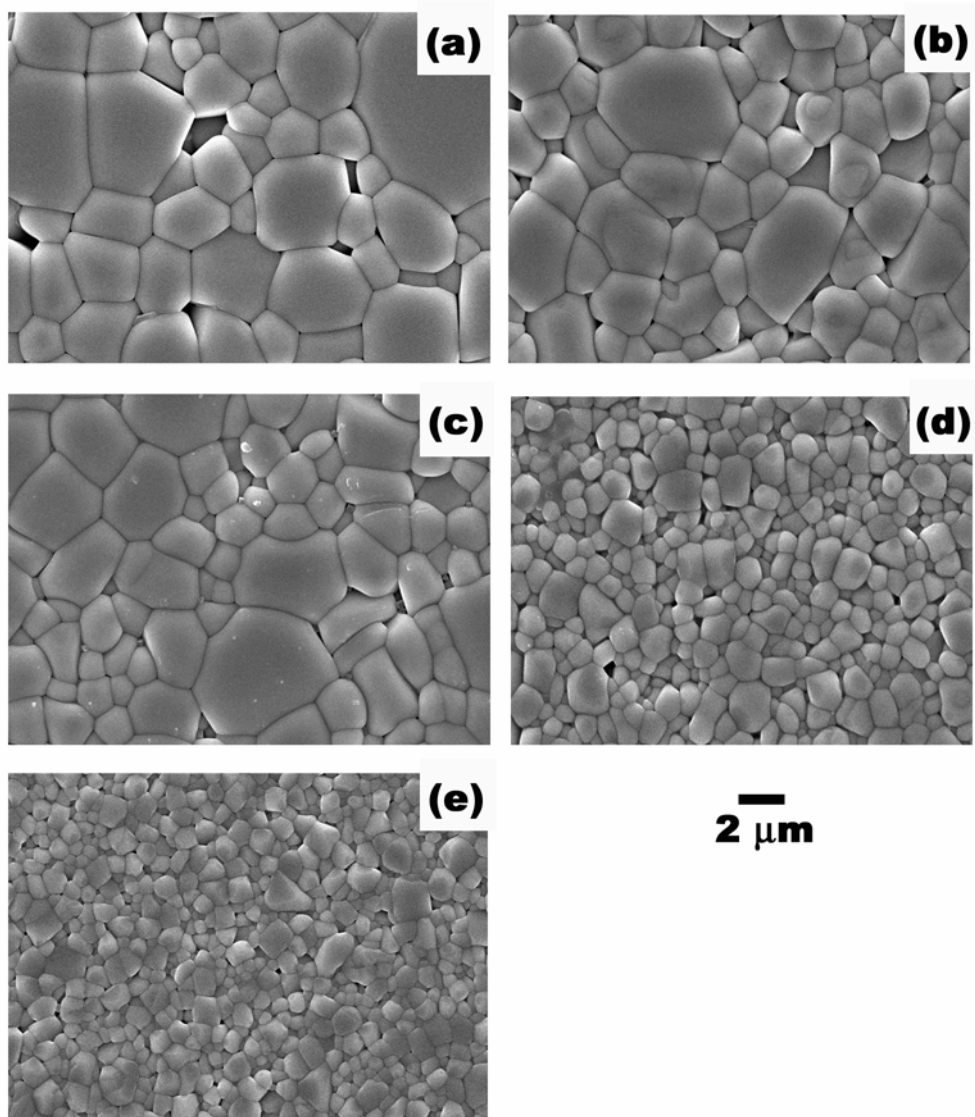
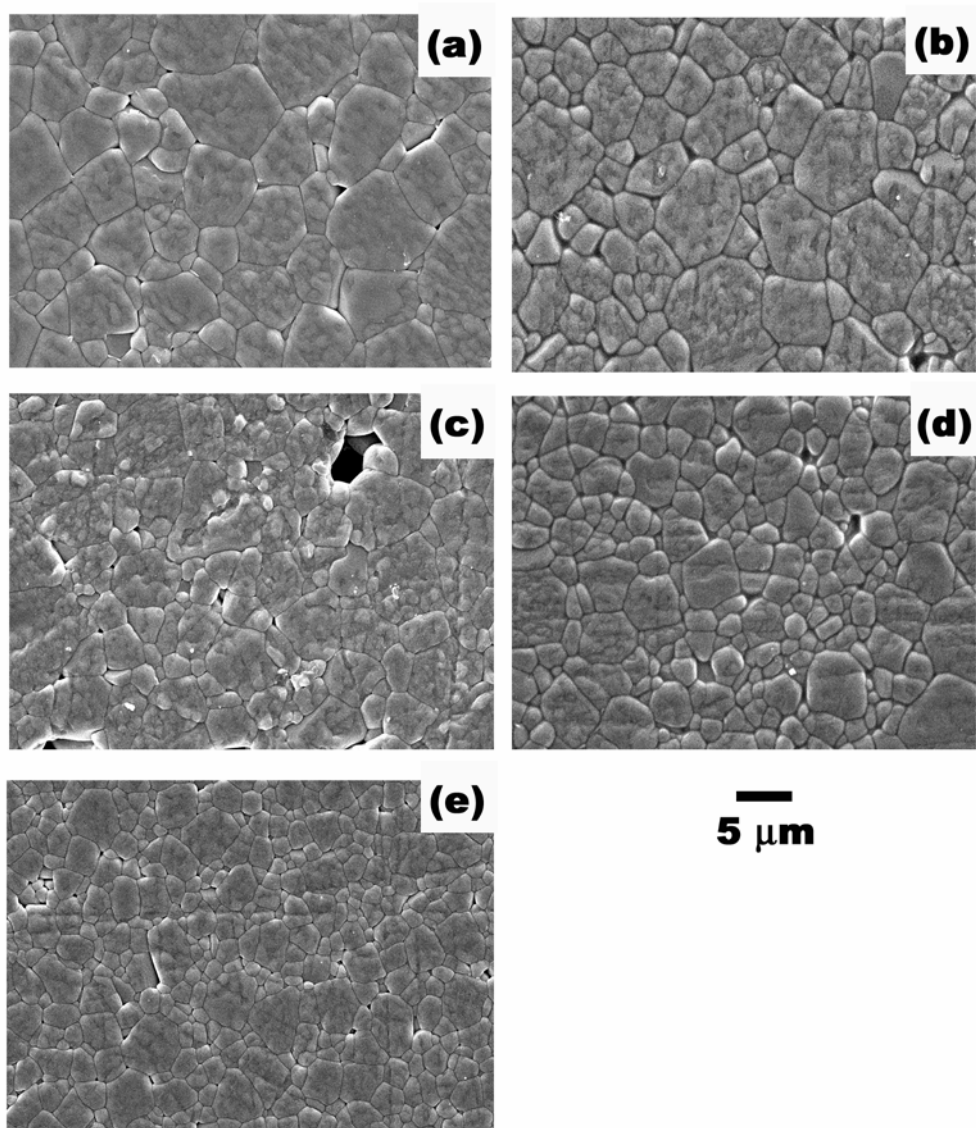
