesized $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and the decomposed $\text{MnFeP}_4\text{O}_{12}$ indicate the pure monoclinic phase with space group $P2_1/n$ and $C2/c$, respectively. The thermal behaviors and superparamagnetic properties of $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{MnFeP}_4\text{O}_{12}$ in this work differed from the single compounds ($\text{M}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{M}_2\text{P}_4\text{O}_{12}$, where $\text{M} = \text{Mn}, \text{Fe}$) and the binary compounds ($\text{Mn}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$) reported in previous works. The kinetic and thermodynamic functions for thermal decomposition of $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ were studied and confirmed as reaction mechanisms. Vibrational frequencies of breaking bonds in two thermal transformation stages were estimated and assigned by comparison with the observed FTIR spectra.

1. INTRODUCTION

Binary metal(II) dihydrogenphosphate hydrates $\text{M}_{1-x}\text{A}_x(\text{H}_2\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$ (M and $\text{A} = \text{Mg}, \text{Ca}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Zn}$, or Cu ; $x = 0\text{--}1$; $n = 1\text{--}4$) have been investigated for over 30 years and have been widely applied as potential pigments, selective catalysts, phosphors, and materials for corrosion-resistant coatings, and they are biocompatible and biodegradable in tissue.^{1–9} This phosphate hydrate group is transformed to binary metal(II) cyclotetraphosphate group $\text{M}_{2-y}\text{A}_y\text{P}_4\text{O}_{12}$ ($y = 0\text{--}2$) via the reactions of dehydration and deprotonation of dihydrogenphosphate groups as well as polycondensation at high temperatures.^{10–16} Both phosphate groups are good sources for macro- and micronutrients (P , Mg , Ca , Mn , Fe , Co , Ni , Zn , Cu) required by plants.^{3–13} Consequently, these phosphate materials have been become a hot research topic in materials science in recent years.

Some binary metal $\text{M}_{1-x}\text{A}_x(\text{H}_2\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$ were prepared for the first time by Trojan et al. using corresponding metal carbonates and phosphoric acid at low temperature (313–353 K) with long time periods (2–60 h),^{1–16} and releasing toxic gas (CO_2). Recently, $\text{M}_{1-x}\text{Ni}_x(\text{H}_2\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ ($\text{M} = \text{Mg}, \text{Mn}, \text{Fe}, \text{Co}, \text{Zn}$, and Cd) were prepared by corresponding metal carbonates and phosphoric acid at 293 K for 2–90 days.⁹ More recently, $\text{Mn}_{1-x}\text{A}_x(\text{H}_2\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ ($\text{A} = \text{Ca}, \text{Fe}, \text{Co}, \text{Ni}$, and Cu) were prepared by metal sources (Mn (c; complexometric) or MnCO_3 and $\text{A}(\text{II}) = \text{CaCO}_3, \text{Fe}, \text{CoCO}_3, \text{NiCO}_3$, or CuCO_3) and phosphoric acid H_3PO_4 at ambient temperature for 20 s. These procedures were strong exothermic reactions and evolved gases (CO_2 and H_2).^{17–21} However, a limited dose of $\text{M}_{1-x}\text{A}_x(\text{H}_2\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$ could be synthesized without toxic gases.

Synthesis of transition phosphates by a soft solid state reaction in media agents (ethanol, acetone, and water, etc.) at ambient temperature has received a great deal of attention due to their conveniences, cost-effectiveness, and that they are environmentally benign.^{22–24} Because of its solubility in water and its ability to associate with metal ions in media, solvent has been used as a binder cum gel for shaping materials (bulk, porous, micro- or nanoparticles) and as a matrix for entrapment of ions to generate a gelled precursor, which resulted in obtaining different material or the same material with different size and morphology. The presence of media agent (solvent) reduces strong exothermic reaction and protects the evolved gases, which will be necessary for elaboration of technology to produce transition metal phosphates. The use of solvent simplifies the process and would provide another alternative process for the environmental and economical synthesis of transition phosphate with different particle size and morphology.

Herein, this work reports the fabrication of $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ through a soft solid state reaction from metals of manganese and iron with phosphoric acid in water–acetone medium at ambient temperature with short time consumption (<30 min). The synthesized $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ decomposed to binary manganese iron cyclotetraphosphate $\text{MnFeP}_4\text{O}_{12}$ at 773 K. Consequently, kinetic (E_a , A) and thermodynamic (ΔH^* , ΔS^* , ΔG^*) functions of thermal transformation of $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ playing an important role in

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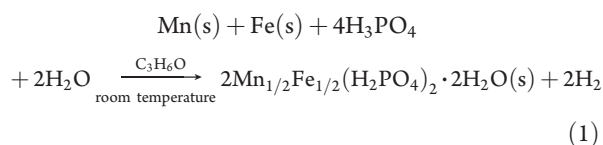
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theoretical study, application development, and industrial production have also been reported for the first time. The synthesized sample and its decomposed product were characterized by X-ray powder diffraction (XRD), Fourier transform infrared (FTIR), scanning electron microscope (SEM), and vibrating sample magnetometer (VSM) techniques. The $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{MnFeP}_4\text{O}_{12}$ may be useful for fertilizers, (Mn- and Fe-micronutrients and P-macronutrients), ceramic pigments, magnetic materials, etc., in the future.

2. EXPERIMENTAL SECTION

2.1. Synthesis and Characterization. The starting reagents are Mn (c; complexometric) (99.99%, Merck), Fe (c; complexometric) (99.99%, Fluka), and phosphoric acid (86.4% w/w H_3PO_4 , Merck). Following this procedure, 1.0988 g of Mn(c) and 1.1186 g of Fe(c) (a mole ratio corresponding to the nominal composition of Mn:Fe ratio of 1:1) were crushed into fine mixed powders using a mortar and pestle. Subsequently, 10 mL of acetone was rapidly added to the fine mixed powders, and then 10 mL of 50% H_3PO_4 (86.4% w/w H_3PO_4 dissolved in DI water) was added slowly to the resulting suspension with continuous stirring at ambient temperature until the cooled crystalline product was developed (30 min). The prepared solid was filtered by a suction pump, washed with acetone, and dried in air.



The water content was investigated by the TG curve in Figure 1, which reveals that its final decomposed product, $\text{MnFeP}_4\text{O}_{12}$, seemed to occur at temperatures above 673 K. The dried white gray precipitation then was calcined in a box furnace at 773 K for 3 h in air atmosphere. The manganese and iron contents of $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{MnFeP}_4\text{O}_{12}$ were determined by dissolving in 0.0126 M hydrochloric acid using atomic absorption spectrophotometer (AAS, Perkin-Elmer, Analyst100). The phosphorus content was determined by colorimetric analysis of the molybdophosphate complex. The structure and crystallite size of the synthesized sample and its decomposed product were studied by X-ray powder diffraction using an X-ray diffractometer (Phillips PW3040, The Netherlands) with Cu K α radiation ($\lambda = 0.15406$ nm). The Scherrer method was used to evaluate the crystallite size.²⁵ The morphologies of the prepared samples were examined with a scanning electron microscope (SEM) using LEO SEM VP1450 after gold coating. The room temperature FTIR spectra were recorded in the range of 4000–370 cm^{-1} with eight scans on a Perkin-Elmer Spectrum GX FT-IR/FT-Raman spectrometer with the resolution of 4 cm^{-1} using KBr pellets (KBr, spectroscopy grade, Merck). The magnetic properties of the $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{MnFeP}_4\text{O}_{12}$ were examined at room temperature (293 K) using a vibrating sample magnetometer (VSM 7403, Lake Shore, U.S.).

2.2. Kinetic and Thermodynamic Studies. To evaluate the activation energies for the thermal decomposition of $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, a TG-DTA Pyris Diamond Perkin-Elmer Instrument was used. The experiments were performed in dynamic dry air, at heating rates of 5, 10, 15, and 20 K min^{-1} over the temperature range from 303 to 673 K and the O_2 flow rate of 100 mL min^{-1} . The sample mass of about 6.0–10.0 mg

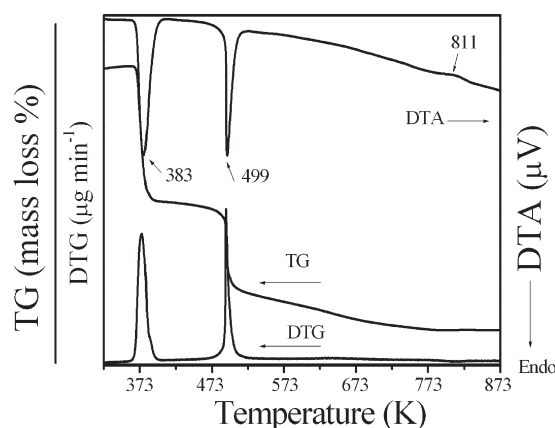


Figure 1. TG-DTG-DTA curves of $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$.

was filled into an aluminum crucible without pressing. The thermogram of sample was recorded in an open aluminum crucible using $\alpha\text{-Al}_2\text{O}_3$ as the reference material. Decomposition of crystal hydrates is a solid-state process of the type^{26–32} $\text{A(solid)} \rightarrow \text{B(solid)} + \text{C(gas)}$. The kinetics of such reactions is described by various equations taking into account the special features of their mechanisms. The activation energies for the thermal transformation steps of $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ were calculated from two peaks on the DTA curves using the Kissinger equation:³³

$$\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E_a}{RT_p} + \ln\left(\frac{AR}{E_a}\right) \quad (2)$$

Here, β is the DTA heating rate (K min^{-1}), E_a is the activation energy for the phase transformation (kJ mol^{-1}), R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and T_p is the phase transformation temperature peak in the DTA curve (K). The fact that the T_p values for various heating rates can be precisely evaluated from nonisothermal data (DTA, DTG, or DSC curves) conferred to the Kissinger method to evaluate the kinetic parameters a high popularity. The plots of $\ln(\beta/T_p^2)$ versus $1/T_p$ should give the straight lines with the best correlation coefficients of the linear regression (R^2), which have been proved to give the values of activation energy and pre-exponential factor by the slope and the intercept for the different thermal transformation stages of $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$. The advantage of Kissinger equation is that the values of E_a and A can be calculated on the basis of multiple thermogravimetric curves and do not require selection of particular kinetic model (type of $g(\alpha)$ or $f(\alpha)$ functions).^{26–31} In addition, the E_a and A values obtained by this method are usually regarded as more reliable than those obtained by a single thermogravimetric curve.

The thermal decomposition mechanism could be determined from the shape factor (n) of the endothermic peak represented by the following equation:³⁴

$$n = \frac{2.5}{\Delta T} \cdot \frac{T_p^2}{E_a/R} \quad (3)$$

where n is the Avrami constant, and ΔT is the full width at half-maximum of the endothermic peak; T_p is the average temperature at different DTA curves; and E_a is the activation energy of the Kissinger method.

From the activated complex theory (transition state) of Eyring,^{35–37} the following general equation may be written:

$$A = \left(\frac{e\chi k_B T_{ap}}{h} \right) \exp\left(\frac{\Delta S^*}{R} \right) \quad (4)$$

$$\Delta S^* = R \ln \left(\frac{Ah}{e\chi k_B T_{ap}} \right) \quad (5)$$

Because

$$\Delta H^* = E_a - RT_{ap} \quad (6)$$

$$\Delta G^* = \Delta H^* - T_{ap}\Delta S^* \quad (7)$$

where A and E_a are the pre-exponential factor and the activation energy, respectively, obtained from the Kissinger method; $e = 2.7183$ is the Neper number; χ is the transition factor, which is unity for monomolecular reactions; k_B is the Boltzmann constant; h is the Planck constant; and T_{ap} is the average phase transformation temperature peak in DTA curves (K). The changes of the enthalpy ΔH^* and Gibbs free energy ΔG^* for the activated complex formation from the reagent can be calculated using the well-known thermodynamic equation. In this Article, we suggest the relation between kinetic (E_a and A) and thermodynamic (ΔH^* , ΔS^* , ΔG^*) parameters of the thermal transformation of $Mn_{1/2}Fe_{1/2}(H_2PO_4)_2 \cdot 2H_2O$ based on the Kissinger method and attract the interest of thermodynamic and kinetic scientists.

The specificity of the thermal decomposition was characterized by identification of the bonds to be selectively activated due to energy absorption at vibrational level.²⁸ These bonds were assigned by comparing the calculated wavenumbers with the observed wavenumbers in the IR spectra. These breaking bonds are assimilated with a Morse oscillator^{28,37,38} coupled nonlinear^{37,38} with the harmonic oscillators of the thermic field. Following a theoretical treatment developed by Vlase et al.,²⁸ the relationship between the average phase transformation temperature peak in four DTA curves (T_{ap} , K) and the wavenumber of the activated bond is given as follows:

$$\omega = \frac{k_b}{hc} T_{ap} = 0.695 T_{ap} \quad (8)$$

where c is the light velocity. Because the breaking bond has an unharmonic behavior, the specific activation is possible also due to more than one quanta, or by a higher harmonic: $\omega_{sp} = q\omega_{calc}$, $q \in N = 1, 2, 3, \dots$, where ω_{sp} is the assigned spectroscopic number for the bond supposed to break, which relates to the evolved gas in the thermal decomposition step. In this Article, we suggested the maximum peak temperature T_{ap} in the DTA curve for the calculated wavenumbers (ω_{sp}) according to eq 8. Therefore, the use of T_p (DTA) will be an alternative method for the calculated wave numbers for identification in each thermal transition step of interesting materials.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization. According to the chemical analysis data, the $P/(Mn + Fe) = 2.01$ and $H_2O/P = 1.82$ molar ratios in the synthesized phosphate differed very little from those calculated for binary metal dihydrogenphosphate

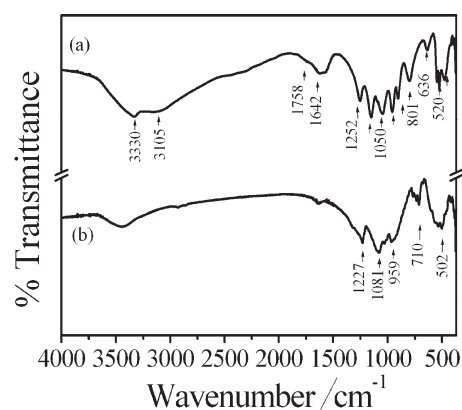
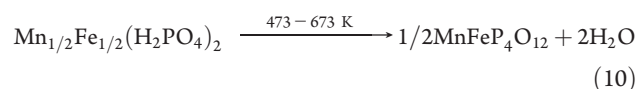
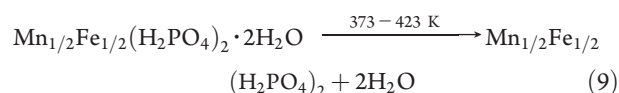


Figure 2. FTIR spectra of $Mn_{1/2}Fe_{1/2}(H_2PO_4)_2 \cdot 2H_2O$ (a) and $MnFeP_4O_{12}$ (b).

with the general formula $Mn_{1/2}Fe_{1/2}(H_2PO_4)_2 \cdot 2H_2O$. Similarly, the $P/(Mn + Fe) = 1.98$ molar ratio in the decomposed product practically corresponds to the $MnFeP_4O_{12}$ stoichiometry, where $Mn(II)$ and $Fe(II)$ stand for divalent cations.

Figure 1 shows the TG-DTG-DTA curves of $Mn_{1/2}Fe_{1/2}(H_2PO_4)_2 \cdot 2H_2O$. The TG curve of $Mn_{1/2}Fe_{1/2}(H_2PO_4)_2 \cdot 2H_2O$ relating to the elimination of water molecules shows two well-defined mass loss stages in the range of 303–873 K. These two steps in the TG curve observed in the ranges of 373–423 and 473–673 K appear in the respective DTG and DTA as two endothermic peaks (383 and 499 K). The corresponding observed mass losses of 11.86 (1.89 mol of H_2O) and 11.73 (1.86 mol of H_2O) % by mass are assigned to the dehydration of coordination water molecules (eq 9) and an intramolecular dehydration of the protonated dihydrogenphosphate groups (eq 10), respectively. The total mass loss of 23.58% (3.74 mol H_2O) is in agreement with those reported for other binary dihydrogenphosphate dihydrate in the literature ($1 < \text{mole of water} < 4$).^{1–9} The thermal decomposition process of $Mn_{1/2}Fe_{1/2}(H_2PO_4)_2 \cdot 2H_2O$ could be formally presented as:



A stable intermediate compound, acid polyphosphate $Mn_{1/2}Fe_{1/2}(H_2PO_4)_2$, has been registered. This intermediate is similarly observed with other binary dihydrogen phosphates, as it is isostructural.^{1–9} The plateau formed between 673 and 873 K on the TG curve indicated the formation of binary manganese iron cyclotetraphosphate, $MnFeP_4O_{12}$, as the final decomposed product. The thermal stability, mechanism, and phase transition temperature of the synthesized $Mn_{1/2}Fe_{1/2}(H_2PO_4)_2 \cdot 2H_2O$ in water–acetone medium of this work are significantly different from those of $Mn(H_2PO_4)_2 \cdot 2H_2O$,⁴⁰ $Fe(H_2PO_4)_2 \cdot 2H_2O$,⁴¹ and $Mn_{0.5}Fe_{0.5}(H_2PO_4)_2 \cdot xH_2O$ ¹⁸ synthesized without media agents. The obtained results are similar to those of the $Mn(H_2PO_4)_2 \cdot 2H_2O$ ²² synthesized by water–acetone medium reported in our previous works. On the basis of thermal results, we can conclude that the different thermal behaviors are caused by the

different interaction and position of Mn and Fe metals in the skeleton, the medium reagents, and reaction condition for precipitation.

The FT-IR spectra of $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (Figure 2a) and $\text{MnFeP}_4\text{O}_{12}$ (Figure 2b) are very similar to those of $\text{M}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{M}_2\text{P}_4\text{O}_{12}$ ($\text{M} = \text{Mn}$ or Fe), respectively.^{1,2,18,22,40,41} The band positions are shifted to the values between those of individual $\text{M}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{M}_2\text{P}_4\text{O}_{12}$ ($\text{M} = \text{Mn}$ or Fe), and sharp or weak bands are observed, indicating the inserting of different metal cations (Mn and Fe) in the skeleton. Consequently, vibrational bands are identified in relation to the crystal structure in terms of the fundamental vibrating units, H_2PO_4^- and H_2O for $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $[\text{P}_4\text{O}_{12}]^{4-}$ ion for $\text{MnFeP}_4\text{O}_{12}$, and are assigned according to the literature.^{1,2,18,42} It is known that the existence of short $\text{OH} \cdots \text{O}$ hydrogen bonds in a variety of strongly hydrogen-bonded solids is manifested by the appearance of the characteristic ABC structure of the $\nu(\text{OH})$ vibration. Usually, the ABC bands are very broad and consist of many ill-resolved components. The strongest band (A) is located in the $3100\text{--}2700\text{ cm}^{-1}$ region, the B band appears at about $2600\text{--}2400\text{ cm}^{-1}$, and the C band is around $1700\text{--}1600\text{ cm}^{-1}$. The problem of the origin of the ABC trio is discussed in many studies on acidic salts, but an explanation of this behavior of strongly hydrogen-bonded systems is still to be found. One of the most popular interpretations of the ABC trio suggests a strong Fermi resonance between the $\nu(\text{OH})$ stretching fundamentals and the overtones $[2\delta(\text{OH})$ and $2\gamma(\text{OH})]$ or combinations involving the $\delta(\text{OH})$ and $\gamma(\text{OH})$ vibrations.^{1,2,18,22} The second type of characteristic vibrations is associated with the phosphate groups. The stretching P–O and bending OPO vibrations of the phosphate groups appear in the ranges of $920\text{--}990\text{ cm}^{-1}$ (ν_1), $990\text{--}1160\text{ cm}^{-1}$ (ν_3), $460\text{--}375\text{ cm}^{-1}$ (ν_2), and $460\text{--}650\text{ cm}^{-1}$ (ν_4). In addition to the internal PO_4 vibrations, other vibrations involving OH motions are the characteristic of the protonated phosphate ions (H_2PO_4^-), both out-of-plane $\delta(\text{OH})$ and in-plane $\gamma(\text{OH})$ bending P–O–H vibrations, which appear at 1252 and 801 cm^{-1} , respectively. The third spectra feature in the FTIR spectrum (Figure 2a) of $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ is the water molecule vibrations. The ν_{OH} stretching modes of HOH appear at 3105 cm^{-1} (ν_1 or band A) and 3330 cm^{-1} (ν_3). The doublet bands (1642 and 1570 cm^{-1}) contribute both to the band C and to the water bending band.² A weak band around 639 cm^{-1} could be tentatively assigned to the rocking mode involving water librations.

The vibrational modes of $\text{P}_4\text{O}_{12}^{4-}$ ion observed in the frequency range $370\text{--}1400\text{ cm}^{-1}$ (Figure 2b) are assigned according to the literature.^{2,18,42} The $\text{P}_4\text{O}_{12}^{4-}$ anion contains the PO_2^{2-} radical and the P–O–P bridge, which are interpreted in the FTIR spectra from the viewpoint of the vibrations of these two groups. As the P–O bond strength in the P–O–P bridge is weaker than in the PO_2^{2-} radical, the stretching frequencies of the P–O–P bridge are expected to be lower than those in the PO_2^{2-} radical. The asymmetric and symmetric stretching frequencies of the PO_2^{2-} radical are generally observed in the areas of $1350\text{--}1220$ and $1150\text{--}1100\text{ cm}^{-1}$, respectively. The P–O–P bridge has its asymmetric and symmetric stretching frequencies around $1000\text{--}900$ and $900\text{--}700\text{ cm}^{-1}$, respectively. The bending modes are expected in the area of $600\text{--}400\text{ cm}^{-1}$ (PO_2^{2-} radical) and $400\text{--}370\text{ cm}^{-1}$ (P–O–P bridge). The metal–O stretching usually appears in the bending mode region as the bending modes of the P–O–P bridge and absorption

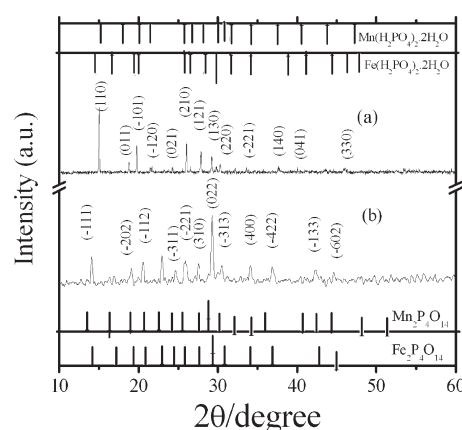


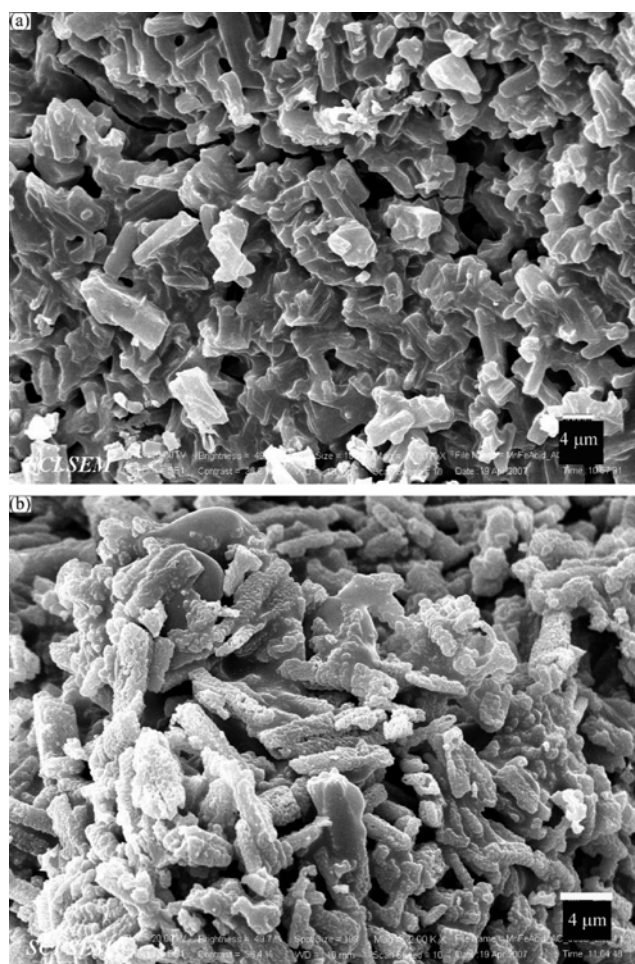
Figure 3. XRD patterns of $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (a) and $\text{MnFeP}_4\text{O}_{12}$ (b).

bands associated with these vibrations are usually very weak. The observation of a strong $\nu_s\text{POP}$ band is known to be the most striking feature of the cyclotetraphosphate spectra, along with the presence of the $\nu_{\text{as}}\text{OPO}^-$ band, which confirmed that the crystal structure is monoclinic (space group $\text{C2}/c$) with a cyclic structure of the $[\text{P}_4\text{O}_{12}]^{4-}$ anion.⁴²

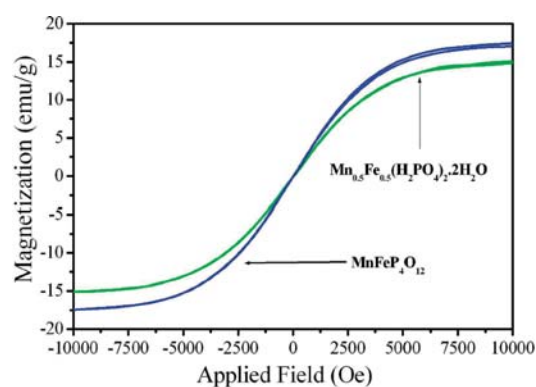
Figure 3 shows the XRD patterns of $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and the decomposed product $\text{MnFeP}_4\text{O}_{12}$, which are similar to those obtained from the individual compounds ($\text{M}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{M}_2\text{P}_4\text{O}_{12}$ ($\text{M} = \text{Mn}$ and Fe)).^{1,2,22,40,41} and the binary compounds ($\text{Mn}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ and $\text{MnFeP}_4\text{O}_{12}$) in our previous work,¹⁸ but the intensities are slightly different. The lower and higher intensities of XRD peaks indicate the differences of crystallization or amorphous phase as well as particle sizes of these materials. According to the hypothesis of isostructural, the systems of binary manganese iron solid solutions and individual metal dihydrogenphosphate (or manganese iron cyclotetraphosphate) show quite a similarity of the XRD peaks because the electronic charges of cations are equivalent and the radii of cations are close to each other. As compared to the published XRD data of the individual metal compounds ($\text{Mn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (PDF# 350010), $\text{Fe}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (PDF# 390699), $\text{Mn}_2\text{P}_4\text{O}_{12}$ (PDF# 380314), and $\text{Fe}_2\text{P}_4\text{O}_{12}$ (PDF# 760223), both studied samples can be assigned to the $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{MnFeP}_4\text{O}_{12}$ product, which are solid solutions and not a mixture of the individual ones. Consequently, all the reflections can be distinctly indexed as a pure monoclinic phase with space group $\text{P2}_1/n$ ($Z = 2$) for $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{C2}/c$ ($Z = 4$) for the decomposed $\text{MnFeP}_4\text{O}_{12}$, which noted that these XRD patterns agreed well with those of standard data of $\text{M}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{M}_2\text{P}_4\text{O}_{12}$ ($\text{M} = \text{Mn}$ or Fe), respectively. The average crystallite sizes and lattice parameters of $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and the decomposed product $\text{MnFeP}_4\text{O}_{12}$ were calculated from XRD patterns and also tabulated in Table 1. The lattice parameters of $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ are larger than those of the standard data of $\text{Mn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (PDF# 350010) and $\text{Fe}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (PDF# 390699). However, the lattice parameters of the decomposed $\text{MnFeP}_4\text{O}_{12}$ are found to range between those of the standard data of $\text{Mn}_2\text{P}_4\text{O}_{12}$ (PDF# 380314) and $\text{Fe}_2\text{P}_4\text{O}_{12}$ (PDF# 760223). The average crystallite size of $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ is larger than that of the calcined $\text{MnFeP}_4\text{O}_{12}$, which resulted from two decomposition

Table 1. Average Crystallite Sizes and Lattice Parameters of $\text{Mn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, $\text{Fe}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, and the Calcined Product $\text{MnFeP}_4\text{O}_{12}$ Calculated from XRD Data

compound	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (deg)	average crystallite size (nm)
PDF# 350010 ($\text{Mn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$)	7.32	10.08	5.37	94.75	
this work ($\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$)	7.90(0)	11.03(6)	6.10 (3)	95.04 (6)	79 ± 11
PDF# 390699 ($\text{Fe}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$)	7.31	9.94	5.37	95.24	
PDF# 380314 ($\text{Mn}_2\text{P}_4\text{O}_{12}$)	11.88	8.59	10.14	119.21	
this work ($\text{MnFeP}_4\text{O}_{12}$)	12.06(8)	8.48(2)	10.12(4)	119.12(5)	62 ± 13
PDF# 760223 ($\text{Fe}_2\text{P}_4\text{O}_{12}$)	11.94	8.37	9.94	118.77	

**Figure 4.** SEM micrographs of $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (a) and $\text{MnFeP}_4\text{O}_{12}$ (b).

processes. The crystallite sizes of 79 ± 11 nm for $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and 62 ± 13 nm for $\text{MnFeP}_4\text{O}_{12}$ in this work are smaller than those prepared from $\text{Mn}(\text{c})\text{--Fe}(\text{c})\text{--H}_3\text{PO}_4$ without the medium system reported by Boonchom et al. (81 ± 14 nm for $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ and 69 ± 21 nm for $\text{MnFeP}_4\text{O}_{12}$).¹⁸ However, the crystallite sizes for both binary compounds in this work are larger than those from the single

**Figure 5.** The specific magnetizations of $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{MnFeP}_4\text{O}_{12}$ as a function of field, measured at 293 K.

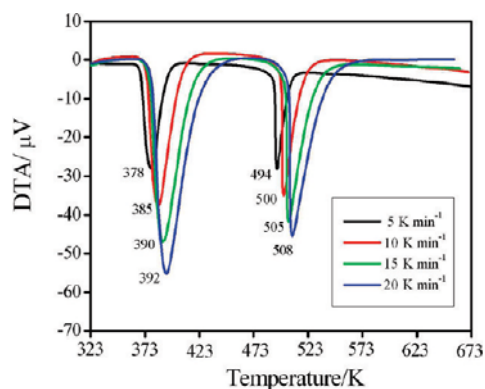
metal compounds (52 ± 14 nm for $\text{Mn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, 28 ± 4 nm for $\text{Fe}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, 29 ± 9 nm for $\text{Mn}_2\text{P}_4\text{O}_{12}$, and 27 ± 6 nm for $\text{Fe}_2\text{P}_4\text{O}_{12}$) in our previous studies.^{22,40,41} These results confirmed that the differences in the crystallite sizes for the synthesized $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{MnFeP}_4\text{O}_{12}$ depend on the medium, water, and metal compositions and the condition for precipitations.

The SEM micrographs of $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{MnFeP}_4\text{O}_{12}$ are shown in Figure 4. The particle shape and size are changed throughout the whole decomposition product. The SEM micrograph of $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (Figure 4a) shows nonuniform particles, which appear as high agglomerates. The morphology of $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ exhibits features different from those of $\text{Mn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, $\text{Fe}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, and $\text{Mn}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ reported in our previous works.^{18,40,41} The morphology of $\text{MnFeP}_4\text{O}_{12}$ shows a high agglomerate of nonuniform particles, which is not similar that for $\text{M}_2\text{P}_4\text{O}_{12}$ ($\text{M} = \text{Mn}$ or Fe) (Figure 4b) in the work previously reported.^{18,40,41} The high agglomerates of $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{MnFeP}_4\text{O}_{12}$ powders are possibly caused by the process of dissolution and a rapid coprecipitation as well as the dehydration process.

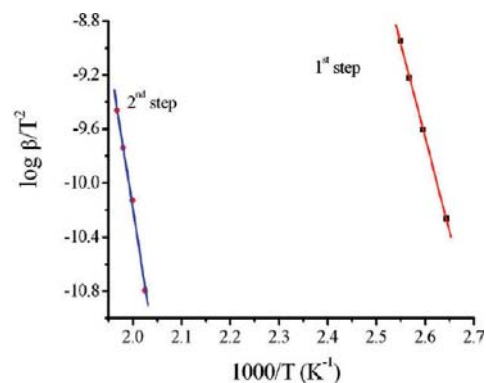
Magnetization curves ($M\text{--}H$ loop) of $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and the decomposed $\text{MnFeP}_4\text{O}_{12}$ powders obtained from room temperature VSM measurements are shown in Figure 5. Both samples demonstrate typical superparamagnetic behavior with negligible coercivity and remanence, in accordance

Table 2. Values of Thermodynamics, Kinetics, and Spectroscopic Data for Two Decomposition Steps of $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$

step	$\Delta G^*/\text{kJ mol}^{-1}$	$\Delta H^*/\text{kJ mol}^{-1}$	$\Delta S^*/\text{J mol}^{-1} \text{K}^{-1}$	A/s^{-1}	$E_a/\text{kJ mol}^{-1}$	R^2	T_{ap}/K	ω_{cal}	q	$q\omega_{\text{cal}}/\text{cm}^{-1}$	band assignment
1	712.34	1119.78	105.46	3.88×10^{20}	115.19	0.9995	386	268	2	537	$\nu_4 (\text{PO}_4^{3-})$
									3	805	$\gamma (\text{OH})$
									4	1074	$\nu_{\text{as}} (\text{PO}_2)$
									6	1611	$\nu_2 (\text{H}_2\text{O})$
									9	2416	B band (H_2PO_4^-)
									11	2953	A band (H_2PO_4^-)
									12	3222	$\nu_1 (\text{H}_2\text{O})$
									13	2490	$\nu_3 (\text{H}_2\text{O})$
2	931.60	1883.50	188.69	1.13×10^{20}	192.54	0.9971	504	350	2	701	$\nu (\text{P}-\text{O}_\text{h})$
									3	1051	$\nu_s (\text{PO}_2)$
									5	1753	C band (H_2PO_4^-)
									7	2454	B band (H_2PO_4^-)
									9	3155	A band (H_2PO_4^-)

**Figure 6.** DTA curves of the synthesized $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ at four different heating rates (5, 10, 15, and 20 K min^{-1}).

with the theory that superparamagnetic behavior is often observed at room temperature.^{43–45} The specific magnetization curves are typical superparamagnetic behavior without any hysteresis in the field range of $\pm 10\,000$ Oe. From the magnetization curves, specific saturated magnetization (M_s) values of the $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{MnFeP}_4\text{O}_{12}$ are 15.097 and 17.459 emu/g, respectively. The superparamagnetic solid solutions formed in $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{MnFeP}_4\text{O}_{12}$ system in this work are different from ferromagnetic for $\text{Fe}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (96.28 emu/g) and $\text{FeP}_4\text{O}_{12}$ (85.01 emu/g),⁴¹ and $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ (25.63 emu/g) and $\text{MnFeP}_4\text{O}_{12}$ (13.14 emu/g),¹⁸ and diamagnetic for $\text{Mn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{MnP}_4\text{O}_{12}$.⁴⁰ It found that the tendency of M_s to increase is consistent with the enhancement of crystallinity or particle sizes, and the saturation values of M_s for $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{MnFeP}_4\text{O}_{12}$ are observed due to the obtained microstructure. These results indicate that the medium reagents for precipitation have the strong effect on the magnetic behaviors of $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{MnFeP}_4\text{O}_{12}$. Superparamagnetic properties of the $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{MnFeP}_4\text{O}_{12}$ samples reported for the first time are important for specific applications because the magnetic materials may be synthesized to have the multifunctions that can be applied in magnetic resonance imaging contrast agents, data lifetime in high density information storage, ferrofluid technology,

**Figure 7.** Kissinger plots indicating the activation energies involving two transformation steps from the synthesized $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ to $\text{MnFeP}_4\text{O}_{12}$.

lithium batteries, magnetocaloric refrigeration catalytic, and/or adsorption processes.⁴⁵

3.2. Kinetic and Thermodynamic Results. The nonisothermal DTA method is desirable to analyze the reaction mechanism and calculate the activation energy of the solid state.^{26–32} Several nonisothermal techniques have been proposed, which are quicker and less sensitive to previous and next transformations. The basic data of T were collected from the DTA curves of the decomposition of $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ at various heating rates (5, 10, 15, and 20 K min^{-1}) (Figure 6). Figure 7 shows the Kissinger plots of two transformation steps of the prepared $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$. From the slopes of the curves (Figure 7), the activation energy values in two decomposition steps of the synthesized $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ were determined as 115.19 and 192.54 kJ mol^{-1} , respectively. The activation energies of two decompositions of $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ are different from those of $\text{Mn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (105–104 kJ/mol for the first step and 199–200 kJ/mol for the second step) and $\text{Fe}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (136–137 kJ/mol for the first step). These activation energies are related to the vibrational frequencies and are the indication of the energy of the breaking bond of intermediate species. The reason may be relevant to the strengths of binding of water molecules in the crystal lattice. Hence, different dehydration temperatures and kinetic parameters are expected. The two mass loss steps

Table 3. Comparing Physical and Chemical Properties of the Studied Materials in the Present Work and in the Literature

ref no.	materials	different synthesis route
this work	$\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{MnFeP}_4\text{O}_{12}$	prepared by $\text{Mn}(\text{c})-\text{Fe}(\text{c})-\text{H}_3\text{PO}_4$ system in water–acetone medium at ambient temperature for 30 min, and its final decomposed product was obtained at 773 K
17	$\text{Mn}_{0.5}\text{Co}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{MnCoP}_4\text{O}_{12}$	prepared by $\text{MnCO}_3-\text{CoCO}_3-\text{H}_3\text{PO}_4$ system at ambient temperature for 15 min, and its final decomposed product was obtained at 773 K
18	$\text{Mn}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{MnFeP}_4\text{O}_{12}$	prepared by $\text{Mn}(\text{c})-\text{Fe}(\text{c})-\text{H}_3\text{PO}_4$ system at ambient temperature for 30 min, and its final decomposed product was obtained at 773 K
19	$\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{CoFeP}_4\text{O}_{12}$	prepared by $\text{Fe}(\text{c})-\text{CoCO}_3-\text{H}_3\text{PO}_4$ system at ambient temperature for 15 min, and its final decomposed product was obtained at 773 K
20	$\text{Mn}_{0.5}\text{Cu}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 1.5\text{H}_2\text{O}$ and $\text{MnCuP}_4\text{O}_{12}$	prepared by $\text{Mn}(\text{c})-\text{CuO}-\text{H}_3\text{PO}_4$ system at ambient temperature for 15 min, and its final decomposed product was obtained at 673 K
21	$\text{Mn}_{0.5}\text{Ca}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{MnCaP}_4\text{O}_{12}$	prepared by $\text{Mn}(\text{c})-\text{CaCO}_3-\text{H}_3\text{PO}_4$ system at ambient temperature for 30 min, and its final decomposed product was obtained at 673 K
22	$\text{Mn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Mn}_2\text{P}_4\text{O}_{12}$	prepared by $\text{Mn}(\text{c})-\text{H}_3\text{PO}_4$ system in water–acetone medium at ambient temperature for 15 min, and its final decomposed product was obtained at 773 K
40	$\text{Mn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Mn}_2\text{P}_4\text{O}_{12}$	prepared by $\text{Mn}(\text{c})-\text{H}_3\text{PO}_4$ and $\text{MnCO}_3-\text{H}_3\text{PO}_4$ systems at ambient temperature for 15 min, and its final decomposed product was obtained at 673 K
41	$\text{Fe}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Fe}_2\text{P}_4\text{O}_{12}$	prepared by $\text{Fe}(\text{c})-\text{H}_3\text{PO}_4$ system at 313 K for 30 min, and its final decomposed product was obtained at 773 K
ref no.	materials	different thermal behavior
this work	$\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{MnFeP}_4\text{O}_{12}$	well-defined two thermal transformation steps in the range of 353–873 K
17	$\text{Mn}_{0.5}\text{Co}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{MnCoP}_4\text{O}_{12}$	four thermal transformation steps in the range of 273–873 K
18	$\text{Mn}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{MnFeP}_4\text{O}_{12}$	three thermal transformation steps in the range of 273–773 K
19	$\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{CoFeP}_4\text{O}_{12}$	three thermal transformation steps in the range of 273–873 K
20	$\text{Mn}_{0.5}\text{Cu}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 1.5\text{H}_2\text{O}$ and $\text{MnCuP}_4\text{O}_{12}$	well-defined two thermal transformation steps in the range of 353–673 K
21	$\text{Mn}_{0.5}\text{Ca}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{MnCaP}_4\text{O}_{12}$	six thermal transformation steps in the range of 353–873 K
22	$\text{Mn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Mn}_2\text{P}_4\text{O}_{12}$	well-defined two thermal transformation steps in the range of 353–1073 K
40	$\text{Mn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Mn}_2\text{P}_4\text{O}_{12}$	more than three thermal transformation steps in the range of 353–773 K
41	$\text{Fe}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Fe}_2\text{P}_4\text{O}_{12}$	three thermal transformation steps in the range of 353–773 K
ref no.	materials	different morphologies
this work	$\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{MnFeP}_4\text{O}_{12}$	high agglomerates of nonuniform particles for both samples
17	$\text{Mn}_{0.5}\text{Co}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{MnCoP}_4\text{O}_{12}$	rod-like shape and nonuniform particles
18	$\text{Mn}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{MnFeP}_4\text{O}_{12}$	rod-like tetrahedral shape and small spherical particles with high agglomerates
19	$\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{CoFeP}_4\text{O}_{12}$	flower like shape for both samples
20	$\text{Mn}_{0.5}\text{Cu}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 1.5\text{H}_2\text{O}$ and $\text{MnCuP}_4\text{O}_{12}$	many small and some large rod like and spherical shapes
21	$\text{Mn}_{0.5}\text{Ca}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{MnCaP}_4\text{O}_{12}$	roughness of many small and some large boundary surfaces and small and large spherical shapes
22	$\text{Mn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Mn}_2\text{P}_4\text{O}_{12}$	small rod like shape and retexturing and coalescence in aggregates of irregularly shape
40	$\text{Mn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Mn}_2\text{P}_4\text{O}_{12}$	large nonuniform polyhedral shape and retexturing and coalescence in aggregates of irregularly shape
41	$\text{Fe}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Fe}_2\text{P}_4\text{O}_{12}$	coalescence in aggregates of irregularly shapes for both samples
ref no.	materials	different magnetic properties
this work	$\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{MnFeP}_4\text{O}_{12}$	superparamagnetic properties ($M_s = 15.097$ emu/g for $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $M_s = 17.459$ emu/g for $\text{MnFeP}_4\text{O}_{12}$)
17	$\text{Mn}_{0.5}\text{Co}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{MnCoP}_4\text{O}_{12}$	not reported
18	$\text{Mn}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ and $\text{MnFeP}_4\text{O}_{12}$	ferromagnetic properties ($M_s = 25.63$ emu/g for $\text{Mn}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ and $M_s = 13.14$ emu/g for $\text{MnFeP}_4\text{O}_{12}$)
19	$\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{CoFeP}_4\text{O}_{12}$	superparamagnetic properties ($M_s = 0.045$ emu/g for $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $M_s = 12.502$ emu/g for $\text{CoFeP}_4\text{O}_{12}$)
20	$\text{Mn}_{0.5}\text{Cu}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 1.5\text{H}_2\text{O}$ and $\text{MnCuP}_4\text{O}_{12}$	not reported
21	$\text{Mn}_{0.5}\text{Ca}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{MnCaP}_4\text{O}_{12}$	not reported
22	$\text{Mn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Mn}_2\text{P}_4\text{O}_{12}$	not reported

Table 3. Continued

ref no.	materials	different magnetic properties
40	Mn(H ₂ PO ₄) ₂ ·2H ₂ O and Mn ₂ P ₄ O ₁₂	not reported
41	Fe(H ₂ PO ₄) ₂ ·2H ₂ O and Fe ₂ P ₄ O ₁₂	ferromagnetic properties ($M_s = 96.28$ emu/g for Fe(H ₂ PO ₄) ₂ ·xH ₂ O and $M_s = 37.78$ emu/g for Fe ₂ P ₄ O ₁₂)
ref no.	materials	different nonisothermal decomposition kinetic data (E_a , A , n)
this work	Mn _{1/2} Fe _{1/2} (H ₂ PO ₄) ₂ ·2H ₂ O and MnFeP ₄ O ₁₂	115.19 kJ mol ⁻¹ , 3.88×10^{15} s ⁻¹ , 2.56 for first step and 192.54 kJ mol ⁻¹ , 1.13×10^{20} s ⁻¹ , 2.06 for second step
17	Mn _{0.5} Co _{0.5} (H ₂ PO ₄) ₂ ·2H ₂ O and MnCoP ₄ O ₁₂	E_a values for four steps as 100.55, 88.90, 90.58, 308.58 kJ mol ⁻¹ , respectively
18	Mn _{0.5} Fe _{0.5} (H ₂ PO ₄) ₂ ·2H ₂ O and MnFeP ₄ O ₁₂	not reported
19	Co _{1/2} Fe _{1/2} (H ₂ PO ₄) ₂ ·2H ₂ O and CoFeP ₄ O ₁₂	not reported
20	Mn _{0.5} Cu _{0.5} (H ₂ PO ₄) ₂ ·1.5H ₂ O and MnCuP ₄ O ₁₂	E_a and n values for two steps as 99.75, 202.84 kJ mol ⁻¹ and 1.34, 1.93, respectively
21	Mn _{0.5} Ca _{0.5} (H ₂ PO ₄) ₂ ·H ₂ O and MnCaP ₄ O ₁₂	E_a values for five steps as 147.85, 129.70, 89.41, 152.94, 236.97 kJ mol ⁻¹ , respectively, A values for five steps as 1.41×10^{20} , 6.55×10^{16} , 4.48×10^9 , 4.04×10^{15} , 1.01×10^{20} , respectively
22	Mn(H ₂ PO ₄) ₂ ·2H ₂ O and Mn ₂ P ₄ O ₁₂	E_a values for two steps as 86.45, 187.92 kJ mol ⁻¹ , respectively
40	Mn(H ₂ PO ₄) ₂ ·2H ₂ O and Mn ₂ P ₄ O ₁₂	not reported
41	Fe(H ₂ PO ₄) ₂ ·2H ₂ O and Fe ₂ P ₄ O ₁₂	E_a value as 136.85 kJ mol ⁻¹
ref no.	materials	different thermodynamic data (ΔH^* , kJ mol ⁻¹ ; ΔG^* , kJ mol ⁻¹ ; and ΔS^* , J mol ⁻¹ K ⁻¹)
this work	Mn _{1/2} Fe _{1/2} (H ₂ PO ₄) ₂ ·2H ₂ O and MnFeP ₄ O ₁₂	1119.78, 712, 105.46 for first step and 1883.50, 931.60, 188.69 for second step
17	Mn _{0.5} Co _{0.5} (H ₂ PO ₄) ₂ ·2H ₂ O and MnCoP ₄ O ₁₂	not reported
18	Mn _{0.5} Fe _{0.5} (H ₂ PO ₄) ₂ ·2H ₂ O and MnFeP ₄ O ₁₂	not reported
19	Co _{1/2} Fe _{1/2} (H ₂ PO ₄) ₂ ·2H ₂ O and CoFeP ₄ O ₁₂	not reported
20	Mn _{0.5} Cu _{0.5} (H ₂ PO ₄) ₂ ·1.5H ₂ O and MnCuP ₄ O ₁₂	not reported
21	Mn _{0.5} Ca _{0.5} (H ₂ PO ₄) ₂ ·H ₂ O and MnCaP ₄ O ₁₂	144.65, 94.38, 130.34 for first step, 126.35, 99.64, 66.18 for second step, 85.50, 119.53–72.26 for third step, 148.71, 127.80, 41.10 for fourth step, and 231.85, 155.59, 123.73 for sixth
22	Mn(H ₂ PO ₄) ₂ ·2H ₂ O and Mn ₂ P ₄ O ₁₂	not reported
40	Mn(H ₂ PO ₄) ₂ ·2H ₂ O and Mn ₂ P ₄ O ₁₂	not reported
41	Fe(H ₂ PO ₄) ₂ ·2H ₂ O and Fe ₂ P ₄ O ₁₂	not reported

correspond to the loss of water of coordinated water in the first steps, subsequently to a continuous intermolecular polycondensation and the elimination of water of constituent in anion in the second step.^{26–28} The second step exhibits higher activation energy in comparison with the first step, and this is understandable because this step relates to true P–OH bond breaking, in connection with the polycondensation reaction.^{1,2,18,40,41} These activation energies are consistent with the former hypothesis that the intermediate nucleates and crystallizes as metastable phase with adequate growth kinetics before the stable phase MnFeP₄O₁₂. This result is consistent with TG-DTG-DTA data as shown in eqs 9 and 10.