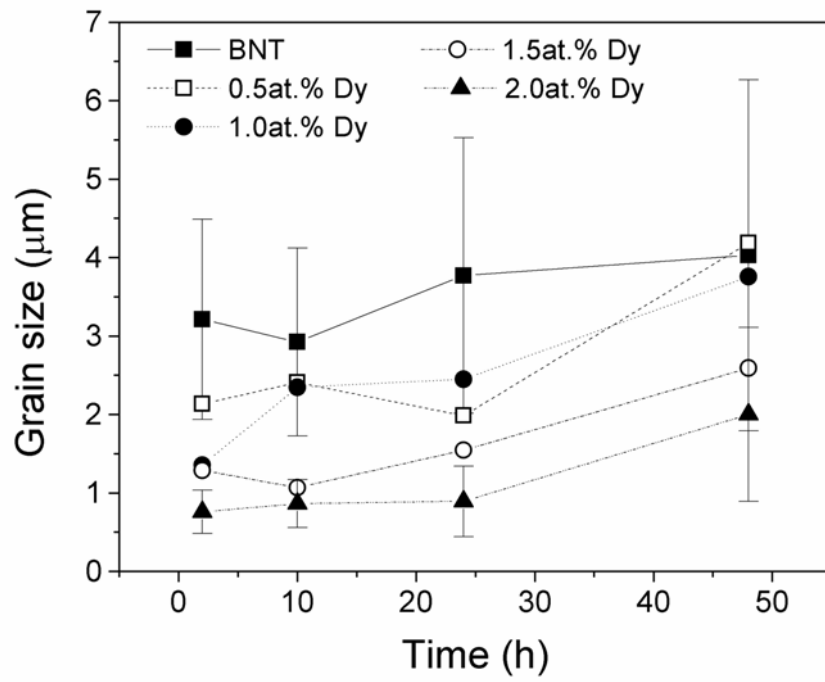