The pre-exponential factor (A) can be estimated from the intercept of the plots of eq 2 (Table 2). All calculations were performed using a program compiled by ourselves. The pre-exponential factor (A) values in the Arrhenius equation for solid-phase reactions are expected to be in a wide range (6 or 7 orders of magnitude), even after the effect of surface area is taken into account.^{26–29} The low factors will often indicate a surface reaction, but if the reactions are not dependent on surface area, the low factor may indicate a “tight” complex. The high factors will usually indicate a “loose” complex. Even higher factors (after correction for surface area) can be obtained for complexes having free translation on the surface. Because in many cases the concentrations in solids are not controllable, it would have been convenient if the magnitude of the pre-exponential factor could provide the information for the reaction molecularity. With such bulk decomposition, any molecule is as likely to react with any

others, and no preference is shown toward corners, edges, surface, defects, or sites of previous decomposition. On the basis of these reasons, the thermal decomposition reaction of Mn_{1/2}-Fe_{1/2}(H₂PO₄)₂·2H₂O may be interpreted as “loose complexes” for the first and second steps, which correspond to the proposed mechanism in eqs 9 and 10.

The value of the Avrami exponent provides information regarding the morphology of the growing crystal.^{17,20–22,32,34} The value of n reflects the mechanism dominating crystallization. Here, smaller n values indicate that the crystallization is dominated by a surface crystallization or that the crystallization dimension is low. On the other hand, larger n values are expected only in case of increasing nucleation rates. For Mn_{1/2}Fe_{1/2}(H₂PO₄)₂·2H₂O, the n values are 2.56 for the first and 2.06 for the second decomposition steps, which are random nucleation and growth of nuclei for both decomposition steps.

As can be seen from Table 2, the entropy of activation (ΔS^*) values for all steps are positive values. It means that the corresponding activated complexes had lower degrees of arrangement than the initial state. Because the decomposition of Mn_{1/2}-Fe_{1/2}(H₂PO₄)₂·2H₂O proceeds as two consecutive reactions, the formation of the second activated complex passed in situ. In terms of the activated complex theory (transition theory),^{35–37} a positive value of ΔS^* indicates a malleable activated complex that leads to a large number of degrees of freedom of rotation and vibration. A result may be interpreted as a “fast” stage. On the other hand, a negative value of ΔS^* indicates a highly ordered

activated complex, and the degrees of freedom of rotation as well as of vibration are less than they are in the nonactivated complex. These results may indicate a “slow” stage.^{26–30} With respect to these results, the first and second decomposed steps of $\text{Mn}_{1/2}\text{-Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ may be interpreted as “fast” stages. The positive values of the enthalpy ΔH^* are in good agreement with two endothermic effects in the DTA results. The positive values of ΔH^* and ΔG^* for two stages show that they are connected with the introduction of heat and are nonspontaneous processes. The results of the kinetic and thermodynamic parameters of the second steps are higher than those of the first step, which correspond to that the second step needs a higher energy pathway and a lower rate reaction than the first step.

To corroborate the calculated data with the spectroscopic ones, we drew up the FT-IR spectra of the studied compound (Figure 2). Table 2 shows the comparison of the ω_{calc} values with the ω_{sp} values determined from this compound, together with the assignments of the corresponding vibrational modes in the literature.^{1,2} These wavenumbers are close to the vibrational modes of water of crystallization and dihydrogen phosphate group (H_2PO_4^-) reported in the literature.^{20–22} The results confirm that the loss of the water of crystallization and deprotonated dihydrogen phosphate group in the first step is followed by a continuous intermolecular polycondensation for the second step.^{20–22} The studied compound exhibited a very good agreement between the calculated wavenumbers from average T_p (DTA) and the observed wavenumbers from IR spectra for the bonds that were suggested to be broken.

4. CONCLUSION

The superparamagnetic $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ was prepared by a soft solution solid-state reaction from the $\text{Mn(c)}\text{--Fe(c)}\text{--H}_3\text{PO}_4$ system in water–acetone medium at ambient temperature with short time consumption (30 min). $\text{Mn}_{1/2}\text{-Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ decomposes in two steps, which correspond to the loss of water of crystallization in the first step, subsequently to a continuous intermolecular polycondensation and elimination of water of constituent in anion (the second step). Thermal kinetic study results indicate the activation energies, which relate to the vibrational frequencies of the breaking bond of thermal transformation of $\text{Mn}_{1/2}\text{Fe}_{1/2}\text{-(H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$. The thermal behaviors, morphologies, particle sizes, superparamagnetic properties, kinetic and thermodynamic data of $\text{Mn}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, and its thermal transformation product ($\text{MnFeP}_4\text{O}_{12}$) in this work are different from those of single metal and binary metal compounds in our previous reports (Table 3). The study results obtained are necessary for elaboration of technology to produce the dihydrogenphosphate and cyclotetraphosphate of transition metals, which may be useful for potential applications as catalytic, ceramic, and biomedical materials, etc.

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A simple synthesis and characterization of binary $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and its final decomposition product $\text{CoFeP}_4\text{O}_{12}$

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ABSTRACT

This paper reports the synthesis of binary $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ by a simple, rapid and cost-effective method using $\text{CoCO}_3\text{--Fe(c)--H}_3\text{PO}_4$ system in water–acetone media at ambient temperature. Thermal transformation of the synthesized powder was investigated by TG/DTG/DTA and DSC techniques, which indicate that its final decomposed product was a binary cobalt iron cyclotetraphosphate $\text{CoFeP}_4\text{O}_{12}$. The FTIR and XRD results of the synthesized $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and the decomposed $\text{CoFeP}_4\text{O}_{12}$ indicate the pure monoclinic phases with space group $\text{P}2_1/\text{n}$ and $\text{C}2/\text{c}$, respectively. The morphologies of $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{CoFeP}_4\text{O}_{12}$ powders appear non-uniform particle shapes and high agglomerates, which are different from the cases of the single compounds $\text{M}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{M}_2\text{P}_4\text{O}_{12}$ (where $\text{M} = \text{Co, Fe}$). The magnetic properties of the studied compounds are superparamagnetic behaviors, which are important for specific applications. The physical properties of the studied powders are comparable with those reported in our previous study, affected by medium and condition of preparation method.

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1. Introduction

Binary metal phosphates with the general formula $\text{M}'_x\text{M}''_{1-x}(\text{H}_2\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$ (M' or $\text{M}'' = \text{Mg, Ca, Ba, Mn, Co, Ni, Fe, Zn}$; $x = 0\text{--}1$; $n = 1\text{--}4$) have the incremented use in order to supply the demands of high modern technology [1–3]. This phosphate group is transformed to the corresponding binary metal(II) cyclotetraphosphate group $\text{M}'_y\text{M}''_{2-y}\text{P}_4\text{O}_{12}$ ($y = 0\text{--}2$) in the reactions of dehydration and deprotonation of dihydrogenphosphate groups at higher temperatures [4–6]. Both $\text{M}'_x\text{M}''_{1-x}(\text{H}_2\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$ and $\text{M}'_y\text{M}''_{2-y}\text{P}_4\text{O}_{12}$ compounds are isostructural with the single metal dihydrogenphosphate ($\text{M}'(\text{H}_2\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$) and single metal(II) cyclotetraphosphate ($\text{M}'_2\text{P}_4\text{O}_{12}$) groups, respectively [8–10]. Consequently, they have similar X-ray diffraction patterns and close unit cell parameters, which crystallize in monoclinic space group $\text{P}2_1/\text{n}$ ($Z = 2$) for the dihydrogenphosphate group and $\text{C}2/\text{c}$ ($Z = 4$) for cyclotetraphosphate group. Both binary metal phosphate groups can be used in a wide range of applications: catalysts and adsorbents,

ion-exchange materials, solid electrolytes for batteries, in linear and non-linear optical components, chelating agents, tooth powder and doughs, artificial teeth and bones, corrosion-resistant coating, sewage purifying agents, glass-ceramics, refractories, fire extinguishers, cements, soap powder, biomaterials and implantates, forages for animals, superionic conductors, piezo- and ferroelectrics, gas and moisture sensors, magnets, phosphors, detergents and high-quality fertilizers [1,4,5,11,12]. Therefore, the design, synthesis and characterization of the field of these phosphates have been very active during the twentieth century. However, the development of the chemistry of these phosphates was very slow, spreading along almost a century. So far, there were reports on the synthesis, the thermal analysis (TA) under quasi-isothermal and quasi-isobaric conditions of binary metal(II) dihydrogenphosphate hydrates $\text{M}'_x\text{M}''_{1-x}(\text{H}_2\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$ (M' or $\text{M}'' = \text{Mg, Ca, Ba, Mn, Co, Ni, Fe, Zn}$; $x = 0\text{--}1$; $n = 1\text{--}4$) [1,4,5,8–12]. Recently, Viter and Nagorny [13], Antrapteva et al. [4] and Koleva and Mehandjiev [12,14] reported the synthesis at low temperature (40–80 °C) with long time consumption (2–90 days) of $\text{M}_{1-x}\text{Ni}_x(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Mg, Mn, Co, Zn}$), $\text{Mn}_{1-x}\text{Zn}_x(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{M}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Co, Ni, Mn, Fe}$), respectively. Most recently, our research group reported the rapid synthesis (10–20 min) of $\text{M}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{M}_{1-x}\text{A}_x(\text{H}_2\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$ (M and $\text{A} = \text{Ca, Mn, Fe, Cu, Co}$) at ambient

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temperature [1,2,15,16]. However, it is obstacle to synthesize binary metal dihydrogenphosphates, binary metal cyclotetraphosphates and their solid solutions, which vary the composition of metal cations for obtaining homogeneity ranges and modified useful properties.

In this work, binary $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ was prepared by solid state method at ambient temperature with short time consumption (<10 min), which is a simple and cost-effective route. Thermal transformation of $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ was investigated by thermogravimetry/differential thermal gravimetry/differential thermal analysis (TG/DTG/DTA) and differential scanning calorimetry (DSC) techniques and its final decomposed product is $\text{CoFeP}_4\text{O}_{12}$. Furthermore, the synthesized $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and its decomposed product $\text{CoFeP}_4\text{O}_{12}$ were characterized by X-ray powder diffraction (XRD), Fourier transform infrared (FTIR), scanning electron microscope (SEM) and vibrating sample magnetometer (VSM) techniques.

2. Experimental

Phosphoric acid (H_3PO_4 , Fluka, 86.4% w/w), cobalt carbonate (CoCO_3 , Merck, AR grade), iron metal (Fe, Merck, AR; c; complexometric) and acetone ($\text{CH}_3\text{CH}_2\text{OCH}_3\text{CH}_2$, Merck, AR grade) were used as precursors for phosphorous, Co(II), Fe(II) and media agent, respectively. Typically process, 2.00 mL of distilled water was added to 8.00 mL H_3PO_4 and then H_3PO_4 solution was added to 2.40 g of CoCO_3 and 1.12 g of Fe(c) (a mole ratio corresponding to the nominal composition of Fe:Co ratio of 1.0:1.0) in the presence of 15 mL acetone. This resulting suspension was continuously stirred at ambient temperature for 10 min and the prepared solid was aged for drying at room temperature. The presence of acetone reduced strong exothermic reaction and prevented the evolved $\text{H}_2(\text{g})$ and $\text{CO}_2(\text{g})$ in the precipitation process and developed the highly crystalline product. This method is a simple, rapid, cost-effective and environmental friendly route for synthesis of $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$. The prepared solid was recovered by filtration (suction pump), washed with acetone, and dried in air.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) was carried out in a flow of air (100 mL min^{-1}) with a heating rate of $10^\circ\text{C min}^{-1}$ over the temperature range from 30 to 800°C using a TG–DTG–DTA Pyris Diamond Perkin Elmer Instruments. Its final decomposed product seemed to occur at temperatures above 600°C , so the prepared solid was calcined at 700°C for 3 h. Differential scanning calorimetry was carried out for a sample (5–10 mg) in an aluminum crucible, over the temperature range of 303–823 K using differential scanning calorimetry (DSC), Perkin Elmer Pyris One. The heating rate employed was 10 K min^{-1} . The cobalt and iron contents of the prepared solid and its final decomposed product were determined by dissolving in 0.0126 M hydrochloric acid using atomic absorption spectrophotometry (AAS, Perkin Elmer, Analyst100). The phosphorus content was determined by colorimetric analysis of the molybdophosphate complex. The structure and crystallite size of the synthesized sample and its decomposed product were studied by X-ray powder diffraction using an X-ray diffractometer (Phillips PW3040, The Netherlands) with Cu K α radiation ($\lambda = 0.15406 \text{ nm}$). The Scherrer method was used to evaluate the crystallite size [17]. The photographs of scanning electron microscope (SEM) were obtained by LEO SEM VP1450 after gold coating. The room temperature FTIR spectra were recorded in the range of $4000\text{--}370 \text{ cm}^{-1}$ with 8 scans on a Perkin–Elmer Spectrum GX FT-IR/FT-Raman spectrometer with the resolution of 4 cm^{-1} using KBr pellets (KBr, spectroscopy grade, Merck). The magnetic properties of the prepared solid and its decomposed product were examined at room temperature (20°C) using a vibrating sample magnetometer (VSM 7403, Lake Shore, USA).

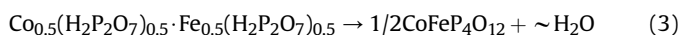
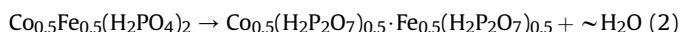
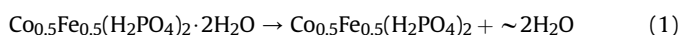
3. Results and discussion

3.1. Chemical analysis

According to chemical analysis data, the $\text{P}/(\text{Co} + \text{Fe}) = 2.13$ and $\text{H}_2\text{O}/\text{P} = 1.92$ molar ratios in the synthesized phosphate differed very little from those calculated for binary metal dihydrogenphosphate with the general formula $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$. Similarly, the $\text{P}/(\text{Co} + \text{Fe}) = 2.01$ molar ratio in the decomposed product practically corresponds to the $\text{CoFeP}_4\text{O}_{12}$ stoichiometry, where Co(II) and Fe(II) stand for divalent cations.

3.2. Thermal analysis

Fig. 1 shows the TG/DTG/DTA curves of $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$. The TG trace shows three mass loss stages in the range of $30\text{--}600^\circ\text{C}$. In the first stage between 45 and 140°C , the mass loss of 11.62% corresponds to the elimination of 1.87 mol water (H_2O) of crystallization. The mass losses of 9.15% for the second stage ($140\text{--}275^\circ\text{C}$) and 5.85% for the third stage ($275\text{--}600^\circ\text{C}$) relate to the eliminations of 1.47 and 0.54 mol water of the deprotonated dihydrogenphosphate groups, respectively. Three endothermic effects in the DTA curve show over the temperature region at 119, 174 and 402°C , which relate to three peaks in DTG curve at 114, 165, and 400°C and closely correspond to the observed mass loss on the TG trace. Further, a small exothermic effect at 712°C without appreciable mass loss is observed in the DTA curve, which can be ascribed to a transition phase form of $\text{CoFeP}_4\text{O}_{12}$. The thermal transformation of $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ involves the dehydration of the coordination water molecule (2 mol H_2O) and an intramolecular dehydration of the protonated dihydrogenphosphate groups (2 mol H_2O) as shown in Eqs. (1) and (3).



An unstable intermediate compounds, such as acid polyphosphate $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2$ and $\text{Co}_{0.5}(\text{H}_2\text{P}_2\text{O}_7)_{0.5} \cdot \text{Fe}_{0.5}(\text{H}_2\text{P}_2\text{O}_7)_{0.5}$ and mixtures of intermediate of both have been registered and

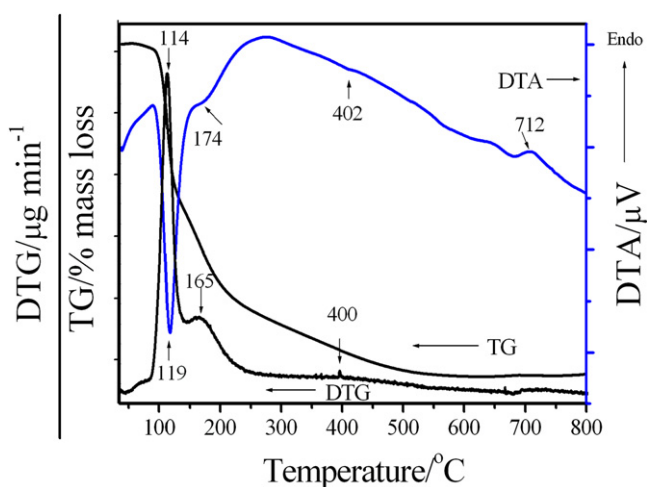


Fig. 1. TG/DTG/DTA curves of $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ at the heating rate of $10^\circ\text{C min}^{-1}$ in air atmosphere.

were similarly observed with the single hydrogen phosphates and other binary metal dihydrogenphosphates [2–8]. The binary cobalt iron cyclotetraphosphate, $\text{CoFeP}_4\text{O}_{12}$ is found to be the final product of the thermal decomposition at $T > 600^\circ\text{C}$. The total mass loss is 26.62% (3.88 mol H_2O), which is in agreement with those reported for other binary dihydrogenphosphate dihydrate in the literature ($1 < \text{mole of water} < 4$) [4,12–16]. The thermal stability, mechanism and phase transition temperature of the studied compound in this work are significantly different from those from the single metal compounds ($\text{Fe}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ [18] and $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ [19]). The different thermal behaviors were considered to be due to the different locations of the incorporation of Fe and Co metals in the skeleton and water constitution, which affect to the strengths of water molecule bonds in the studied compound.

The DSC curve of $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (Fig. 2) shows four endothermic peaks at 121, 167, 215 and 402°C (onset peak at 98, 162, 204 and 389°C) which relate to the dehydration reactions for the first two peaks and the polycondensation reactions for the last two peaks, respectively. Three endothermic peaks at 121, 167 and 402°C in the DSC curve are in good agreement with DTG and DTA curves as shown in Fig. 1. According to DSC experiment, the heat of dehydration reactions and the polycondensation reactions of this compound can be estimated and were found to be 154.80, 7.80, 20.98 and 34.04 J g^{-1} , respectively.

3.3. X-ray powder diffraction

Fig. 3 shows the XRD patterns of the $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ sample and its final decomposed product, which are very similar to those obtained from the single metal compounds of M (H_2PO_4) $_2 \cdot 2\text{H}_2\text{O}$ and $\text{M}_2\text{P}_4\text{O}_{12}$ (when $\text{M} = \text{Co}$ and Fe), respectively. Compared with the published XRD data of the individual metal compounds ($\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (PDF no 390698), $\text{Fe}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (PDF no 751444), $\text{Co}_2\text{P}_4\text{O}_{12}$ (PDF no 842208) and $\text{Fe}_2\text{P}_4\text{O}_{12}$ (PDF no 782285)), both studied samples can be assigned to the $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{CoFeP}_4\text{O}_{12}$ products. According to hypothesis of isostructural, the systems of binary cobalt iron solid solutions and individual metal dihydrogenphosphate (or cobalt iron cyclotetraphosphate) show quite similarity of the XRD peaks because the electronic charges of cations are equivalent and the radii of cations are close to each other. Consequently, we can draw a conclusion that the synthesized $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and its

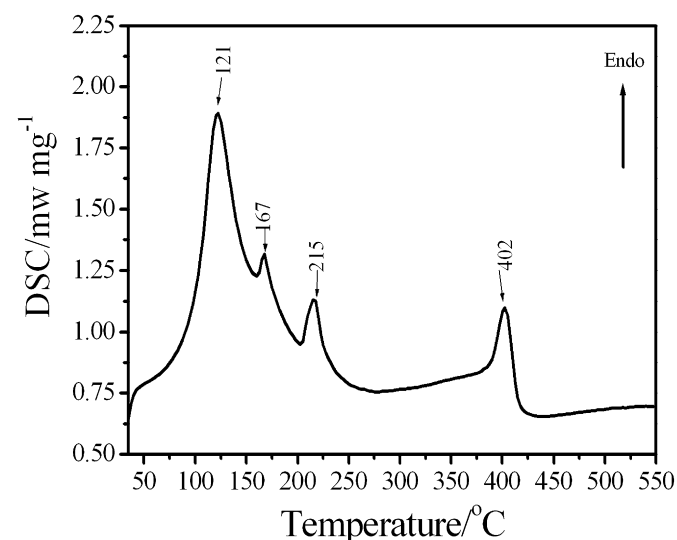


Fig. 2. DSC curve of $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ at the heating rate of $10^\circ\text{C min}^{-1}$ in N_2 atmosphere.

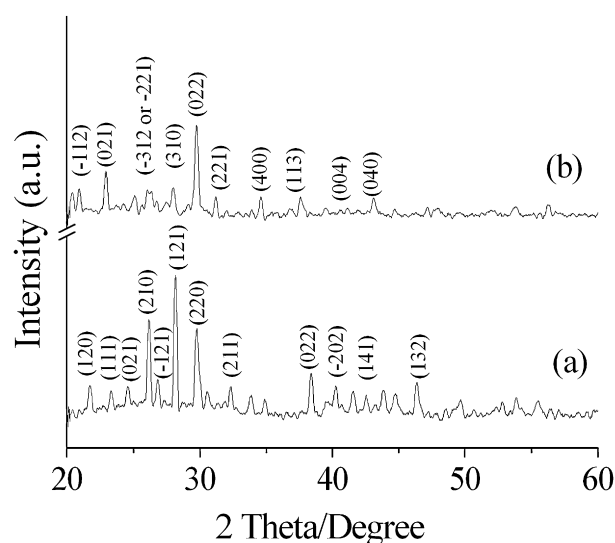


Fig. 3. XRD patterns of $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (a) and its decomposed product $\text{CoFeP}_4\text{O}_{12}$ (b).

final decomposed product are solid solutions and not a mixture of the individual ones. On the basis of XRD results, all the reflections can be distinctly indexed as pure monoclinic phases with space group $\text{P}2_1/\text{n}$ ($Z = 2$) for $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{C}2/\text{c}$ ($Z = 4$) for $\text{CoFeP}_4\text{O}_{12}$. The average crystallite sizes and lattice parameters of both samples were calculated from the XRD patterns and were summarized in Table 1. The lattice parameters and crystallite sizes of $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{CoFeP}_4\text{O}_{12}$ are comparable to those of the single metal compounds reported in the standard data and our previous works [18,19]. As can be seen from Table 1, the crystallite sizes for both binary compounds in this work are larger than those from the single metal compounds in our previous reports [18,19].

3.4. FTIR spectroscopy

The FTIR spectra of $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and its final decomposed product $\text{CoFeP}_4\text{O}_{12}$ are shown in Fig. 4. On the basis of isostructural, the FTIR spectra peaks of the binary metal and single metal of dihydrogenphosphate (or cyclotetraphosphate) are quite similar. Consequently, vibrational bands are identified in relation to the crystal structure in terms of the fundamental vibrating units namely H_2PO_4^- and H_2O for $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $[\text{P}_4\text{O}_{12}]^{4-}$ ion for $\text{CoFeP}_4\text{O}_{12}$, which are assigned according to the literature [4,12–16]. The FTIR spectrum of $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (Fig. 4a) is very similar to those observed by Koleva and Mehandjiev [12] and Boonchom et al. [18,19]. The highest site symmetry of H_2PO_4^- ion is C_{2v} , in the crystallographic unit cell ($\text{P}2_1/\text{n}$, $Z = 2$), but the four H_2PO_4^- ions are located on the set of non-equivalent site symmetry of C_1 . A pair of H_2PO_4^- ions is related to each other by a center of symmetry. It is known that the existence of short $\text{OH} \cdots \text{O}$ hydrogen bonds in a variety of strongly hydrogen-bonded solids is manifested by the appearance of the characteristic ABC structure of the $\nu(\text{OH})$ vibrational. Usually, the ABC bands are very broad and consist of many ill-resolved components. The strongest band (A) is located in the $3100\text{--}2700 \text{ cm}^{-1}$ region, the B band appears about $2600\text{--}2400 \text{ cm}^{-1}$ and the C band around $1700\text{--}1600 \text{ cm}^{-1}$. The problem of the origin of the ABC trio is discussed in many studies on acidic salts, but an explanation of this behavior of strongly hydrogen-bonded systems is still to be found. One of the most popular interpretations of the ABC trio suggests a strong Fermi resonance between the $\nu(\text{OH})$ stretching fundamentals and the overtones [$2\delta(\text{OH})$ and $2\gamma(\text{OH})$] or combinations involving the $\delta(\text{OH})$ and $\gamma(\text{OH})$ vibrations. The IR

Table 1Average crystallite sizes and lattice parameters of $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and its decomposed product $\text{CoFeP}_4\text{O}_{12}$ calculated from XRD data.

Compound	Method	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$\beta/^\circ$	Average crystallite sizes/nm
$\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$	PDF no 390698	7.27	9.88	5.33	94.86	26 ± 2
	Ref. [19]	7.21(3)	9.91(1)	5.29(5)	94.88(6)	
$\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$	This work	7.29(0)	9.90(0)	5.35(0)	95.10(0)	59 ± 13
$\text{Fe}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$	PDF no 751444	7.30	9.92	5.34	95.14	—
	Ref. [18]	7.25(1)	10.10(0)	5.32(0)	95.71(0)	
$\text{Co}_2\text{P}_4\text{O}_{12}$	PDF no 842208	11.8	8.297	9.923	118.72	40 ± 10
	Ref. [19]	11.83(8)	8.22(6)	9.94(0)	118.51(1)	
$\text{CoFeP}_4\text{O}_{12}$	This work	11.62(1)	8.30(0)	9.65(2)	119.17(4)	62 ± 15
$\text{Fe}_2\text{P}_4\text{O}_{12}$	PDF no 782285	11.94	8.37	9.93	118.74	—
	Ref. [18]	12.80(0)	8.80(4)	10.56(0)	118.67(4)	

spectrum of $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ in the region of the OH stretching modes is characterized by the appearance of a complex broad band between 3600 and 1600 cm^{-1} . Two bands centered at 3145 and 2431 cm^{-1} in the FTIR spectra are referred to as bands A and B, respectively. The third component (band C) is observed around $1744\text{--}1640\text{ cm}^{-1}$. The intense band at about 1260 cm^{-1} is due to the in plane P–O–H bending (A_2), while the out of plane bending (A_1) vibration is observed at about 815 cm^{-1} . A strong band at about 1141 cm^{-1} is assigned to PO_2 asymmetric stretching (B_1), while the other one at about 1043 cm^{-1} corresponds to PO_2 symmetric stretching modes (A_1). The FTIR frequency of the $\text{P}(\text{OH})_2$ asymmetric stretching (B_2) shows the strong band at about 945 cm^{-1} . The weak band at about 906 cm^{-1} is assigned to $\text{P}(\text{OH})_2$ symmetric stretching modes (A_1). The medium band at about 560 cm^{-1} is corresponding to PO_2 bending modes (B_1). Two strong bands appeared at about 520 and 470 cm^{-1} are attributed to PO_2 rocking modes as B_1 and A_2 vibrations, respectively. The bands of water vibrations are illustrated in Fig. 4a as doublet bands (1640 and 1568 cm^{-1}) contribute both to the band C and to the water bending band. A weak band occurs in the FTIR spectra at approximately 638 cm^{-1} is assigned to rocking mode involving water librations. The ν_{OH} stretching modes of HOH in $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ appear at 3145 cm^{-1} (ν_1 or A band) and 3322 cm^{-1} (ν_3). The bands associated with the ν_{OH} stretching frequencies in H_2PO_4^- ions are observed at about 2929 and 2431 cm^{-1} .

The FTIR spectrum of $\text{CoFeP}_4\text{O}_{12}$ is shown in Fig. 4b, which are very similar to those obtained from the individual $\text{M}_2\text{P}_4\text{O}_{12}$ ($\text{M} = \text{Co}$

and Fe) [18,19]. The vibrational modes of $\text{P}_4\text{O}_{12}^{4-}$ ion observed in the frequency range of $370\text{--}1400\text{ cm}^{-1}$ are assigned according to the literature [20,21]. One of the most noteworthy features of the spectra is the presence of strong bands in the ranges of 1332–1227, 1150–1100, 1080–959, 780–700 and $600\text{--}400\text{ cm}^{-1}$. These bands can be assigned to $\nu_{\text{as}}\text{OPO}^-$, $\nu_{\text{s}}\text{OPO}^-$, $\nu_{\text{as}}\text{POP}$, $\nu_{\text{s}}\text{POP}$ and metal–O vibrations, respectively. The observation of a strong $\nu_{\text{s}}\text{POP}$ band is known to be the most striking feature of cyclotetraphosphate spectra, along with the presence of the $\nu_{\text{as}}\text{OPO}^-$ band. From X-ray diffraction data [20,21], it was shown that the crystal structure is monoclinic (space group C2/c) with a cyclic structure of the $[\text{P}_4\text{O}_{12}]^{4-}$ anion. This has been confirmed by the FTIR measurements.

3.5. Scanning electron microscopy

The SEM micrographs of $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{CoFeP}_4\text{O}_{12}$ are shown in Fig. 5. The particle shape and size are changed throughout the whole decomposition product. The SEM micrographs of $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{CoFeP}_4\text{O}_{12}$ show non-uniform particles and high agglomerates, which are different from those of the single metal compounds $\text{M}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{M}_2\text{P}_4\text{O}_{12}$ ($\text{M} = \text{Co}$ or Fe) [18,19]. Additionally, the particle sizes and surface morphologies of both compounds in this work are significantly different from those of these binary compounds ($\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{CoFeP}_{14}\text{O}_{12}$) reported by our previous work [22,23]. The different morphologies of the single metal compounds ($\text{M}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{M}_2\text{P}_4\text{O}_{12}$, $\text{M} = \text{Co}$ or Fe) and these binary compounds indicate the presence of Co ions in substitution position of Fe ions and the different conditions of preparation method, respectively.

3.6. VSM magnetometer

Fig. 6 shows the specific magnetization curves of $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{CoFeP}_4\text{O}_{12}$ obtained from VSM measurements measured at 20°C . Both samples demonstrate typical superparamagnetic behavior without any hysteresis in the field range of $\pm 10,000\text{ Oe}$, which is in agreement with the theory of superparamagnetic behavior, is often observed at room temperature. Specific saturated magnetization (M_s) values of 25.61 and 11.89 emu/g are observed for the $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{CoFeP}_4\text{O}_{12}$, respectively. The superparamagnetic behaviors of the studied compounds are different from the ferromagnetic properties of Fe ($\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Fe}_2\text{P}_4\text{O}_{12}$ and the diamagnetic properties of Co ($\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Co}_2\text{P}_4\text{O}_{12}$. In addition, it is seen that magnetizations of the $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{CoFeP}_4\text{O}_{12}$ are lower than those of $\text{Fe}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (96.28 emu/g) and $\text{Fe}_2\text{P}_4\text{O}_{12}$ (85.01 emu/g) [18]. The M_s of $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ in this work is higher than that of $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (0.045 emu/g) prepared from other method and reported by Boonchom et al. [23]. But the M_s of

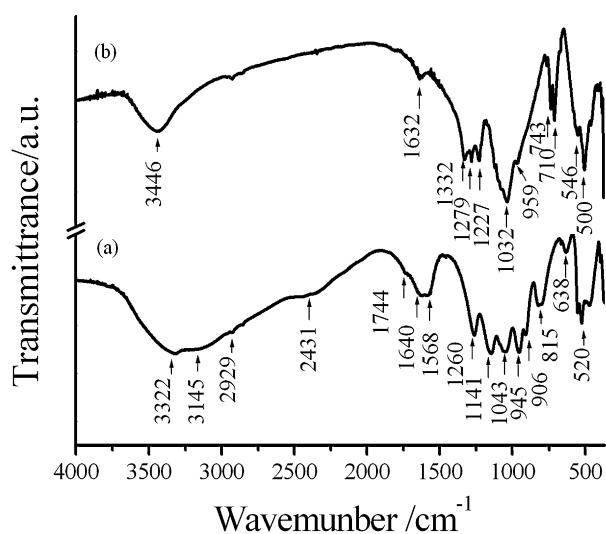


Fig. 4. FTIR spectra of $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (a) and its decomposed product $\text{CoFeP}_4\text{O}_{12}$ (b).

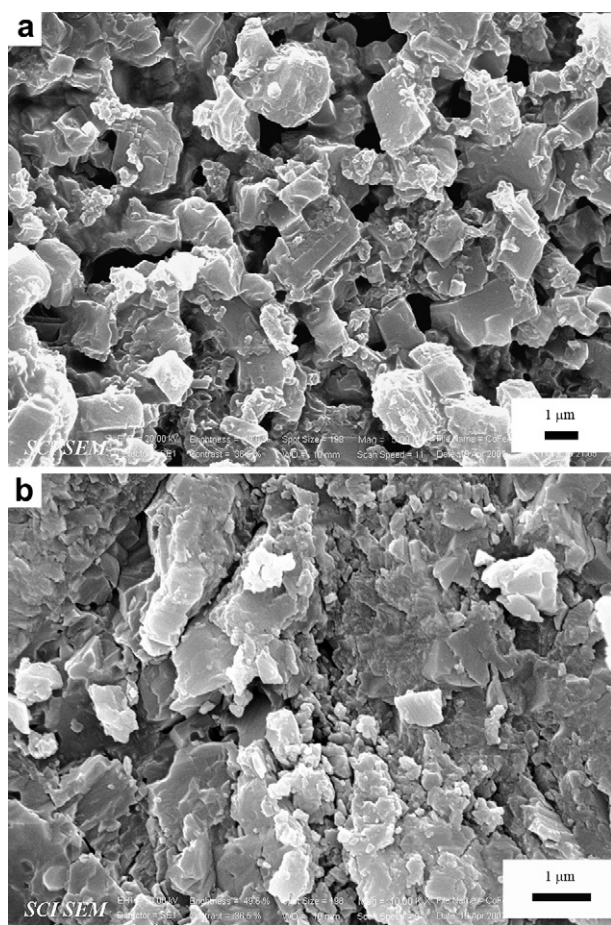


Fig. 5. SEM micrographs of $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (a) and its decomposed product $\text{CoFeP}_4\text{O}_{12}$ (b).

$\text{CoFeP}_4\text{O}_{12}$ in this work is smaller than that of the calcined $\text{Co}_{1/2}\text{Fe}_{1/2}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (12.502 emu/g) precursor at 700 °C and the obtained $\text{CoFeP}_4\text{O}_{12}$ (14.243 emu/g) in our previous study [22,23]. These results confirmed that the differences in magnetic properties

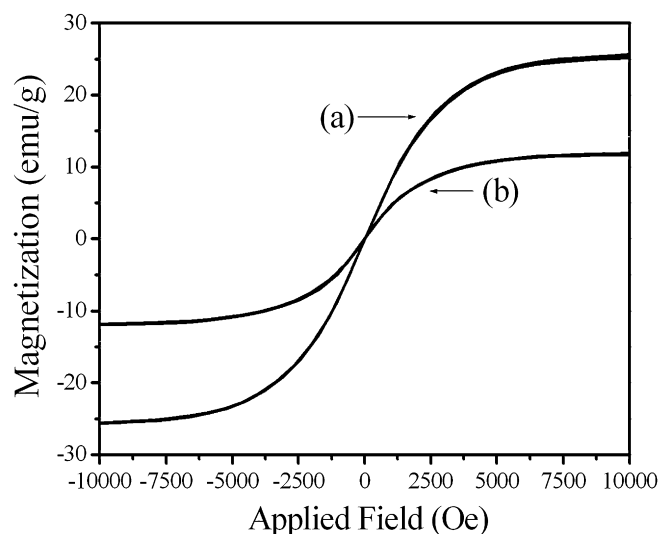


Fig. 6. The specific magnetizations of $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (a) and its decomposed product $\text{CoFeP}_4\text{O}_{12}$ (b) as a function of field, measured at 293 K.

for the synthesized $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{CoFeP}_4\text{O}_{12}$ depend on the medium and condition for preparations.

4. Conclusion

$\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ was successfully synthesized by a simple solid state method using $\text{CoCO}_3\text{--Fe--H}_3\text{PO}_4$ system at ambient temperature with short time consuming (10 min). Thermal transformation of $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ was investigated by TG/DTG/DTA and DSC techniques, which indicate the dehydration and the deprotonated dihydrogenphosphate reactions and its final decomposed product is $\text{CoFeP}_4\text{O}_{12}$. The structures, morphologies and magnetic properties of $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and its decomposed product $\text{CoFeP}_4\text{O}_{12}$ were investigated. The XRD patterns and FTIR spectra suggest the formation of pure monoclinic phases of $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{CoFeP}_4\text{O}_{12}$. Both samples are superparamagnetic at room temperature, having no hysteresis loop in the range of $-10,000 \text{ Oe} < H < +10,000 \text{ Oe}$. This work presents the simple, cost-effective and short time consuming method for the alternative preparation of $\text{Co}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{CoFeP}_4\text{O}_{12}$ compounds, which may be used in many important applications such as catalytic, superionic conductors, piezo- and ferroelectrics, magnets, ceramic and electrochemical performance.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at [doi:10.1016/j.solidstatesciences.2010.10.012](https://doi.org/10.1016/j.solidstatesciences.2010.10.012).

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Effect of BiAlO₃ modification on the stability of antiferroelectric phase in PbZrO₃ ceramics prepared by conventional solid state reaction

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ABSTRACT

In this paper, we report on the polycrystalline $(\text{Pb}_{1-3x/2}\text{Bi}_x)(\text{Zr}_{1-3x/4}\text{Al}_x)\text{O}_3$ (PZO–BAO) ceramics, with $x = 0.0$ – 0.3 , prepared by conventional solid state reaction. The crystal structure and thermal and dielectric properties of the sintered ceramics were investigated as a function of composition by means of X-ray diffraction (XRD), differential scanning calorimetry (DSC) and dielectric spectroscopy. The results indicated that the presence of BiAlO₃: BAO in the solid solution decreased the structural stability of the overall perovskite phase. Dielectric, thermal and P–E hysteresis results confirmed that no ferroelectric intermediate phase was seen in the PZO–BAO system. An antiferroelectric phase can be stable in a wide temperature range, indicating that BAO enhanced antiferroelectric phase stability in perovskite PZ manifests by “square” antiferroelectric behavior. Therefore, the $(\text{Pb}_{1-3x/2}\text{Bi}_x)(\text{Zr}_{1-3x/4}\text{Al}_x)\text{O}_3$ solid solution offers a material system for high-energy-storage capacitors and electromechanical transducers.

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1. Introduction

Pure and compositionally modified lead zirconate (PbZrO_3 ; PZO) ceramics are important materials used in energy storage applications for DC fields, due its antiferroelectric (AFE) nature. PZO has an orthorhombic structure, with the lattice parameters, $a = 5.884$ Å, $b = 11.768$ Å and $c = 8.22$ Å [1]. The phase transition sequence has been found to follow the progressive heating of PZO orthorhombic AFE to rhombohedral ferroelectric (FE) ($228 < T < 230$ °C) to paraelectric (PE) cubic at $T_c = 230$ °C. The FE phase of between 228 and 230 °C is sometimes called the FE intermediate phase. The AFE–FE phase transition could occur spontaneously, due to several factors, for example, a change in stress configuration promoted by external mechanical driving fields, an increase in the amplitude of the applied AC electric field, hydrostatic pressure and/or temperature variations [2,3]. For electric field induced AFE to FE phases, transformation requires a very strong electric field in the AFE PZO, otherwise dielectric breakdown occurs instead. Therefore, most AFE ceramics are modified chemically by adding metal oxide at the A- and B-sites of the perovskite structure. The FE intermediate phase can be induced by adding Ba^{2+} , Sr^{2+} , and La^{3+} at the

Pb^{2+} -site [2,4–7]. Moreover, our recent research found that the FE intermediate phase also can be induced by adding, for example, hybrid-doped $\text{Ni}^{2+}/\text{Nb}^{5+}$, $\text{Zn}^{2+}/\text{Nb}^{5+}$, $\text{Co}^{2+}/\text{Nb}^{5+}$ and $\text{Mg}^{2+}/\text{W}^{6+}$ at the Zr^{4+} -site [8–14].

BiMO_3 ; $\text{M} = \text{Fe}^{3+}$, Mn^{3+} and Nd^{3+} has received a lot of attention recently as a multiferroic, and investigation of the solid solutions, BiMO_3 – PbTiO_3 , has shown that they improve ferroelectric properties of PbTiO_3 , reduce the amount of lead, and find new morphotropic phase boundary piezoelectrics [15–18]. However, very little has been known so far about experimental BiMO_3 with non-magnetic ions ($\text{M} = \text{Al}$, Sc , Ga , and In). Furthermore, due to the relatively small size of Bi^{3+} , $\text{Bi}(\text{M})\text{O}_3$ is not stable in perovskite form, and can be only synthesized under high pressure [19]. The smaller tolerance factor of $\text{Bi}(\text{M})\text{O}_3$, and easily polarized Bi^{3+} ion, can enhance the transition temperature further, and with larger piezoelectric effect when solid solution with PbTiO_3 [15]. Crystallized BiAlO_3 is a noncentrosymmetric structure and isotypic with the well-known multiferroic, BiFeO_3 . Theoretical studies by Baetig et al. [20], on a unique ferroelectric phase bismuth aluminate (BiAlO_3 ; BAO), predicted that BAO could be a promising novel candidate ferroelectric material, with a high curie temperature of ~ 530 °C. In 2005, Belik et al. [21] synthesized the compound of BAO by using a high-pressure, high-temperature technique at 6 GPa and 1000–1200 °C. BAO has rhombohedral ($R3c$) symmetry with lattice parameters given as $a = b = 5.37546(5)$ Å and $c = 13.3933(1)$ Å. Unfortunately, pure stable perovskite BAO ceramics have never been synthesized using a conventional sintering process, due to

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the small value of t and electronegativity difference between A- and B-site cations. Zuo et al. [22] investigated the phase transitional behavior and various electrical properties of $(1-x)\text{K}_{1/2}\text{Na}_{1/2}\text{NbO}_3$; KNN- x BAO ceramics. The results indicate that the addition of BAO significantly influences the sintering, microstructure, phase transition and electrical properties of KNN ceramics. The identification of phase transitional behavior confirms the formation of a MPB between orthorhombic and tetragonal ferroelectric phases in the composition range of $0.005 \leq x \leq 0.01$. Ranjan et al. [23] studied the crystal structure and solid solubility in the PbTiO_3 – BiAlO_3 system. Their study suggested that decrease in stability of the ferroelectric state, due to dilution of the Ti-sublattice by smaller sized Al^{3+} ions, was compensated for by the increase in ferroelectric stability by Bi^{3+} ions. Although the compositions of $\text{Bi}(\text{M})\text{O}_3$ – PbTiO_3 have been investigated widely, few reports on $\text{Bi}(\text{M})\text{O}_3$ with other lead perovskite end members are available. To the authors' knowledge, the literature has not reported BAO as incorporated into PZO for solid solutions. Moreover, the effects of substitution in both A- and B-sites on the antiferroelectric phase stability of PZO are still unclear. The Bi^{3+} ion and Al^{3+} ion are both smaller than the Pb^{2+} and Zr^{4+} ion, respectively. Therefore, in this paper, we report on the how antiferroelectric phase stability is changed by A- and B-site substitution and determine the solubility limit of BAO in PZO.

2. Experimental procedures

2.1. Synthesis

Ceramics of $(\text{Pb}_{1-3x/2}\text{Bi}_x)(\text{Zr}_{1-3x/4}\text{Al}_x)\text{O}_3$, with $x=0.0$ – 0.3 , were synthesized using the conventional ceramic processing procedures [24]. Reagent grade oxide powders of Bi_2O_3 ($\geq 99.9\%$ purity, Cerac), PbO ($\geq 99\%$ purity, Kanto), ZrO_2 ($\geq 99.9\%$ purity, Advance Material) and Al_2O_3 ($\geq 99.5\%$ purity, Fluka) were weighed according to stoichiometric formula, and ball-milled with ethanol and yttrium-stabilized zirconia media for 18 h. The dried powders were calcined in crucibles at 700 – 900°C for 4 h, then ball-milled again for 6 h. The dried calcined powders were mixed with 5 wt% polyvinyl alcohol (PVA) and then pressed into pellets of 15 mm diameter and ~ 2 mm thickness. After burning out PVA binder at 550°C , the pellets covered with extra powders were sintered in sealed crucibles at between 1100°C and 1250°C for 4 h.

2.2. Characterizations

The densities of ceramics were obtained using the Archimedes method. The density of the sintered PZO–BAO pellets was measured by the Archimedes water immersion method. The relative density of all the sintered pellets was approximately 97–98% of the theoretical density. X-ray diffraction (XRD; Bruker-AXS D8) using CuK_α radiation was utilized to determine the phases formed and optimum firing temperatures for formation of the desired phase for $0.02 \leq x \leq 0.3$ compositions. For measuring the dielectric and ferroelectric characteristics, the specimens were polished to 1 mm thickness using sand paper after ultrasonic cleaning in an ethanol bath. Silver-paste (Heraeus C1000) was coated on both sides of the sintered samples by the screen printing method, and then subsequently fired at 650°C for 30 min. For investigating the dielectric properties, capacitance was measured at 1 kHz using an automated measurement system. This system consisted of an LCR meter (HP-4284, Hewlett-Packard Inc.). The dielectric constant was then calculated from $\epsilon_r = C/d/\epsilon_0 A$, where C was the capacitance of the sample; d and A were the thickness and area of the electrode, respectively; and ϵ_0 was the dielectric permittivity of vacuum (8.854×10^{-12} F/m). Polarizations, as a function of electric field (P – E loop) at 4 Hz of the samples, were observed using a ferroelectrics test system (RT66B; Radiant Technologies, Inc.). The peak field was maintained at 40 kV/cm during measurement.

3. Results and discussion

3.1. Crystal structure and physical properties of PZO–BAO solid solutions

The X-ray diffraction patterns of the sintered ceramics, $(\text{Pb}_{1-3x/2}\text{Bi}_x)(\text{Zr}_{1-3x/4}\text{Al}_x)\text{O}_3$; $x=0.02$ – 0.3 , at room temperature are shown in Fig. 1. The presence of diffraction peaks can be used to evaluate the structural order at long range or periodicity of the material [25]. The patterns indicate that the ceramics possess a phase of perovskite structure, and the crystalline symmetry is

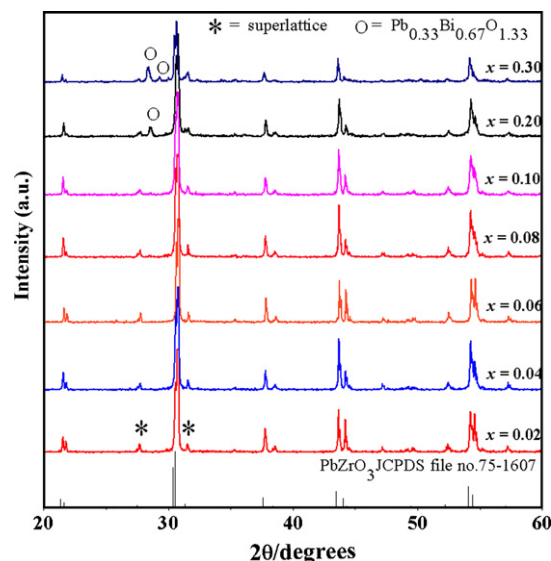


Fig. 1. XRD diffraction patterns of sintered $(\text{Pb}_{1-3x/2}\text{Bi}_x)(\text{Zr}_{1-3x/4}\text{Al}_x)\text{O}_3$; $x=0.02$ – 0.30 ceramics.

orthorhombic. Phase-pure perovskite structures, with orthorhombic symmetry, were obtained for $x \leq 0.1$; however $x \geq 0.1$, A cubic pyrochlore phase $\text{Pb}_{0.33}\text{Bi}_{0.67}\text{O}_{1.33}$ (Powder diffraction Files no. 85-0448), identified by "o", began to develop at $x \geq 0.1$, and increased in intensity with increasing BAO concentration. These results indicated that the presence of BAO in the solid solution decreases the structural stability of PZO perovskite phase, due to the instability of BAO perovskite under normal conditions and the tolerance factor. The solubility limit of $(\text{Pb}_{1-3x/2}\text{Bi}_x)(\text{Zr}_{1-3x/4}\text{Al}_x)\text{O}_3$ ceramics is the composition, $x=0.1$. The peak positions shifted to higher angles, indicating a slight decrease in the lattice parameter. This phenomenon can be explained qualitatively with respect to the unit cell volume caused by the Bi^{3+} and Al^{3+} incorporation. The ionic radii of Bi^{3+} (Shannon radius = $1.17 \text{ \AA}$ for CN = 8) and Al^{3+} (Shannon radius = $0.535 \text{ \AA}$ for CN = 6) are less than those of Pb^{2+} (Shannon radius = $1.29 \text{ \AA}$ for CN = 8) and Zr^{4+} (Shannon radius = $0.72 \text{ \AA}$ for CN = 6), respectively [26]. Therefore, Bi^{3+} can enter the eight-fold coordinated A-site of the perovskite structure to substitute Pb^{2+} , and Al^{3+} can enter the six-fold coordinated B-site of the perovskite structure to substitute Zr^{4+} , due to radius matching. The lattice parameters were calculated using the least square refinement from the UNITCELL-97 program [27]. Table 1 shows the lattice parameter and cell volume of $(\text{Pb}_{1-3x/2}\text{Bi}_x)(\text{Zr}_{1-3x/4}\text{Al}_x)\text{O}_3$ ceramics. The substitution of the relatively smaller Bi^{3+} and Al^{3+} for the comparatively larger Pb^{2+} and Zr^{4+} led to a decrease in the unit cell volume. This seems to be the case for $x \leq 0.01$ only, as composition, $x \geq 0.01$, is close to the solubility limit, but this argument does not apply due to the inhomogeneous distribution factor.

Fig. 2 shows enlarged profiles of the $1/4(hkl)$ superlattice reflection (*) and $(240)/(004)$ for determining the crystal structure of as-sintered ceramics. By increasing BAO concentration, the remaining $1/4(hkl)$ superlattice reflection peaks indicated the remainder of antiparallel displacements of A-site ions in the perovskite structure. It is interesting to note that the substitution of BAO does not change the crystalline structure of PZO ceramics within the studied doping level. The influence of BAO addition on the phase structure of the PZO–BAO system is similar to that of the PT–BAO system [23,28]. The tolerance factor (t) for perovskite structure can be described by the general formula for ABO_3 ; $t = (R_A + R_O)/(\sqrt{2})(R_B + R_O)$, where R_A is the radius of A (CN = 8), R_B the radius of B (CN = 6) and R_O the radius of oxygen (CN = 8). When t is >1 , the FE phase is stabilized, and when t is <1 , the AFE phase is sta-

Table 1
Summary of the lattice parameters of $(\text{Pb}_{1-3x/2}\text{Bi}_x)(\text{Zr}_{1-3x/4}\text{Al}_x)\text{O}_3$; $x = 0.02\text{--}0.1$ ceramics.

Composition (x)	Lattice parameters			Volume of unit cell ($\text{\AA}^3$)
	a	b	c	
0.00	5.8835 ± 0.0003	11.7672 ± 0.0008	8.2177 ± 0.0007	568.93
0.02	5.8629 ± 0.0207	11.7258 ± 0.0414	8.2171 ± 0.0273	564.89
0.04	5.8609 ± 0.0225	11.7221 ± 0.0453	8.2116 ± 0.0253	564.15
0.06	5.8584 ± 0.0237	11.7167 ± 0.0473	8.2023 ± 0.0195	563.01
0.08	5.8545 ± 0.0258	11.7113 ± 0.0494	8.2022 ± 0.0159	562.37
0.10	5.8522 ± 0.0275	11.7106 ± 0.0527	8.2007 ± 0.0124	562.01

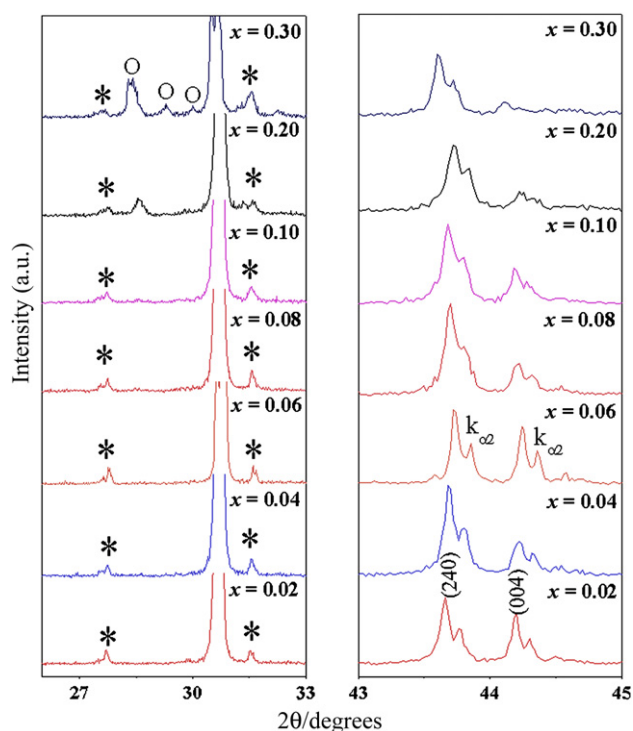


Fig. 2. X-ray diffraction profiles for the $1/4$ (hkl) superlattice reflection (*), pyrochlore phase (O) and $(240)/(004)$ peaks of $(\text{Pb}_{1-3x/2}\text{Bi}_x)(\text{Zr}_{1-3x/4}\text{Al}_x)\text{O}_3$; $x = 0.02\text{--}0.30$ ceramics.

bilized [29]. The average ionic radius of the A- and B-site ions in the $(\text{Pb}_{1-3x/2}\text{Bi}_x)(\text{Zr}_{1-3x/4}\text{Al}_x)\text{O}_3$ can be calculated from the following equation:

$$r_{\text{A-site}} = \left(1 - \frac{3x}{2}\right) r_{\text{Pb}^{2+}} + x r_{\text{Bi}^{3+}} \quad (1)$$

$$r_{\text{B-site}} = \left(1 - \frac{3x}{4}\right) r_{\text{Zr}^{4+}} + x r_{\text{Al}^{3+}} \quad (2)$$

where the ionic radii of Pb^{2+} , Bi^{3+} , Zr^{4+} and Al^{3+} are 1.29 Å, 1.17 Å, 0.72 Å and 0.535 Å, respectively [26]. The average ionic radius of the A- and B-site ions and tolerance factor in the $(\text{Pb}_{1-3x/2}\text{Bi}_x)(\text{Zr}_{1-3x/4}\text{Al}_x)\text{O}_3$ ceramics are shown in Table 2. The calculated tolerance factor of the $(\text{Pb}_{1-3x/2}\text{Bi}_x)(\text{Zr}_{1-3x/4}\text{Al}_x)\text{O}_3$; $x = 0.02\text{--}0.3$ is between 0.8904 and 0.8202, indicating that AFE behavior is expected to be seen at room temperature. Dielectric and ferroelectric properties; later explained, support this assumption. Furthermore, as expected, the stability of perovskite structure decreases with increasing BAO concentration, due to the small tolerance factor value.

3.2. Dielectric properties

Temperature dependence of relative permittivity (ϵ_r) and dielectric loss ($\tan \sigma$) for $(\text{Pb}_{1-3x/2}\text{Bi}_x)(\text{Zr}_{1-3x/4}\text{Al}_x)\text{O}_3$; $x = 0.02\text{--}0.3$

Table 2
Average ionic radius of A-site, B-site ions and tolerance factor in the $(\text{Pb}_{1-3x/2}\text{Bi}_x)(\text{Zr}_{1-3x/4}\text{Al}_x)\text{O}_3$ ceramics.

Compositions (x)	$R_{\text{A-site}}$	$R_{\text{B-site}}$	Tolerance factor (t)
0.02	1.2747	0.7199	0.8904
0.04	1.2594	0.7198	0.8854
0.06	1.2441	0.7197	0.8804
0.08	1.2288	0.7196	0.8754
0.10	1.2135	0.7195	0.8704
0.20	1.1370	0.7190	0.8453
0.30	1.0605	0.7185	0.8202

ceramics were measured at 1, 10 and 100 kHz, as shown in Fig. 3. It is well known that pure PZO has two dielectric anomaly peaks reported at 228 and 230 °C, which corresponds to the phase transitions of orthorhombic antiferroelectric (AFE) phase to rhombohedral FE intermediate phase and rhombohedral FE intermediate phase to cubic paraelectric phase, respectively. Furthermore, the FE intermediate phase can be induced easily by adding Ba^{2+} , Sr^{2+} , and Ca^{2+} at the Pb^{2+} -site [2,4–7] or $\text{Ni}^{2+}/\text{Nb}^{5+}$, $\text{Zn}^{2+}/\text{Nb}^{5+}$, $\text{Co}^{2+}/\text{Nb}^{5+}$ and $\text{Mg}^{2+}/\text{W}^{6+}$ at the Zr^{4+} -site [8–14]. As shown in Fig. 3, a single sharp dielectric permittivity peak arises in all ceramic samples. Interestingly, the dielectric results showed one sharp dielectric peak anomaly, indicating that the FE intermediate phase did not exist in $(\text{Pb}_{1-3x/2}\text{Bi}_x)(\text{Zr}_{1-3x/4}\text{Al}_x)\text{O}_3$; $x = 0.02\text{--}0.3$ samples. Increasing BAO concentration resulted in a very small decrease in transition temperature. No frequency dependence of dielectric response or shift in transition temperature with frequency was observed under transition temperature, which indicated no evidence of relaxor-like $\text{Pb}(\text{Zr},\text{Ni},\text{Nb})\text{O}_3$ [8,10] or $(\text{Pb},\text{Ba})\text{ZrO}_3$ [5,7]. Nevertheless, at high temperature, the dielectric data revealed an enhanced dielectric loss with increasing BAO concentration. At 1 kHz measurement, frequent higher losses were found to persist to a significantly lower temperature. These results demonstrated that the enhanced dielectric losses at higher temperatures are due to a space charge mechanism [30]. For the composition, $x \geq 0.2$, the maximum relative permittivity decreases steadily with increasing BAO content (ϵ_r decreases from ~3700 in composition $x = 0.1$ –700 in composition $x = 0.3$), and the lower value is attributed to the detrimental effect of the secondary pyrochlore phase.

3.3. Thermal properties

The DSC technique was used as the second tool to confirm the phase transition of PZO–BAO ceramics. Fig. 4 shows the temperature dependences of the heat flow (DSC curves) obtained when heating the $(\text{Pb}_{1-3x/2}\text{Bi}_x)(\text{Zr}_{1-3x/4}\text{Al}_x)\text{O}_3$; $x = 0.02\text{--}0.3$ samples at the rate of 10 K/min^{−1}. A single endothermic peak was observed for all compositions. The peaks shifted slightly to lower temperatures with increasing BAO concentrations. This transition temperature corresponds to the Curie temperature of the AFE to PE transformation. However, there is no significant difference in the temperature of AFE to PE phase transition in the composition, $x \geq 0.08$. This could be related to appearance of the pyrochlore phase. The DSC results

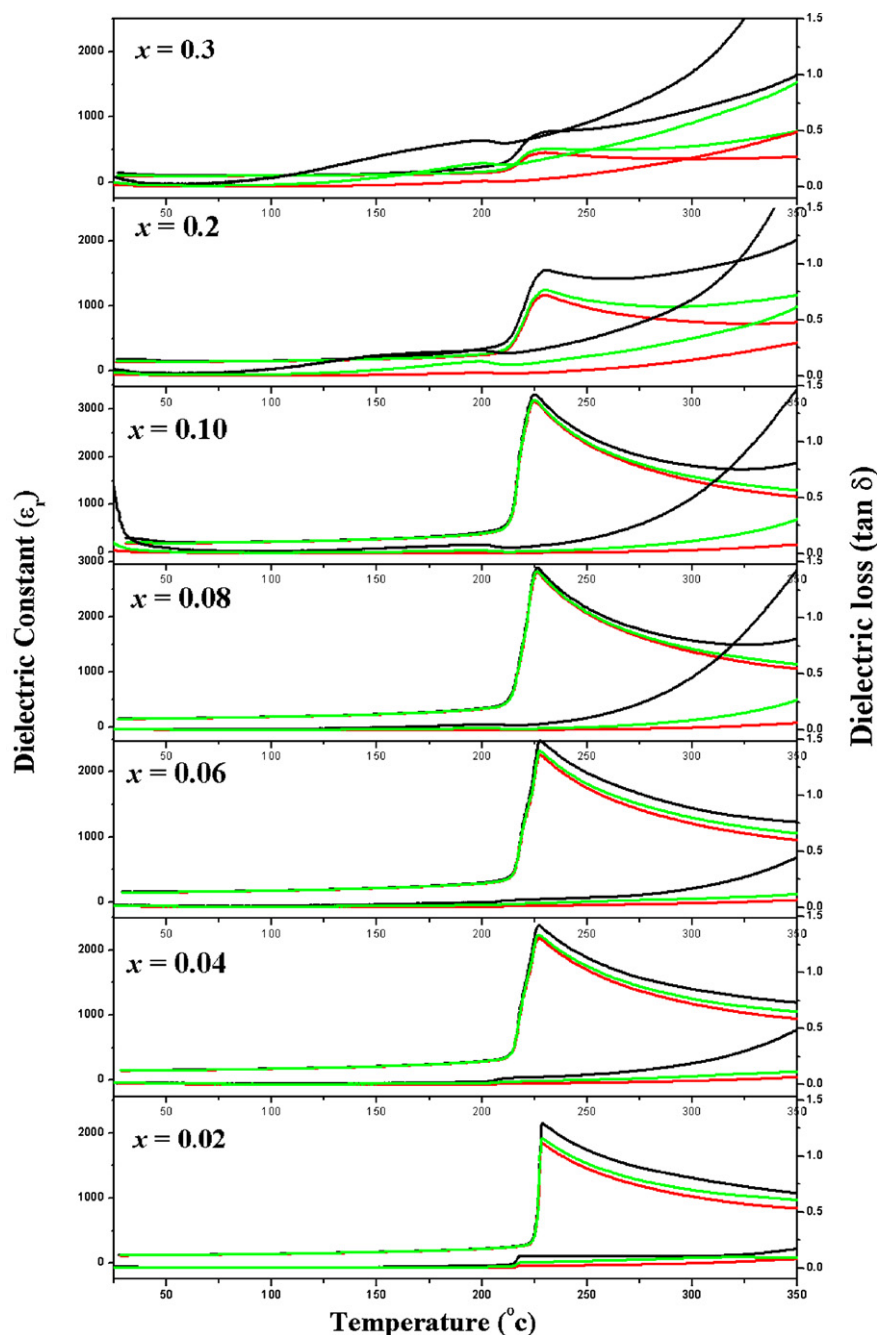


Fig. 3. Relative permittivity (ϵ_r) and dielectric loss ($\tan \delta$) as a temperature function of $(\text{Pb}_{1-3x/2}\text{Bi}_x)(\text{Zr}_{1-3x/4}\text{Al}_x)\text{O}_3$; $x = 0.02$ – 0.3 ceramics.

observed are consistent with dielectric measurement results. It should be pointed out that the difference in AFE-PE transition temperature values in dielectric, ferroelectric and DSC measurement techniques is due to the difference in heating rate and well time of the measurement.

Thermodynamic parameter, enthalpy ($\Delta H^*/\text{J g}^{-1}$), heat capacity ($C_p/\text{J g}^{-1} \text{K}^{-1}$), entropy change ($\Delta S^*/\text{J g}^{-1} \text{K}^{-1}$), and Gibbs energy change ($\Delta G^*/\text{J g}^{-1}$), were calculated from the DSC results. The enthalpy change was calculated directly from the amount of heat change involved in each step per unit mass of the sample. ΔH^* , thus determined, was implemented to calculate the specific heat capacity (C_p) using the following equation [31,32]

$$C_p = \frac{\Delta H}{\Delta T} \quad (3)$$

where $\Delta T = T_2 - T_1$; T_1 is the temperature at which the DSC peak begins to depart from the baseline; and T_2 is the temperature at which the peak lands. Consequently, the changes of entropy (ΔS^*) and Gibbs energy (ΔG^*) were calculated using the following equations [31,32]

$$\Delta S^* = 2.303C_p \log \left(\frac{T_2}{T_1} \right) \quad (4)$$

$$\Delta H^* = \Delta G^* - T_p \Delta S^* \quad (5)$$

On the basis of the DSC data, the value of ΔH^* , ΔS^* , C_p and ΔG^* for the phase transition can be calculated according to Eqs. (3)–(5), and is presented in Table 3. The peak value of heat capacity became weaker, and anomaly of heat capacity gradually broader, with increasing BAO concentration. These results indicated that the phase transition deviates gradually from the first

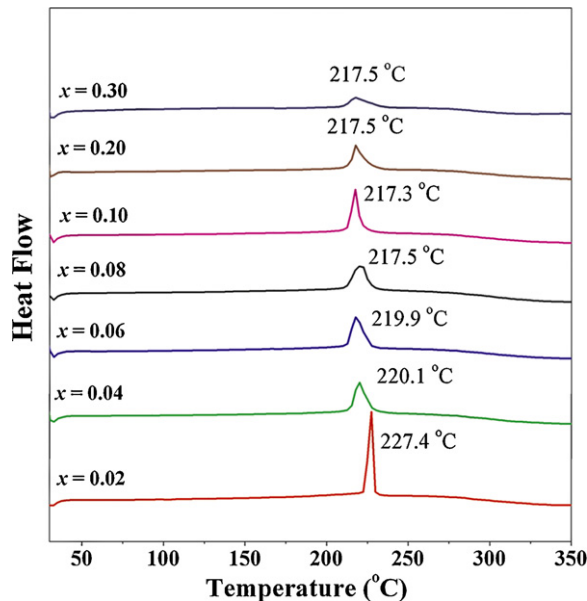


Fig. 4. Typical DSC curves for $(\text{Pb}_{(1-3x/2)}\text{Bi}_x)(\text{Zr}_{1-3x/4}\text{Al}_x)\text{O}_3$; $x = 0.02\text{--}0.3$ ceramics.

order type. Furthermore, the enthalpy (ΔH^*) continues to decrease with increasing BAO content, indicating that BAO decreases the energy requirement for transition from AFE to FE. Stenger and Burggraaf [33] observed that the change in entropy (ΔS^*) correlates with the fluctuation probability in conjunction with a small spontaneous lattice deformation and polarization. With increasing BAO content, there is no significant change in ΔS^* , indicating the stability of energy required to reorient the antiferroelectric sublattices in the PZO–BAO system [33]. On the other hand, the thermodynamic parameter, ΔH^* and ΔG^* , calculated according to Eqs. (3)–(5), gives the positive values, indicating that the AFE to PE phase transitions are connected to the introduction of heat, and phase transitions are non-spontaneous processes.

3.4. Ferroelectric properties

In order to examine how the phase transition occurs with temperature, electrical polarization hysteresis loop measurements were performed under a peak field of 40 kV/cm at a series of temperatures for $(\text{Pb}_{(1-3x/2)}\text{Bi}_x)(\text{Zr}_{1-3x/4}\text{Al}_x)\text{O}_3$ ceramics. A disk specimen, with a diameter of about 10 mm and thickness around 600 μm was used. The loop was recorded after the temperature was stabilized for at least 5 min. At 30 °C, no ferroelectric hysteresis loop was observed for any compositions ($0.0 \leq x \leq 0.3$). The linear polarization was observed, due perhaps to the extremely high coercive field, indicating that the composition, $x \leq 0.3$, belongs to the AFE phase at room temperature. The $\text{Pb}_{0.94}\text{Bi}_{0.04}\text{Zr}_{0.97}\text{Al}_{0.04}\text{O}_3$ ceramic was selected for further investigation of the polarization behavior sequence during heating to 220 °C. The polarization behavior of $\text{Pb}_{0.94}\text{Bi}_{0.04}\text{Zr}_{0.97}\text{Al}_{0.04}\text{O}_3$ ceramic as a function of temperature is

shown in Fig. 5. For the $\text{Pb}_{0.94}\text{Bi}_{0.04}\text{Zr}_{0.97}\text{Al}_{0.04}\text{O}_3$ composition, such linear behavior with minimum polarization remains at temperatures of up to 195 °C. When the temperature was raised to 200 °C, a double hysteresis loops started to develop, indicating the occurrence of electric field-induced antiferroelectric-to-ferroelectric phase transition. The transition from a minor loop at low field to a saturated double-shaped hysteresis loop at high field occurs at 205 °C by increasing the electric fields. This is expected because an antiferroelectric crystal generally has a zero net switchable dipole moment, due to the antiparallel alignment of elementary dipoles in its unit cell. When the external electric field is weak, the induced polarization is proportional to the electric field and demonstrates no macroscopic polarization hysteresis [34]. While the electric field exceeds a threshold value, called the critical field, the crystal becomes ferroelectric and the polarization displays hysteresis with respect to the field. A hysteresis loop also forms in the negative field, with the two loops being associated with antiparallel dipoles in adjacent unit-cell sublattices. As the temperature increases to 215 °C, the critical field is slowly reduced. This is caused by a higher temperature that provides higher thermal fluctuation to the polarization order parameter, which reduces the ferroelectric interaction among the dipoles.

In addition, when the temperature was increased to above 225 °C, a linear curve also was seen as an indication of the cubic paraelectric (PE) phase. Fig. 6 shows the polarization versus electric field hysteresis loops at 205 °C for the $(\text{Pb}_{(1-3x/2)}\text{Bi}_x)(\text{Zr}_{1-3x/4}\text{Al}_x)\text{O}_3$; $x = 0.02\text{--}0.08$ ceramics. The double hysteresis behavior in polarization, with an applied electric field, clearly demonstrates the antiferroelectric nature of $(\text{Pb}_{(1-3x/2)}\text{Bi}_x)(\text{Zr}_{1-3x/4}\text{Al}_x)\text{O}_3$; $x = 0.02\text{--}0.08$ ceramics. The remanent polarization, P_r , slightly decreases between $x = 0.02$ and 0.08, from 23.26 $\mu\text{C}/\text{cm}^2$ to 19.4 $\mu\text{C}/\text{cm}^2$. The AFE–FE switching field decreases for $x = 0.02$ and 0.08 from 29.23 kV/cm to 13.81 kV/cm. In Berlincourt's [35] study of doped $\text{Pb}(\text{Zr},\text{Sn},\text{Ti})\text{O}_3$ ceramics, two different types of AFE to FE transitions based on the character of the P–E hysteresis loop were described; the two types of double hysteresis loops have been termed “square” and “slanted”. The “slanted” double hysteresis loop ceramics have far less hysteresis, small volume difference between AFE and FE phases, lower transition fields and a wider temperature range, over which the transition can be induced by electric fields. The “slanted” double hysteresis loop ceramics exhibit a small remanent polarization at zero fields, while the “square” loop ceramics do not. The P–E hysteresis loop measurements demonstrate that the ferroelectric properties of ceramics in the PZO–BAO system shift gradually from “square” to “slanted” antiferroelectric behavior, with increasing BAO concentrations. Interestingly, with increasing temperatures from room temperature to 250 °C, antiferroelectric to ferroelectric intermediate phase transition was not observed in any compositions, which indicated no ferroelectric intermediate phase in the PZO–BAO ceramics. Chu et al. [36] pointed out that the area enclosed by the decreasing field part of the polarization–electric field trace represented a stored electrical energy density. The ferroelectric results show that the PZO–BAO ceramics have large polarization at a high electric field and a large area between the polarization axis and curve. There are indications that this

Table 3

Values of thermodynamic parameters for phase transition of the $(\text{Pb}_{(1-3x/2)}\text{Bi}_x)(\text{Zr}_{1-3x/4}\text{Al}_x)\text{O}_3$ ceramics calculated from DSC data.

Compositions (x)	T_p/K	$\Delta H^*/\text{J g}^{-1}$	$C_p/\text{J g}^{-1} \text{K}^{-1}$	$\Delta S^*/\text{J g}^{-1} \text{K}^{-1}$	$\Delta G^*/\text{J g}^{-1}$
0.02	499	3.825	7.665×10^{-3}	6.145×10^{-5}	3.856
0.04	497	3.749	7.543×10^{-3}	6.163×10^{-5}	3.795
0.06	491	3.348	6.819×10^{-3}	6.438×10^{-5}	3.382
0.08	490	2.815	5.745×10^{-3}	6.336×10^{-5}	2.849
0.10	489	2.676	5.461×10^{-3}	6.193×10^{-5}	2.901
0.20	490	2.360	4.816×10^{-3}	6.851×10^{-5}	2.408
0.30	489	1.429	2.922×10^{-3}	5.985×10^{-5}	1.455

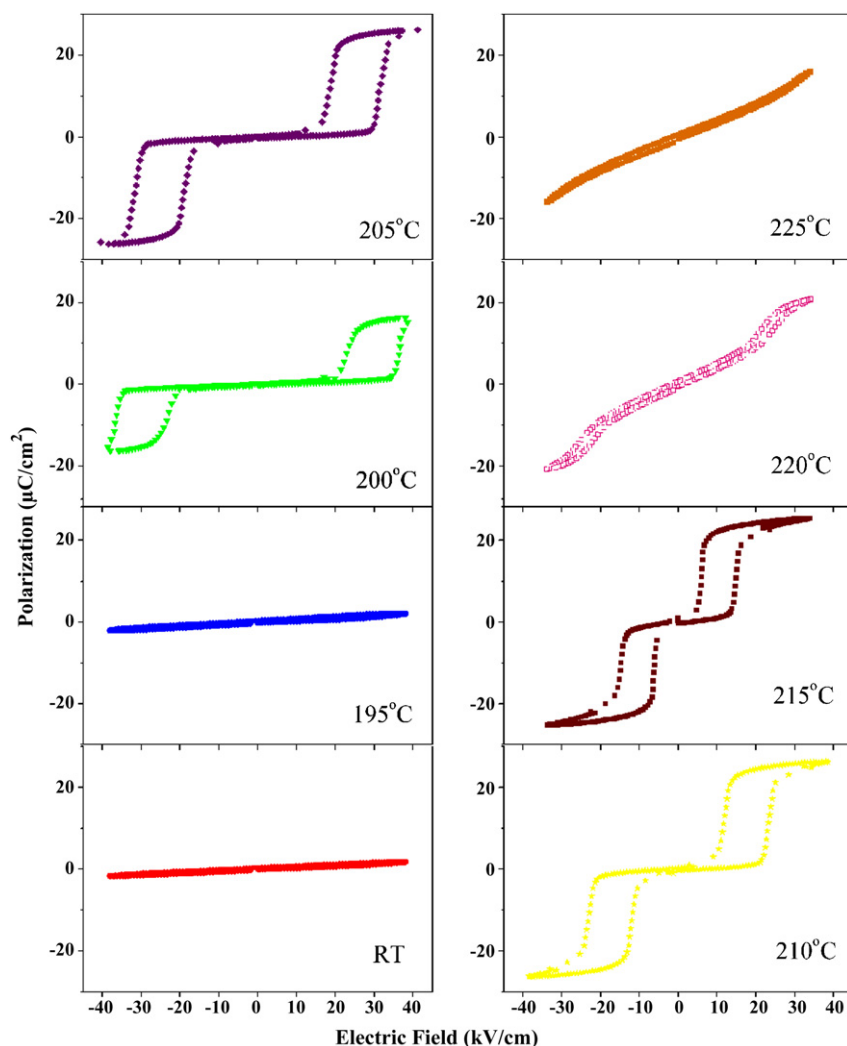


Fig. 5. Polarization hysteresis loops recorded from $\text{Pb}_{0.94}\text{Bi}_{0.04}\text{Zr}_{0.97}\text{Al}_{0.04}\text{O}_3$ ceramic at 4 Hz during heating.

material can therefore store much more energy than either the ferroelectric or linear dielectric materials.

There is good agreement between results of the three different investigation techniques. The results indicated that BAO modification can stabilize an antiferroelectric state in perovskite PZO. It is well known that the ionic size and distribution of substituent on the A- and B-site have been shown to affect antiferroelectric phase stability. If A-site ions are replaced by larger ones or a B-site ion by a smaller one, ferroelectric phase stability is enhanced. However, if A-site ions are replaced by smaller ones, or a B-site ion by a larger one, then antiferroelectric phase stability is enhanced [37]. However, in the PZO–BAO system, the ionic radius of Bi^{3+} (1.17 Å) and Al^{3+} (0.535 Å) are both smaller than Pb^{2+} (1.29 Å) and Zr^{4+} (0.72 Å), respectively. These results clearly demonstrate that the stability in antiferroelectric phase PZO, by substituting Pb^{2+} (1.29 Å) with Bi^{3+} (1.17 Å) in the A-site of the ABO_3 perovskite structure, are much more pronounced than substitution of Zr^{4+} by Al^{3+} in the B-site of the perovskite structure. This is because the decreasing average rate of radii in the A-site (0.765 Å/mol) is much higher than that in the B-site radii (0.005 Å/mol) as shown in Table 1. The decreasing average of radii in the A-site causes decreasing space in which the B-site cation is allowed to “rattle”. This in turn decreases the polarizability, which facilitates a decrease in the Curie point. The results clearly demonstrated that the ionic radii of the substituent are an important factor in controlling the structure-property relations by compositional design.

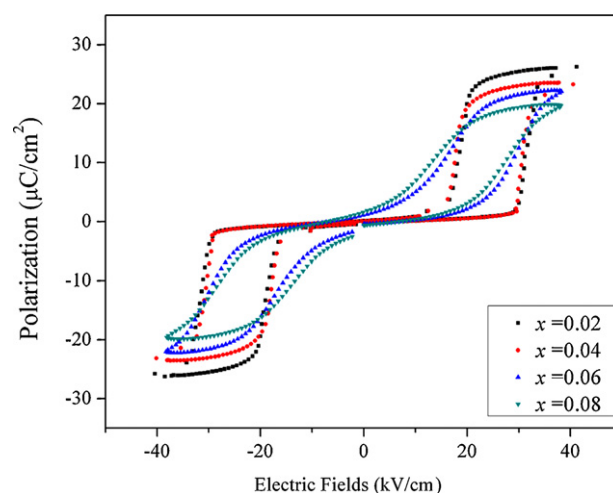


Fig. 6. Electric hysteresis loops of $(\text{Pb}_{1-3x/2}\text{Bi}_x)(\text{Zr}_{1-3x/4}\text{Al}_x)\text{O}_3$; $x = 0.02\text{--}0.08$ ceramics at 205 °C.

4. Conclusions

The investigation of $(\text{Pb}_{1-3x/2}\text{Bi}_x)(\text{Zr}_{1-3x/4}\text{Al}_x)\text{O}_3$; $x = 0.02\text{--}0.3$ using X-ray diffraction, dielectric behavior, thermal properties and ferroelectric measurements have shown clearly that phase

pure perovskite ceramics in the $(\text{Pb}_{(1-3x/2)}\text{Bi}_x)(\text{Zr}_{1-3x/4}\text{Al}_x)\text{O}_3$ system can be prepared by the solid-state reaction method with up to 10 mol% of BiAlO_3 . Phase-pure perovskite structures with orthorhombic symmetry were obtained for $x \leq 0.1$; however $x \geq 0.1$, A cubic pyrochlore phase $\text{Pb}_{0.33}\text{Bi}_{0.87}\text{O}_{1.33}$ began to develop at $x \geq 0.1$ and increased in intensity with increasing BAO concentration. The substitution of the relatively smaller Bi^{3+} and Al^{3+} for the comparatively larger Pb^{2+} and Zr^{4+} led to a decrease in the unit cell volume. Dielectric, thermal and P–E hysteresis results confirmed that there was no ferroelectric intermediate phase in the PZO–BAO system, and only antiferroelectric to paraelectric phase transition was obtained for a wide temperature range. The results confirmed that BAO is shown to be a stable antiferroelectric state in PZO in a wide temperature range. The stability in antiferroelectric phase PZO by substituting Pb^{2+} (1.29 Å) with Bi^{3+} (1.17 Å) in the A-site of the ABO_3 perovskite structure is much more pronounced than substitution of Zr^{4+} by Al^{3+} in the B-site of the perovskite structure. The $(\text{Pb}_{(1-3x/2)}\text{Bi}_x)(\text{Zr}_{1-3x/4}\text{Al}_x)\text{O}_3$ solid solution offers a material system for possible applications in high-energy-storage capacitors and electromechanical transducers.

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Solution combustion synthesis and characterization of lead-free piezoelectric sodium niobate (NaNbO_3) powders

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ABSTRACT

Nano-crystalline sodium niobate (NaNbO_3) powder was synthesized by the solution combustion synthesis of sodium nitrate (NaNO_3) and Nb_2O_5 using glycine as the fuel. The chemical reaction, nucleation mechanisms and influence of the fuel-to-oxidizer ratio to phase formation were studied. The precursor and product powders were characterized, using thermo gravimetric analysis (TGA), differential thermal analysis (DTA), the X-ray diffraction technique (XRD), scanning electron microscope (SEM) and Fourier transform infrared (FTIR) spectroscopy. As-prepared powder possesses an orthorhombic crystal structure with an X-ray diffraction pattern that could be matched with the perovskite, NaNbO_3 JCPDS no. 82-0606. Perovskite NaNbO_3 phase, with a mean crystalline size (calculated by X-ray line broadening) ranging from 44.51 ± 11.99 nm (ratio of 0.7) to 26.11 ± 13.69 nm (ratio of 2.0) was obtained. The SEM image shows polyhedral-shaped powder with a mean particle size of 137 ± 52 nm and 226 ± 46 nm for as-prepared and calcined powder, respectively.

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1. Introduction

Sodium niobate (NaNbO_3) is a perovskite with an inorganic complex oxide and the empirical formula, ABO_3 . It is among the candidates for lead-free substances that avoid toxicity of lead-based piezoelectric materials (e.g. PZT [1,2]), and is concerned about the environment. NaNbO_3 has been studied widely for its unusual structural transition series [3–7]. It has a ferroelectric rhombohedral phase below -100°C , and is antiferroelectric with orthorhombic symmetry between -100°C and 640°C [4]. Finally, it possesses cubic paraelectric above 640°C [5], and in addition, its antiferroelectric, perovskite-type nature can transform into a ferroelectric one by chemical doping, i.e. K^+ [6,7] and Li^+ [8].

Generally, alkali niobate powders are synthesized by conventional solid state reaction, where alkali metal carbonate or oxide compound of starting materials are heated at high temperature (800°C or above) for a long duration [8,9]. High calcination temperature can cause volatilization of alkali metal, thus causing this

classical method difficulty in achieving a homogeneous mixture of the component [8–10]. Powder agglomeration can occur during heating, which could affect properties such as low surface area and low sinterability [10]. Thus, this method does not always allow for the production of dense, homogeneous single phase ceramics. Therefore, development of alternative methods that can produce powder with high sinterability and controlled stoichiometric composition is necessary. In recent years, ultra fine ceramic powder, which is synthesized using mechanochemical synthesis [11], polymeric precursors [12], and hydrothermal and polymerized complex methods [13], has been described in the literature to enable production of desired compositions. While synthesizing powder rapidly, with the desired composition, high porosity and high sinterability remains a challenge, combustion synthesis (CS) has been found as a potential solution for this problem.

Combustion synthesis (CS) or self-propagating high temperature synthesis (SHS) is an effective, low-cost method for producing various industrially useful materials. It has been introduced as a quick, straightforward preparation process for producing homogeneous, very fine, crystalline and unagglomerated multicomponent oxide ceramic powders, without intermediate decomposition and/or calcination steps [14,15]. The combustion synthesis technique begins with a mixture of easily oxidized reactants (such as nitrates) and a suitable organic fuel (such as urea [16], tartaric acid

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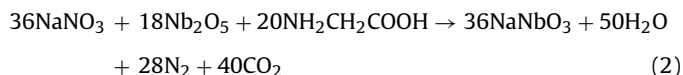
[17], alanine [18], glycine [19], etc.), which acts as a reducing agent. The mixture is then heated until it ignites, which is when the temperature of rapid exothermal chemical reaction commences, and a self-sustaining combustion reaction starts. This highly exothermic reaction produces a high temperature and duration long enough for the synthesis to occur, even in the absence of an external heating source [20]. Ultrafine nano-sized powder also can be prepared by releasing a large amount of gas from the system. This process results in a dry, fluffy, crystalline, unagglomerated and fine oxide powder. Metal nitrate was found to be the salt preferred, due to its water solubility, and homogeneous solution could be achieved easily by melting at a low temperature [16].

However, it was reported that an exothermic redox reaction (oxidation and reduction reaction taking place simultaneously) could be initiated only when the oxidizer and fuel are mixed intimately in a fixed proportion. The basis of the combustion synthesis process derives from the thermochemical concepts used in propellant chemistry [21,22]. The method consists of establishing a simple valency balance, irrespective of whether the elements are present in the oxidizer or fuel components of the mixture, and then calculating the stoichiometric composition of the starting mixture, which is equivalent to the release of maximum energy. The assumed valencies, which are presented as usual products of the combustion reaction, consist of CO_2 , H_2O and N_2 . Therefore, carbon and hydrogen are considered as reducing elements with the corresponding valencies of +4 and +1, whereas oxygen is thought to be an oxidizing agent with a valency of –2, and nitrogen a valency of 0. To extrapolate the concept of combustion synthesis of ceramic oxide means considering metals as reducing agents with their valencies in the corresponding oxide or nitrate, i.e. +2 for magnesium (oxide), +3 for cerium (nitrate) and +4 for cerium (oxide). In the case of multiple valence elements, the final product is used for calculation.

The elemental stoichiometric coefficient, φ , which is the ratio between the total valencies of fuel (glycine; $\text{NH}_2\text{CH}_2\text{COOH}$) and that of the oxidizer (sodium nitrate), can be calculated following the method proposed by Jain et al. [21]:

$$\varphi = \frac{n(\text{O}_{(\text{N})} + 2 \times 1_{(\text{H})} + 4_{(\text{C})} + 2 \times 1_{(\text{H})} + 4_{(\text{C})} - 2_{(\text{O})} - 2_{(\text{O})} + 1_{(\text{H})})}{1_{(\text{Na})} + 0_{(\text{N})} + 3 \times -2_{(\text{O})}} \quad (1)$$

where n is the mole of glycine. According to the propellant chemistry for stoichiometric redox reaction between fuel and an oxidizer, the φ ratio should be united (stoichiometric). A $\varphi < 1$ means oxidant-rich condition and $\varphi > 1$ means fuel-rich condition. To satisfy the principle in the present system, the sodium nitrate (oxidizing valency = 5–) to glycine (reducing valency = 9+) molar ratio was found to be 1:0.56. The comprehensive reaction that formed NaNbO_3 can be written as:



It should be noted that various fuel-to-oxidizer ratios should be carried out for investigating and comparing the effect of fuel-rich/fuel-lean mixtures on the synthesis of sodium niobate powder. In this study, sodium niobate powder was synthesized via the combustion synthesis technique for the first time. This process used sodium nitrate and niobium pentoxide as starting materials, and glycine was used as fuel. The different fuel-to-oxidizer molar ratios such as fuel-deficient (<0.56), equivalent stoichiometric (0.56) and fuel-rich (>0.56) condition were applied.

2. Experimental procedure

For the combustion synthesis of perovskite sodium niobate powder, AR grade sodium nitrate (NaNO_3 99.5%) and niobium pentoxide (Nb_2O_5 99.95%) were used as the oxidizer, and glycine ($\text{NH}_2\text{CH}_2\text{COOH}$ 99.7%) as fuel. The appropriate amount

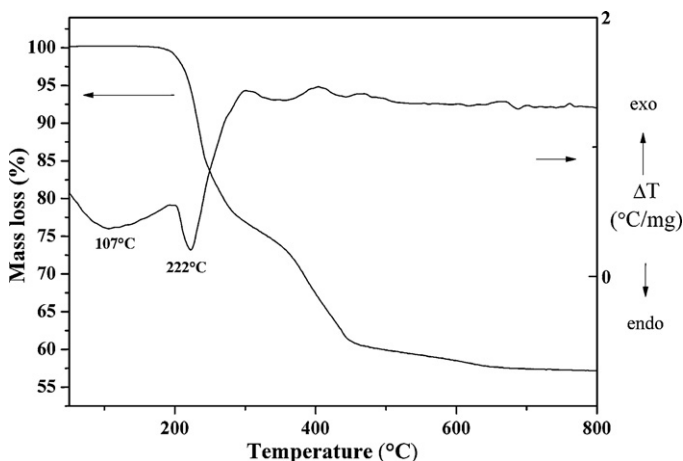


Fig. 1. TG-DTA curves of the precursor mixed in the stoichiometric proportion of NaNbO_3 .

of starting materials was weighed, mixed with de-ionized water in a glass beaker and stirred regularly for 30 min. The fuel (glycine) was then added and the mixture stirred for 30 min. After that, the solution precursor was boiled on a hotplate and then evaporated. Once the solution had thickened and begun to dry, the ignition took place when the temperature rapidly increased, which resulted in self-sustaining combustion with rapid evolution of a large volume of gas products, and formation of voluminous powder. For investigating thermal behavior of the precursor, the mixture of starting material was determined using thermo gravimetric analysis (TGA) and differential thermal analysis (DTA). The X-ray diffraction (XRD, Advance D8) technique was carried out on the combustion synthesized powder, using Ni-filtered $\text{CuK}\alpha$ radiation for phase identification and mean crystalline size estimation. The final powder product was characterized by using the Fourier transform infrared (FTIR) technique and scanning electron microscope (SEM, Hitachi S4700).

3. Results and discussion

Fig. 1 shows the TG/DTA plots of the stoichiometric precursor for NaNbO_3 powder synthesis. From observations of the TGA curve, there appeared to be three-stages of weight loss from room temperature to 800 °C. The definition of initial temperature (T_{in}) is when the sample weight starts changing rapidly during the chemical reaction [23]. As the precursor was heated, a significant weight loss was observed as the temperature reached 170 °C, indicating that the T_{in} was around this heat. The weight loss did not stop until the temperature reached 480 °C. It was indicated clearly that this reaction belongs to a multi-stage reaction. The overall weight loss was found to be about 40%, which is close to the theoretical value of 36.87% that corresponds to the release of 50 mol H_2O , 28 mol N_2 and 40 mol CO_2 related to Eq. (2). This outcome supported our conception that a hotplate can be used as a heating source because it is capable of initiating the combustion reaction at a temperature as low as that of the T_{in} .

The evolution XRD pattern of the combustion synthesized ceramic powder, with the fuel-to-oxidizer molar ratio, is illustrated in Fig. 2. The fuel-deficient (0.5) and equivalent stoichiometric ratio (0.56), were found (according to experimental observation) to have no ignition and combustion reaction in those compositions. Their XRD patterns correlated to detection results of the diffraction peaks of Nb_2O_5 (●) (JCPDS file no. 30-0873) and NaNO_3 (■) (JCPDS file no. 85-0859) starting materials, with no evidence of perovskite NaNbO_3 phase found. Although the equivalent stoichiometric ratio (0.56) was calculated for maximum energy release, auto-ignition did not occur in this study. This could indicate that oxygen deficiency in the system and its environment might lead to combustion reaction and fail to follow the theory. The fuel-to-oxidizer molar ratio was increased by using the fuel-rich condition (>0.56), which was found to produce the perovskite NaNbO_3 ceramic powder, due to its diffraction peaks being detected for all different fuel contents

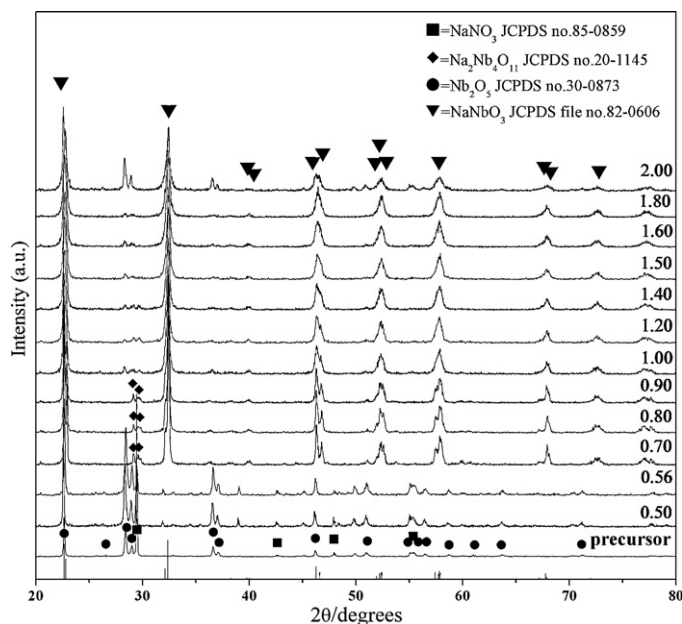


Fig. 2. X-ray diffraction patterns of NaNbO₃ powder obtained from various fuel-to-oxidant molar ratios.

(fuel-to-oxidizer molar ratio ranging from 0.7 to 2.0). This NaNbO₃ phase (▼) was consistent with JCPDS file no. 82-0606, which corresponded to an orthorhombic structure with the space group, P2₁ma (26). For a fuel-rich condition (fuel-to-oxidizer molar ratio of 0.7, 0.8 and 0.9), the NaNbO₃ phase (▼) was detected with the accompanying pyrochlore phase of Na₂Nb₄O₁₁ (◆), which matched JCPDS file no. 20-1145. No evidence of unreacted Nb₂O₅ and/or NaNO₃ diffraction peak was found. As fuel content increased from the fuel-to-oxidizer molar ratio of 1.0–2.0, unreacted Nb₂O₅ (●) (JCPDS file no. 30-0873) was found together with a majority of NaNbO₃ diffraction peaks. From the reflection peak, the average crystalline size (*D*) of NaNbO₃ powders was considered as a function of fuel content by using X-ray line broadening through Scherrer's equation [24]:

$$D = \frac{k\lambda}{\beta \cos \theta_B} \quad (3)$$

where *D* is the average crystalline size, *k* a constant taken as 0.89, λ the wavelength of X-ray radiation, β the full width at half maximum (FWHM) and θ_B the diffraction angle. The consequent values are reported in Table 1. As the fuel content increased, the average crystalline size (*D*) was found to decreased from 44.51 ± 11.99 nm (ratio of 0.7) to 26.11 ± 13.69 nm (ratio of 2.0). This suggested that elevated fuel content could lead to the production of a smaller crystalline size (related to a small particle size) of powder. Nevertheless, as a consequence of additional cost and more carbon residual, an extremely high fuel-to-oxidizer molar ratio (fuel-rich ratio) did not always result in the desired production of powder [25].

Therefore, from findings on the fine nucleation condition of monophasic NaNbO₃ phase, the fuel-to-oxidizer molar ratio of 1.0 was selected to investigate the effect of calcination temperature. From this ratio, the volume fraction of the perovskite phase formation (%perovskite) of as-prepared powder was found to be as high as 93%. This relative value was considered by approximately calculating the ratio of the main X-ray peak intensities of NaNbO₃ and Nb₂O₅ phases [26], according to the following equation; % perovskite = $(I_{\text{perovskite}} / (I_{\text{perovskite}} + I_{\text{Nb}_2\text{O}_5})) \times 100$. Thus, the as-prepared powder was calcined at different temperatures for 4 h with a heating/cooling rate of 20 °C/min. The X-ray diffraction (XRD) patterns of sodium niobate (NaNbO₃) powder, calcined for 4 h at different temperatures, are illustrated in Fig. 3. As the XRD

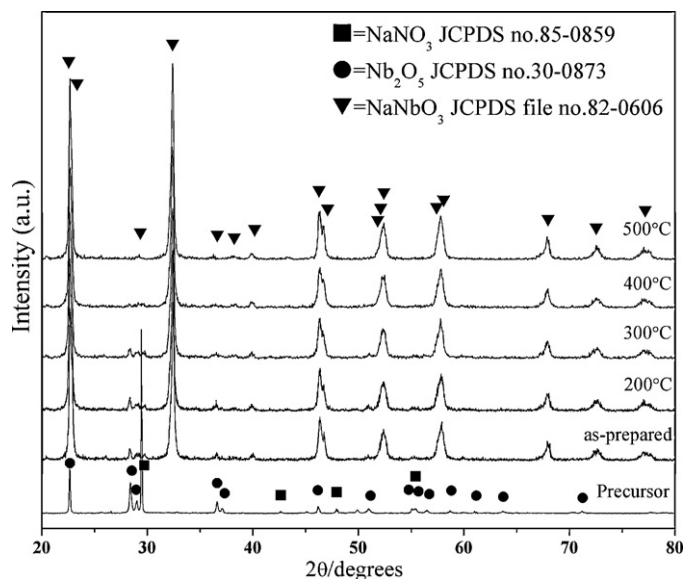


Fig. 3. X-ray diffraction patterns of NaNbO₃ powder (obtained from the fuel-to-oxidant molar ratio of 1.0) calcined at various temperatures for 4 h with a heating/cooling rate of 20 °C/min.

pattern of as-prepared powder was composed of a slight Nb₂O₅ (●) (JCPDS file no. 30-0873) phase, the intensity of that phase was found to decrease with increasing calcination temperature. The diffraction peak corresponded to the Nb₂O₅, which disappeared after calcination at 400 °C for 4 h, whereas monophasic perovskite NaNbO₃ phase was obtained. This result suggested that the perovskite NaNbO₃ powder could be synthesized by using the combustion synthesis process and calcinations at 400 °C for 4 h. This process was found to be a simple, rapid and cost-effective method when compared with the traditional solid-state reaction, which takes longer time and requires higher temperature [8,9]. In addition, the mean crystalline size (*D*), which is reported in Table 1, was not significantly varied between as-prepared powder (29.28 ± 5.29 nm) and increasing calcination temperatures of up to 400 °C (27.84 ± 7.12 nm). It can be suggested that calcina-

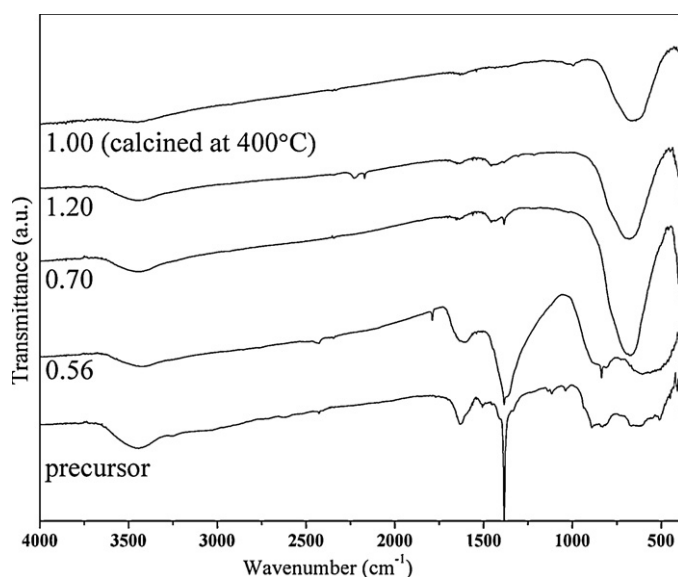


Fig. 4. FT-IR spectra of the precursor mixed in the stoichiometric proportion of NaNbO₃ powder obtained from various fuel-to-oxidant molar ratios and after the calcination step.

Table 1
Mean crystalline size, D , of NaNbO_3 powder obtained from various fuel-to-oxidant molar ratios.

	Fuel-to-oxidant molar ratios								
	0.7	0.8	0.9	1.0	1.2	1.4	1.6	1.8	2.0
As-prepared	44.51 ± 11.99	42.59 ± 11.54	37.31 ± 8.54	29.09 ± 5.29	27.45 ± 5.86	26.29 ± 5.97	24.40 ± 4.92	23.79 ± 5.52	26.12 ± 13.69
	Calcination temperature ($^{\circ}\text{C}$)								
	200 $^{\circ}\text{C}$	300 $^{\circ}\text{C}$	400 $^{\circ}\text{C}$	500 $^{\circ}\text{C}$	600 $^{\circ}\text{C}$	700 $^{\circ}\text{C}$	800 $^{\circ}\text{C}$	900 $^{\circ}\text{C}$	
Calcined powder	29.95 ± 4.51	31.51 ± 4.02	27.84 ± 7.12	$30 \pm 82 \pm 5.43$	38.84 ± 8.09	60.72 ± 8.09	70.87 ± 9.22	85.27 ± 15.65	

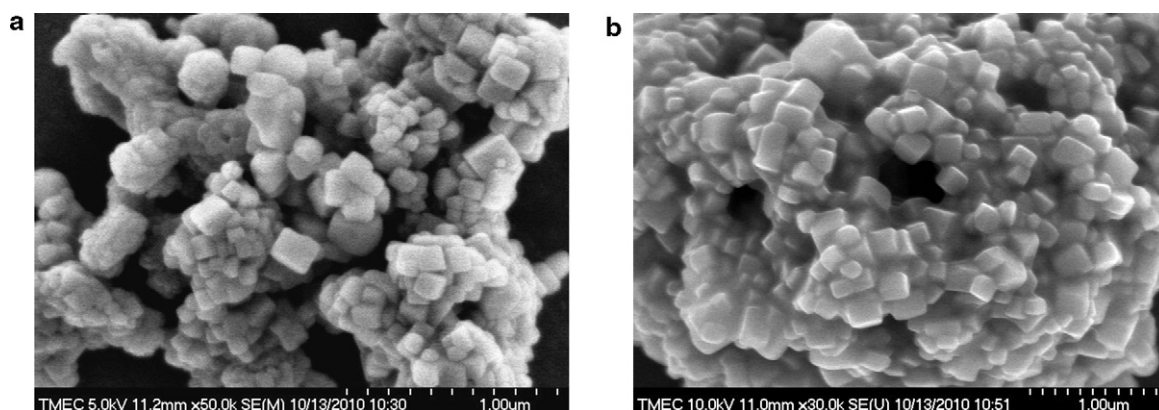


Fig. 5. SEM micrograph showing as-prepared NaNbO_3 powder synthesized using the fuel-to-oxidant molar ratio of 1.0 (a) and powder calcined at 400 $^{\circ}\text{C}$ for 4 h (b).

tions at this low temperature also produced a lower crystalline size when compared with the traditional solid state reaction method.

Fig. 4 shows the FT-IR spectroscopic studies of the crystalline NaNbO_3 obtained after combustion synthesis, its precursor without heat treatment and powder calcined at 400 $^{\circ}\text{C}$ for 4 h. For all powder, an IR band of around 3400 cm^{-1} was assigned to O–H asymmetric stretching (ν_3) [27], and on observation, it related to the moisture content of KBr. Regarding the precursor of NaNbO_3 powders without heat treatment, and as-prepared powder with a stoichiometric ratio (0.56), the IR spectrum indicated peaking of the characteristic band at ~ 1612 , ~ 1385 and ~ 890 cm^{-1} , which corresponded to the anti-symmetric carboxyl group stretching vibration, anti-symmetry NO_3^{-1} stretching and bending vibration, respectively [28]. This result proved existence of the carboxyl and NO_3^{-1} group (belonging to the starting material) in those samples. With regard to fuel-rich ratios (0.7 and 1.2), the new broad absorption bands appeared after combustion at a low wave number of ~ 673 cm^{-1} , suggesting that the Nb–O bond formation did occur. This Nb–O bond was believed to be the vibration (ν_3) mode in the corner-shared NbO_6 octahedron, according to reported IR spectra of niobate glass ceramics [28]. This result led to the assumption that the perovskite NaNbO_3 phase was synthesized (which correlated to XRD analysis). However, the IR band of anti-symmetric COO^- and that of anti-symmetry NO_3^{-1} stretching vibration also were observed. This clearly indicated traces of existent carboxyl group and nitrate in as-prepared NaNbO_3 powder, which cannot be detected when using the XRD technique. For powder calcined at 400 $^{\circ}\text{C}$ for 4 h, the spectra band of vibration (ν_3) mode belonging to the Nb–O bond was found without observation of any starting material band. This can indicate that monophasic perovskite NaNbO_3 has been synthesized successfully after calcination at a temperature as low as 400 $^{\circ}\text{C}$ for 4 h. Fig. 5 shows an SEM micrograph of the as-prepared NaNbO_3 powder using the fuel-to-oxidizer molar ratio of 1.0 (a) and powder calcined at 400 $^{\circ}\text{C}$ for 4 h (b). The powder was found to be polyhedral in shape, with uni-

form features. No evidence of a different or pyrochlore phase was found, which suggested the homogeneous character of the prepared powder. The average particle size, which can be estimated from micrographs, was found to be 137 ± 52 nm and 226 ± 46 nm for as-prepared and calcined powder, respectively. These particle size values are greater than the average crystalline size calculated from X-ray line broadening because a particle can be formed generally of many crystallites [29–31]. The particle growth for calcined powder seemed to be detected. It can be said that the firing process tends to produce agglomerated particles and grain growth, as reported by other works [32,33].

4. Conclusions

Crystalline NaNbO_3 powder, with a volume fraction of the perovskite phase formation (% perovskite) as high as 93%, was synthesized directly via the solution combustion process using NaNO_3 , Nb_2O_5 and glycine. Monophasic perovskite NaNbO_3 powder was obtained after calcination at 400 $^{\circ}\text{C}$ for 4 h. The fuel-to-oxidizer molar ratio was found to affect the combustion reaction and character of the powder obtained. The average crystalline size (D) was found to decrease from 44.51 ± 11.99 nm (ratio of 0.7) to 26.11 ± 13.69 nm (ratio of 2.0). This method is a simple, rapid, cost- and time-saving way of synthesizing stoichiometric, homogeneous and fine NaNbO_3 powder with a low calcination temperature. The powder obtained was found to be a uniform soft agglomerated particle.

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Synthesis of potassium niobate (KNbO₃) nano-powder by a modified solid-state reaction

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Synthesis of potassium niobate (KNbO₃) nano-powder by a modified solid-state reaction

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Abstract Crystalline lead-free piezoelectric potassium niobate (KNbO₃) powders have been synthesized through a modified solid-state reaction method. The thermal behavior of the K₂C₂O₄·H₂O and Nb₂O₅ raw material mixture was investigated by thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The X-ray diffraction technique (XRD) was used to investigate the phase formation and purity. The morphology of the powder obtained was characterized using a scanning electron microscope (SEM). The XRD pattern showed that the monophasic perovskite phase of KNbO₃ could be synthesized successfully at a

temperature as low as 550 °C for 240 min, with an average crystallite size of 36 ± 8 nm. The SEM images suggested that the average particle size of the powder obtained was 278 ± 75 nm.

Introduction

Lead zirconate titanate (PZT) ceramics are used widely in piezoelectric applications, due to their superior piezoelectric properties near the morphotropic phase boundary (MPB) [1, 2]. However, more than 50% of the lead-based piezoelectric material contains poisonous lead, which is a major drawback [3]. It has been reported that the use of lead-based ceramics causes serious environmental problems and numerous physical symptoms [3]. Furthermore, EU legislation will enforce draft directives for waste from electrical and electronic equipment (WEEE), and restrictions on the use of certain hazardous substances in electrical and electronic equipment (RoHS) and end-of life vehicles (ELV) [4–6]. According to these issues, lead and other heavy metals should be phased out, and alternative lead-free piezoelectric materials are receiving considerable attention.

Among various alternative families, perovskite type (ABO₃) ceramics have attracted much consideration. Among alkali metal niobates, potassium niobate (KNbO₃) is a well-known perovskite oxide that possesses attractive physical and piezoelectric properties [6–9]. Furthermore, the electromechanical coupling factor of the thickness-extensional mode, k_t , was reported to reach as high as 0.69 for the 49.5°-rotated X-cut on the Y-axis. This value of k_t is the highest among current lead-free piezoelectrics [10]. However, the main hindrance regarding this alkali niobate-based material lies in the difficulty of preparing dense and stoichiometric controlled ceramics using the conventional

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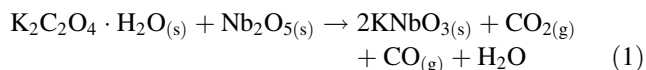
solid-state reaction and ordinary air sintering methods [11, 12]. These difficulties are caused by potassium volatility at high temperatures and excessive reactivity with moisture [13, 14]. Thus, different additive methods, hot pressing and spark plasma sintering have been used to improve ceramic densification [12, 15–19].

Several alternative ways for preparing alkali niobates have been investigated and developed: the hydrothermal [20] and hydrothermal-assisted sol–gel method [22], and glycothermal [23], nitrate–tartarate precursor technique [21], etc. However, most chemical synthesis routes require high purity reactants, which are more expensive and demand complicated procedures and specific apparatus. A modified solid-state reaction method has been used to synthesize the NaTaO_3 perovskite type material successfully, with reduced reaction temperature [24]. In this method, the carbonate compound was replaced by oxalate, and the addition of urea played an important role. Recently, this method also has been applied to synthesize lead-free sodium niobate (NaNbO_3) powders (without fuel) [25]. By replacing sodium carbonate using oxalate as the raw material, a lower calcination temperature and fine powders with an average crystallite size of 31.45 ± 5.28 nm were achieved.

In this study, a modified solid-state reaction method, with an expected lower reaction temperature, was used to synthesize KNbO_3 particles, using potassium oxalate as raw material without the addition of any fuel. Effects of the calcination conditions on the KNbO_3 phase development were investigated by the X-ray diffraction technique (XRD) and a scanning electron microscope (SEM).

Experiment

KNbO_3 was synthesized by a modified solid-state reaction method. Reagent-grade potassium oxalate monohydrate ($\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, 99.9%) and niobium oxide (Nb_2O_5 , 99.9%) were employed as the starting material. The raw materials were weighed in stoichiometric quantities following the equation below.



These starting materials were mixed by the ball-milling method using ethyl alcohol and partially stabilized zirconia balls for 18 h. Then, the mixture was dried on a hot plate with regular stirring for a suitable period. After drying, the precursor mixture was determined by thermo gravimetric analysis (TGA, Perkin Elmer) and differential thermal analysis (DTA, Perkin Elmer) for investigating the thermal behavior during heat treatment and finding the appropriate

calcination temperature. Based on TG–DTA results, the mixture was placed subsequently in a closed alumina crucible, and calcined for different periods of time at various temperatures ranging from 300 to 700 °C, to investigate formation of the KNbO_3 phase.

Subsequently, calcined powders were inspected by room temperature X-ray diffraction (XRD, Advance D8), using Ni-filtered CuK_α radiation to examine the effect of thermal treatment on the phase development and optimal calcination condition of crystalline KNbO_3 powder formation. The room temperature FTIR spectra were recorded in the range of $4,000\text{--}400\text{ cm}^{-1}$ (Perkin-Elmer, Spectrum GX spectrometer), with eight scans and a resolution of 4 cm^{-1} using KBr pellets. Powder morphologies and particle size were figured directly using a scanning electron microscope (SEM, Hitachi S4700).

Results and discussion

Figure 1 shows the TG–DTA curves of the stoichiometric precursor of KNbO_3 . The thermogravimetric (TG) curve of the KNbO_3 precursor shows three stages of weight loss from room temperature to 1,300 °C. Four endothermic peaks at 123, 398, 524 and 1,066 °C were observed in the differential thermal analysis (DTA) curve. Three weight-loss steps were observed in the ranges of 50–121, 121–172, and 416–532 °C. The corresponding weight losses seen were 3.92, 1.07, and 16.00%. The overall weight loss was found to be about 21%, which is close to the theoretical value of 20.01%, and corresponds to the release of 1 mol H_2O , 1 mol CO , and 1 mol CO_2 related to Eq. 1. In the temperature range from 50 to 121 °C (first stage), the initial weight loss of 3.92% showed decomposition of the oxalate molecule releasing water molecules (0.98 mol

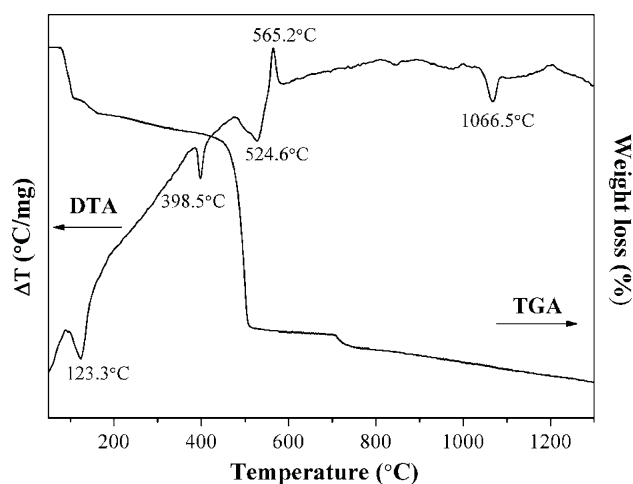


Fig. 1 TG–DTA curves of an uncalcined powder mixed in the stoichiometric proportion of KNbO_3

H₂O), which concurred with the theoretical value for releasing 1.00 mol H₂O (4.00%). This weight-loss corresponded to the endothermic peak, centered at 123 °C.

The second and third weight-loss steps illustrated the highest weight loss (~17%), which indicated a large elimination of organic compound that could be related to the release of CO and CO₂ by combustion reactions according to Eqs. 2 and 3 (16% theoretically). In the temperature range from 121 to 532 °C, the DTA curve shows corresponding endothermic peaks (398 and 524 °C) that agree with the TG result.



However, an exothermic DTA peak was found centered at 565 °C. This implied that the third decomposition stage could lead to the formation of potassium niobate compound, which could be expected from the exothermic peak at 565 °C (as confirmed by XRD analysis in Fig. 2). As the temperature increased to 695 °C, weight loss was found to start again in the TGA curve, which could be correlated to the decomposition of the activated-K₂CO₃ residue. It is well known that K₂C₂O₄ decomposes to K₂CO₃ at a higher temperature; however, this carbonate residue could decompose at a lower temperature when its degree of arrangement is lower than its initial state [26]. When heating further, an endothermic peak (without the observed weight-loss stage) could correspond to the phase transformation at 1,066 °C. Therefore, temperatures from the above TG–DTA analysis, which ranged from 300 to 700 °C, were selected for calcinations and investigation of the phase formation. The mixture of raw materials in the

required stoichiometric ratio was calcined in air using a heating/cooling rate of 20 °C/min at various temperatures and followed by the phase analysis using an X-ray diffractometer.

The X-ray diffraction (XRD) patterns of potassium niobate (KNbO₃) powders, calcined for 4 h at different temperatures, are illustrated in Fig. 2. The diffraction pattern of the powder calcined at 300 °C suggests a composition of potassium oxalate (◇) (JCPDS no.22-1232) and niobium oxide (●) (JCPDS no.30-0873) raw materials. No evidence of the KNbO₃ perovskite phase was found. As calcination temperatures increased to 500 °C, diffraction peaks of un-reacted raw materials were also found, but with lower intensity. This could demonstrate that the completed reaction cannot occur at such a low temperature range. As the diffusion coefficient is a temperature dependent parameter, the rate of diffusion is affected greatly by higher temperatures [27], which also could improve higher atomic mobility [28]. Nonetheless, the powders calcined from 550 to 700 °C showed diffraction peaks that could correspond to the orthorhombic potassium niobate perovskite phase (KNbO₃) JCPDS no.32-0822 (▼). Amplified peak intensities can be seen after calcinations at increased temperatures. However, this result indicates the formation of KNbO₃ perovskite phase powder, which passes through the calcination temperatures from 550 to 700 °C in 4 h. These temperatures were lower than those in the chemical synthesis of KNbO₃, which used the polymerized complex method (PC method). This technique achieved the KNbO₃ compound after the calcination step at 900 °C [29], or once the citrate precursor route had obtained KNbO₃ nanopowder after heat treatment at 800 °C [30]. In addition, other chemical methods always require high purity reagent, which is more expensive, and involves complex procedures.

For a verdict on fine KNbO₃ nucleation condition, a temperature of 550 °C was chosen to find the effect of calcination dwell time. The mixture of raw material powder was calcined at 550 °C for 15–360 min. The XRD analysis of calcined powder, with a different dwell time (Fig. 3), revealed an amorphous phase for a calcination period of 15 min, and no distinct crystalline phase could be detected. The absence of reflection peaks that correspond to K₂C₂O₄·H₂O and Nb₂O₅ indicated the amorphous nature of the powder obtained. The presence of reflection peaks for the XRD pattern of powder calcined at 550 °C for 20 min or longer could be ascribed to the crystalline phase of the sample. The different diffraction pattern of the powder, calcined for 20 min, suggests the nucleation condition of the KNbO₃ phase, which was confirmed by further soaking time. After the calcination step at 550 °C for 20 min or longer, the powder showed an XRD pattern that could be matched with the perovskite potassium niobate (KN) phase

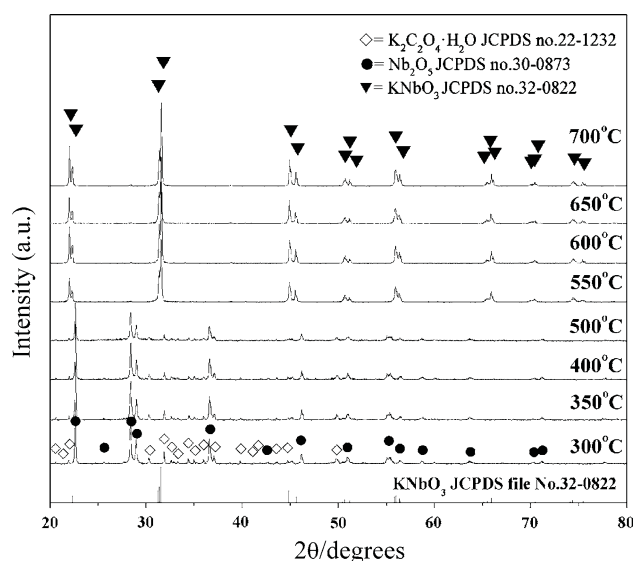


Fig. 2 X-ray diffraction patterns of KNbO₃ powder calcined at various temperatures for 4 h with a heating/cooling rate of 20 °C/min

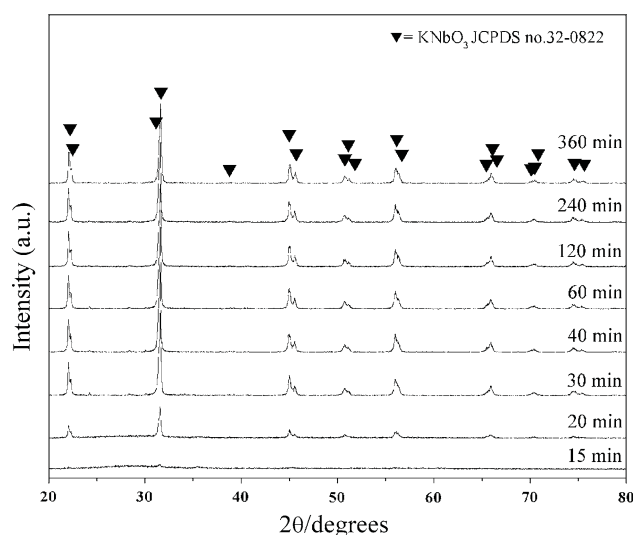


Fig. 3 X-ray diffraction patterns of KNbO_3 powder calcined at the calcination temperature of $550\text{ }^\circ\text{C}$ for various dwell times with a heating/cooling rate of $20\text{ }^\circ\text{C/min}$

JCPDS no.32-0822. These XRD analyses agreed with the TG-DTA analysis, in which crystallization of the KNbO_3 phase was found around the previously mentioned temperature range. During the course of calcinations, the rise in calcination temperature and dwell time resulted in increased diffraction peak intensities, which related to higher crystallinity of the powder. This was supported by the increase in lattice parameters and average crystallite size, as revealed below. Nevertheless, it has been confirmed that this modified solid state reaction method can synthesize pure KNbO_3 phase powder by using potassium oxalate monohydrate as starting material at the calcination temperature of $550\text{ }^\circ\text{C}$ for 20 min. This calcination temperature is much lower than that used in a mixed oxide powder process, which lies in the range of $800\text{ }^\circ\text{C}$ [9, 11, 13, 31, 32], or solution process (sol-gel and precipitation

methods) that requires calcination temperatures of over $600\text{ }^\circ\text{C}$ [33, 34]. Since XRD analysis suggested an orthorhombic crystal structure for preparing KNbO_3 powder, lattice parameters of the sample could be deliberate by means of the UnitCell program package (<http://rock.esc.cam.ac.uk/pub/minp/UnitCell/>). The corresponding cell parameters, which are close to those reported from JCPDS file No.32-0822 ($a = 5.695\text{ nm}$, $b = 5.721\text{ nm}$, and $c = 3.973\text{ nm}$) are given in Table 1. The suggested orthorhombic crystal structure, obtained from matching with the JCPDS file, could be supported by this correlation of lattice parameters.

The average crystallite size of KNbO_3 powders was considered as a function of calcination temperature, and time for broadening the X-ray line of the reflection peak using Scherrer's equation [35]: $D = k\lambda/\beta\cos\theta_B$, where D is the average crystallite size, k a constant taken as 0.89, λ the wavelength of X-ray radiation, β the full width at half maximum (FWHM), and θ_B the diffraction angle. The corresponding values are reported in Table 2. The average crystallite size of powders, calcined from 550 to $700\text{ }^\circ\text{C}$ for 4 h, was found to be about 36 ± 8 to $58 \pm 6\text{ nm}$. As the dwell time increased, it was found that the average crystallite size of calcined powders was increasing from 33 ± 9 to $36 \pm 8\text{ nm}$. The low D values suggest that the surface area of calcined powder was high enough to support high sinterability sufficiently [36]. The increase in crystallinity of the KNbO_3 phase was affected by increasing dwell time and calcination temperature. This consequence may confirm that the dwell time and calcination temperature also play an important role in developing the pure phase creation.

Figure 4 shows the FT-IR spectroscopic studies of the crystalline potassium niobate (KNbO_3) before and after the calcination step. The IR band for the uncalcined precursor was observed at $3,253\text{ cm}^{-1}$, due to O–H asymmetric

Table 1 Lattice parameters of the KNbO_3 powder calcined at various calcination temperatures for 4 h

KNbO_3 Lattice parameter	Calcinations temperature ($^\circ\text{C}$)			
	550	600	650	700
a	5.6929 ± 0.0005	5.6876 ± 0.0070	5.7019 ± 0.0022	5.6952 ± 0.0028
b	5.6989 ± 0.0080	5.6994 ± 0.0048	5.7153 ± 0.0108	5.6980 ± 0.0060
c	3.9802 ± 0.0005	3.9768 ± 0.0006	3.9912 ± 0.0155	3.9777 ± 0.0030

Table 2 Mean crystalline size, D , of the KNbO_3 powder calcined at different temperatures for 4 h and for a different dwell time at $550\text{ }^\circ\text{C}$

KNbO_3	Calcination temperature ($^\circ\text{C}$)					
	550	600	650	700		
D	36.40 ± 8.25	41.46 ± 8.84	53.59 ± 6.56	57.81 ± 6.31		
550 $^\circ\text{C}$	Dwell time (min)					
	20	30	40	60	120	240
D	33.15 ± 9.22	34.36 ± 7.92	34.54 ± 8.128	35.30 ± 8.30	35.97 ± 6.47	36.40 ± 8.25

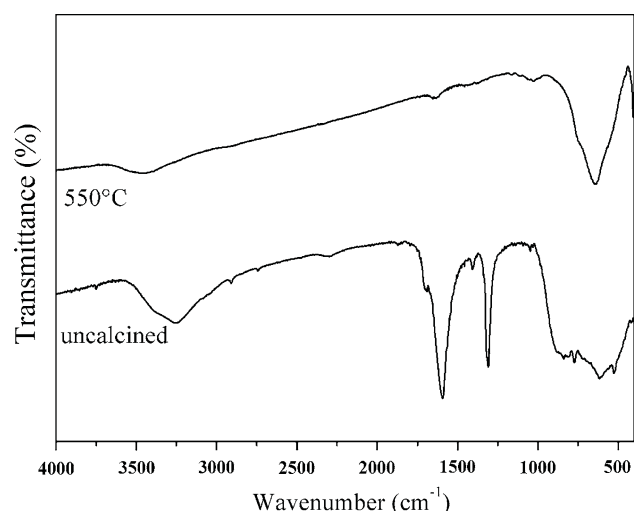


Fig. 4 FT-IR spectra of an uncalcined powder mixed in the stoichiometric proportion of KNbO_3 and KNbO_3 particles calcined at 550 °C

stretching (ν_3), which related to the moisture content of the KBr pellet and scissor bending mode (ν_2) of HO–H at 1,600 cm^{-1} and 1,310 cm^{-1} . When KNbO_3 powders were calcined at 550 °C for 4 h, the absorption of bands at a low wave number range of 620 cm^{-1} suggested occurrence of Nb–O bond formation, which was believed to be the vibration (ν_3) mode in the corner-shared NbO_6 octahedron, according to the reported IR spectra of niobate glass ceramics [37]. This result shows that the perovskite KNbO_3 phase was synthesized, which correlated with other results. The TG result indicated that the mass loss in the TG curve at around 700 °C could be the result of the K_2CO_3 residue decomposition, however, the FTIR band corresponding to the C–O stretching mode of carbonate at 1,450 cm^{-1} [38] was not found in KNbO_3 powders calcined at 550 °C for 4 h. This observation could be described as the effect of dwell time.

Figure 5 shows SEM micrographs of KNbO_3 powder prepared using a modified solid state reaction method at 550 and 700 °C for 240 min. The KNbO_3 powder was found to be polyhedral in shape, with uniform features. The secondary phase could not be observed, which suggested the homogeneous character of the powder prepared. The mean particle sizes, which can be estimated from the micrographs, were found to be 278 ± 75 and 341 ± 80 for powder obtained at 550 and 700 °C, respectively. Particle growth was detected in powder calcined at a higher temperature. This value is greater than the average crystallite size, calculated from X-ray line broadening. It was believed that this contradictory value could indicate the agglomerate of the calcined powders. As reported by other studies [39, 40], the firing process tends to produce agglomerated particles and grain growth. No evidence of a different or pyrochlore phase was found. This outcome relates to the XRD result, in which the monophasic perovskite phase of KNbO_3 can be established after calcinations at 550 °C for 240 min.

Conclusion

Crystalline KNbO_3 powder was prepared from a modified solid state reaction of $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and Nb_2O_5 . The final product was confirmed by XRD and SEM techniques. This is a simple cost- and time-saving method for synthesizing stoichiometric, homogeneous, and fine KNbO_3 powder, with a low calcination temperature of 550 °C for 240 min. This temperature is about 250 °C lower than others used, even in conventional methods. The powder obtained was found to be a uniform agglomerated particle that possesses an average crystallite size (defined by XRD) of between 36 ± 8 and 58 ± 6 nm, and a mean particle size (defined by SEM micrograph) of 278 ± 75 nm.

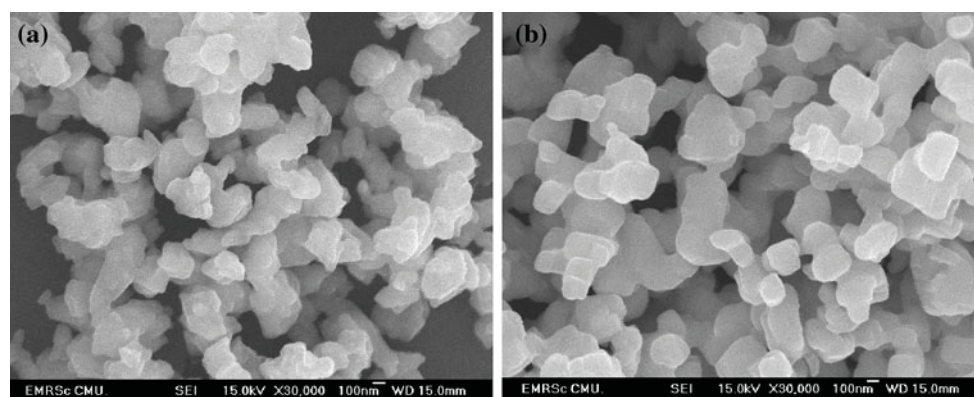
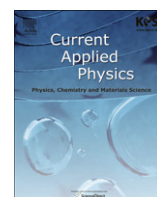


Fig. 5 SEM micrographs showing KNbO_3 powder synthesized at 550 °C (a) and 700 °C (b), for 4 h with a heating/cooling rate of 20 °C/min

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Phase transition behaviour and electrical properties of lead-free $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3\text{--LiNbO}_3\text{--LiSbO}_3$ piezoelectric ceramics

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ABSTRACT

The ternary system of $0.945(\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3)\text{--}(0.055 - x)\text{LiNbO}_3\text{--}x\text{LiSbO}_3$ [$0.945\text{KNN--}(0.055 - x)\text{LN--}x\text{LS}$]; $x = 0.0\text{--}0.055$ lead-free piezoelectric ceramics was fabricated by the conventional mixed oxide method with normal sintering. The crystal structure was studied by means of X-ray diffraction (XRD). The results of XRD patterns show that complete solid solutions of the mixed phase between the orthorhombic and tetragonal perovskite phase were observed. The DSC and dielectric data show that the amount of LiSbO_3 in $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3\text{--LiNbO}_3$ solid solution slightly decreases the paraelectric cubic-ferroelectric tetragonal phase transition (T_C) to a low temperature. Furthermore, good dielectric and piezoelectric properties were observed at composition, $x = 0.03$. The polymorphic phase transition between the orthorhombic and tetragonal phases plays a very important role in enhancement of the piezoelectric properties of KNN–LN–LS ceramics.

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1. Introduction

Lead-based piezoelectric materials such as $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) ceramics are the most widely used, due to their superior piezoelectric performances [1]. However, the toxicity of lead oxide, which contains more than 60 wt%, can cause damage to the kidney, brain and nervous system [2]. In recent years, many countries have required that all electronic equipment be lead-free for human health and environmental protection. Therefore, urgent development of lead-free piezoelectric ceramics, with outstanding properties for replacing lead-based ceramics, is necessary, and recent attention on this topic has been paid to $(\text{K,Na})\text{NbO}_3$ and (KNN)-based ceramics, due to their good piezoelectric properties and high Curie temperature [3]. It is well known that not only the morphotropic phase boundary (MPB) between orthorhombic and tetragonal phase, but also the polymorphic orthorhombic and tetragonal phase transition

temperature play an important role in the electrical properties of KNN-based ceramics [4,5]. It was reported that the polymorphic orthorhombic-tetragonal phase transition temperature (PPT) strongly affects the electrical properties of KNN-based ceramics, and a PPT near room temperature would be helpful in obtaining enhanced electrical properties. Recently, Guo et al observed excellent electrical properties in the $(1 - x)(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3\text{--}x\text{LiNbO}_3$ system [6]. The coexistence of orthorhombic-tetragonal phase was found at $0.05 < x < 0.07$. Excellent piezoelectric and electromechanical responses; $d_{33} = 235$ pC/N, $k_p = 44\%$, and $k_t = 48\%$, were obtained as samples, with the composition, $x = 0.052$. Recent studies have also found that the binary system of $(1 - x)\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3\text{--}x\text{LiSbO}_3$; $[(1 - x)\text{KNN--}x\text{LS}]$ at the composition, $x \sim 0.052$, exhibited good piezoelectric properties at room temperature, with electromechanical coupling factors of $k_{33} \sim 62\%$ and $k_{31} \sim 30\%$, and piezoelectric coefficients of $d_{33} \sim 265$ pC/N and $d_{31} \sim -116$ pC/N [7]. The piezoelectric, electromechanical, and elastic properties were determined as a function of temperature, showing anomalous behaviour at around room temperature, which related to the orthorhombic to tetragonal polymorphic phase transition (PPT) [7]. Since both the $0.945\text{KNN--}0.055\text{LN}$ [6] and $0.948\text{KNN--}0.052\text{LS}$ [7]

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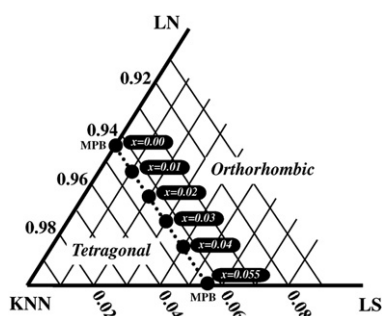


Fig. 1. Composition studied in the $0.945\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3-(0.055-x)\text{LiNbO}_3-x\text{LiSbO}_3$ ternary solid solution.

compositions have excellent electrical properties; the combination of these two systems to form a KNN–LN–LS ternary solid solution is very interesting. In this study, the ternary solid solution of $0.945\text{KNN}-(0.055-x)\text{LN}-x\text{LS}$, where $x=0-0.055$, was synthesized. To obtain a homogeneous perovskite solid solution and better electrical properties, the samples were prepared by a conventional solid state reaction process. Fig. 1 schematically shows the composition range that was studied in this work. In this study, the influence of LiNbO_3 (LN) and LiSbO_3 (LS) addition on phase transitions, and electrical properties of KNN ceramics are also reported.

2. Experiment

The sample, $0.945\text{KNN}-(0.055-x)\text{LN}-x\text{LS}$, where $x=0.00, 0.01, 0.02, 0.03, 0.04$ and 0.055 , was prepared using the conventional solid state reaction process with normal sintering. Reagent-grade oxide and carbonate powders of K_2CO_3 (99.0%), Na_2CO_3 (99.5%), Li_2CO_3 (99.9%), Nb_2O_5 (99.5%) and Sb_2O_3 (99.9%) were used as starting raw materials. The powders were weighed according to the stoichiometric formula and ball milled in absolute ethanol for 24 h. The dried slurries were calcined at 850°C for 4 h, then ball milled again for 24 h. The granulated powders were pressed into disks of 15 mm diameter and 1 mm thickness and then pressed using a cold isostatic pressing (CIP) technique under 300 MPa. These disks were sintered in air at $1030-1070^\circ\text{C}$ for 2 h. The density of the fired samples was determined by Archimedes method and found to be greater than 95% theoretical. Silver paste (Heraeus C1000) was fired on both sides of the samples at 550°C for 10 min, as electrodes for dielectric measurements. The crystal structures were determined by X-ray diffraction (XRD) analysis

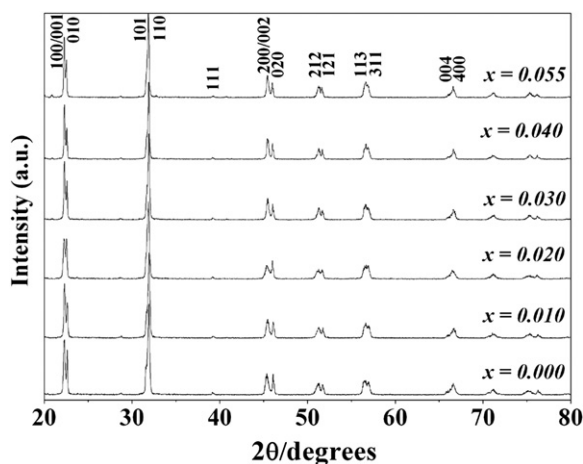


Fig. 2. XRD patterns of $0.945\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3-(0.055-x)\text{LiNbO}_3-x\text{LiSbO}_3$ ceramics at room temperature.

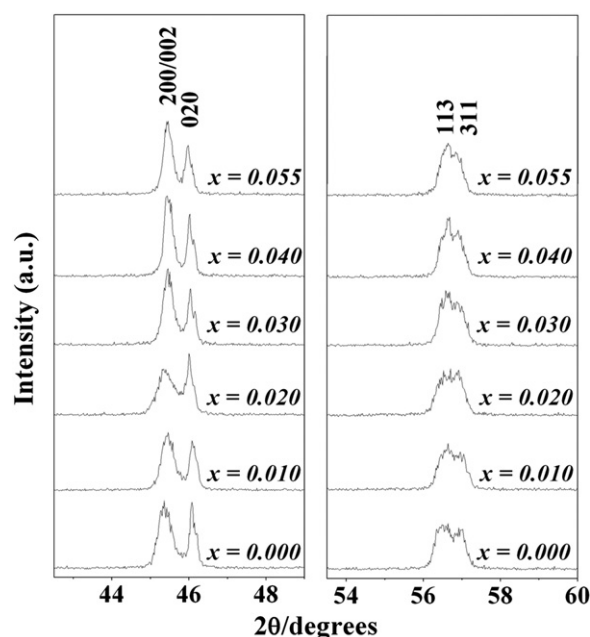


Fig. 3. XRD patterns of the (200) and (113) peaks of $0.945\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3-(0.055-x)\text{LiNbO}_3-x\text{LiSbO}_3$ ceramics.

obtained by using $\text{CuK}\alpha$ radiation (Bruker-D8 Advance). The temperature dependence of the samples' dielectric constant was examined using a programmable furnace with an LCR analyzer (HP-4284, Hewlett–Packard Inc.). A differential scanning calorimeter (DSC) was used to follow the phase transitions of sintered ceramics. The ceramics were poled for piezoelectric measurement in a silicone oil bath at room temperature for 30 min and field strength of $3-4\text{ kV/mm}$. The piezoelectric coefficient, d_{33} , of the samples, which were left for 24 h after poling, was measured using a d_{33} meter (Model 8000, Penne baker). The planar electromechanical coupling factor, k_p , was calculated from the resonance and anti-resonance frequencies, based on IEEE standards.

3. Results and discussion

Fig. 2 displays the XRD pattern of $0.945\text{KNN}-(0.055-x)\text{LN}-x\text{LS}$ ceramics sintered at 1050°C . A series of continuous solid solutions between KNNLN and KNNLS was clearly formed. The phase structure in all samples was a pure perovskite phase and no secondary

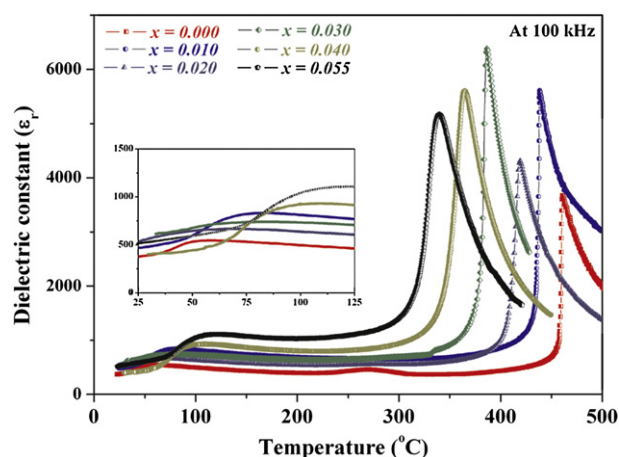


Fig. 4. Temperature dependence of the dielectric constant (ϵ_r) at 100 kHz of $0.945\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3-(0.055-x)\text{LiNbO}_3-x\text{LiSbO}_3$ ceramics as a function of x .

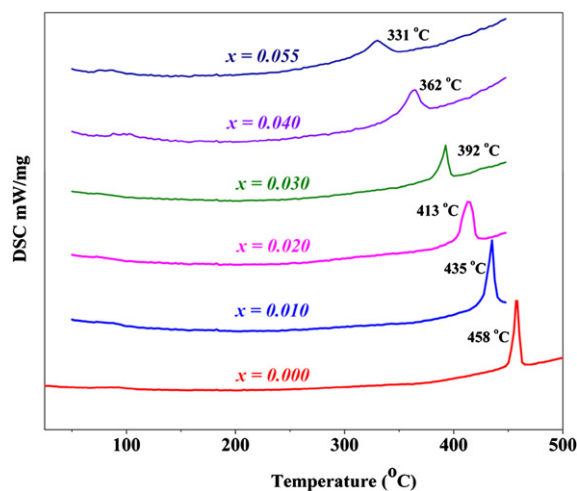


Fig. 5. DSC heating curves of 0.945K_{0.5}Na_{0.5}NbO₃–(0.055 – x)LiNbO₃–xLiSbO₃ ceramics as a function of x.

impurity could be certified. The result indicated that the dopants were completely diffused into the (K_{0.5}Na_{0.5})NbO₃ lattices, with Li⁺ entering the (Na_{0.5}K_{0.5})⁺ sites and Sb⁵⁺ occupying the Nb⁵⁺ sites, to form a new solid solution in all compositions. Fig. 3 shows the XRD patterns of 0.945KNN–(0.055 – x)LN–xLS ceramics in the 2θ range of 43–48° and 54–60°. The compositions in this study were selected across the orthorhombic–tetragonal coexistence region between the KNN–LS and KNN–LN system. As expected, coexistence of the orthorhombic–tetragonal phase was observed in all compositions. Interestingly, with an increasing x value, the diffraction peaks located at a higher angle, and (113) and (311) peaks near 2θ = 57°, tended to merge into a single peak, which indicated that the crystalline structure varied from the orthorhombic–tetragonal phase to the orthorhombic-rich phase. Similar behaviour was observed in the xPb(Zn_{1/3}Nb_{2/3}O₃)–(0.2 – x)Pb(Ni_{1/3}Nb_{2/3})O₃–0.8Pb(Zr_{1/2}Ti_{1/2})O₃ ternary system [8].

The temperature dependence of the dielectric constant, (ε_r) of 0.945KNN–(0.055 – x)LN–xLS ceramics, at the frequency of 100 kHz is shown in Fig. 4, together with the temperature dependence of ε_r for all ceramic samples; showing two phase transitions that correspond to those of ferroelectric tetragonal to paraelectric cubic (T_C) and polymorphic ferroelectric orthorhombic to tetragonal ferroelectric (T_{O–T}) for high and low transition temperatures, respectively. The T_C decreases with increased composition x, however; T_{O–T} tends to decrease with increasing composition x up to 0.03 and continues to increase with a further increase of x. The T_{O–T} was approximately 52, 53, 49, 48, 85 and 95 °C for compositions x = 0.00, 0.01, 0.02, 0.03, 0.04 and 0.055, respectively. Interestingly, the T_{O–T} phase transition temperature for the composition, x = 0.03, is close to room temperature and this composition is expected to attribute to high piezoelectric responses. The phase transition temperature; clearly confirmed by DSC measurement, is presented in Fig. 5. At the composition, x = 0.00, a sharp peak was observed near the

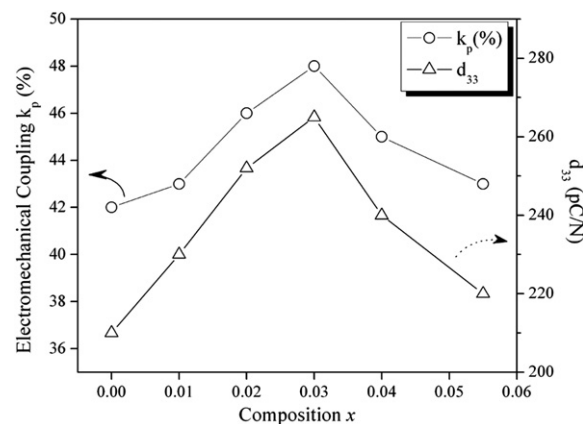


Fig. 6. Planar electromechanical coefficient and piezoelectric constant of 0.945K_{0.5}Na_{0.5}NbO₃–(0.055 – x)LiNbO₃–xLiSbO₃ ceramics as a function of x.

ferroelectric tetragonal to paraelectric cubic phase transition temperature, and the transition is of the first order, due to its association with a significant value of ΔH. The transition temperature defined by maximum heat capacity, which closely followed the ferroelectric to paraelectric transition temperature revealed by the dielectric measurement, is shown in Fig. 4. The peak value of heat capacity became weaker, and heat capacity anomaly gradually broader, with increasing LS concentration. These results indicated that the phase transition deviates gradually from the first order type. Stenger and Burggraaf et al. [9] observed that the change in entropy (ΔS) and ΔS/T_i correlates with the fluctuation probability in conjunction with a small spontaneous lattice deformation and polarization. They explained that large values of the ratio, ΔS/T_i, give sharp transition and lower values, which lead to diffuse behaviour. Table 1 shows that the ΔS and ΔS/T_i values are small for the LS doped sample, when compared to the KNN–LN sample. This indicates the existence of diffuseness in the phase transition behaviour, which increases with increasing LS content, and coincides well with the dielectric results in the composition range investigated. This behaviour can originate from the more complex occupation of the A and B sites in an ABO₃ perovskite structure and heterogeneous compositions, which also give rise to random fields that tend to make the phase transition “diffuse” instead of sharp, as in a normal ferroelectric. Fig. 6 shows the piezoelectric constant, d₃₃, and planar electromechanical coupling factor, k_p, of polarized 0.945KNN–(0.055 – x)LN–xLS ceramics as a function of LiSbO₃ concentration. It can be seen that the property exhibits a compositional dependence when d₃₃ and k_p of the composition, x = 0.00, show values of 210 pC/N and 0.42, respectively, with increasing x, d₃₃ and k_p to the maximum values of 265 pC/N and 0.48 at x = 0.03. As expected, the composition, x = 0.3, shows the maximum d₃₃ and k_p value in the KNN–LN–LS system. Therefore, it can be concluded that the polymorphic phase transition between the orthorhombic and tetragonal phases plays a very important role in enhancement of the piezoelectric properties of KNN–LN–LS ceramics. Similar behaviour was observed in the KNN–LN [6] KNN–LT [10] and KNN–LT–BNT–BT [11] system. The KNN–LN–LS samples showed good piezoelectric properties when compared with the KNN–LN [6] and KNN–LS system [7].

Table 1
The values of ε_{max}, T_{max}, T_i, ΔH, ΔS and ΔS/T_i of KNN–LN–LS ceramics.

Compositions	ε _{max}	T _{o–T} (°C)	T _{max} (°C)	T _i (°C)	ΔH (J g ^{–1})	ΔS × 10 ³ (J g ^{–1} K ^{–1})	(ΔS/T _i) × 10 ⁶ (J g ^{–1} K ^{–2})
x = 0.000	4800	52	460	458	4.174	9.114	19.900
x = 0.010	5750	53	439	435	3.471	7.979	18.343
x = 0.020	4400	49	419	413	2.858	6.920	16.755
x = 0.030	6700	48	388	392	1.800	4.592	11.714
x = 0.040	5700	85	363	362	0.987	2.727	7.533
x = 0.055	5250	95	340	331	0.014	0.042	0.127

4. Conclusion

In this study, 0.945K_{0.5}Na_{0.5}NbO₃–(0.055 – x)LiNbO₃–xLiSbO₃ ceramics were prepared by the conventional solid state reaction process with normal sintering. All ceramics with a perovskite structure are mixed phase of orthorhombic and tetragonal phase. The phase transition temperature of tetragonal–cubic (T_C) was

decreased with increasing x . Furthermore, good dielectric and piezoelectric properties were observed at composition, $x = 0.03$. The polymorphic phase transition between the orthorhombic and tetragonal phases plays a very important role in enhancement of the piezoelectric properties of KNN–LN–LS ceramics.

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