รูป 4.43 โครงสร้างจุลภาคของพื้นผิวของเซรามิกที่ถูกเผาซินเตอร์ที่ 1050 °C เป็นเวลา 10 ชั่วโมง (a) 0at.%Dy (b) 0.5at.%Dy (c) 1.0at.%Dy (d) 1.5at.%Dy และ (e) 2.0at.%Dy



รูป 4.44 โครงสร้างจุลภาคของพื้นผิวของเซรามิกที่ถูกเผาซินเตอร์ที่ 1050 °C เป็นเวลา 48 ชั่วโมง (a) 0at.%Dy (b) 0.5at.%Dy (c) 1.0at.%Dy (d) 1.5at.%Dy และ (e) 2.0at.%Dy



รูป 4.45 กราฟแสดงความสัมพันธ์ระหว่างขนาดเกรนและเวลาของเซรามิกบิสมาต์โซเดียมไททาเนตเจือด้วยไดสโพรเซียม

บทที่ 5

สรุปผลการวิจัยและข้อเสนอแนะ

5.1 สรุปผลการวิจัย

ผลของงานวิจัยในโครงการนี้ ได้ทำให้ทราบถึงอิทธิพลของสารเจือประเภทต่างๆที่มีต่อการแน่นตัวและเฟสที่เกิดขึ้นของเซรามิกเลดแลนทานัมเซอร์โคเนตไททาเนตและบิสมาลไธเดียมไททาเนต ซึ่งพบว่า ในกรณีของเลดแลนทานัมเซอร์โคเนตไททาเนตนั้น เซรามิกที่ถูกเจือด้วยทั้งสแตนซึ่งถือว่าเป็นตัวให้จะมีลักษณะของเซรามิกที่ดีที่สุดโดยดูจากลักษณะของเกรนที่ค่อนข้างสมบูรณ์และเรียงชิดติดกัน รวมถึงมีความหนาแน่นโดยเฉลี่ยสูงกว่าในกรณีของเหล็กและอะลูมิเนียม ในวัสดุเลดแลนทานัมเซอร์โคเนตไททาเนต การเจือด้วยตัวให้อาจจะไปเสริมตัวให้ที่มีอยู่แล้วคือแลนทานัมทำให้เกิดเป็นเซรามิกที่ค่อนข้างสมบูรณ์ อย่างไรก็ตาม จากภาพถ่ายกล้องจุลทรรศน์แสง พบว่าเซรามิกที่ได้ยังไม่มี ความโปร่งใส ซึ่งอาจจะมีสาเหตุมาจากสภาวะในการเผายังไม่เหมาะสมจึงอาจจะต้องมีการศึกษาเพิ่มเติม

สำหรับในส่วนของบิสมาลไธเดียมไททาเนตนั้น พบว่าการเจือด้วยเซอร์โคเนียมทำให้มีความหนาแน่นลดลงและมีการกระจายตัวของขนาดเกรนกว้างขึ้น ส่วนการเติมไดสโพรเซียมนั้น ทำให้เกรนมีขนาดเล็กลงแต่ก็ทำให้ความหนาแน่นลดลงเช่นกัน สำหรับในกรณีของเหล็ก ทองแดงและสังกะสีซึ่งถือว่าเป็นตัวรับทั้งหมด จะให้ผลไปในทิศทางเดียวกัน นั่นคือ สามารถทำให้เซรามิกบิสมาลไธเดียมไททาเนตถูกเผากลายเป็นเซรามิกมีความหนาแน่นสูงและเกรนใหญ่โดยใช้อุณหภูมิซินเตอร์ต่ำได้ ดังนั้นในการผลิตเซรามิกดังกล่าว สารเจือที่เป็นตัวรับจึงสามารถถูกนำมาใช้ปรับปรุงกระบวนการผลิตเซรามิกบิสมาลไธเดียมไททาเนตได้

5.2 ข้อเสนอแนะ

เนื่องจากการวิจัยยังไม่ครอบคลุมถึงสารเจือทั้งหมดที่สามารถนำมาใช้ปรับปรุงกระบวนการผลิตได้ จึงต้องมีการศึกษาค้นคว้าต่อไปถึงกลไกของการที่สารเจือชนิดใดชนิดหนึ่งสามารถช่วยให้เซรามิกมีการแน่นตัวที่ดีขึ้น กลไกดังกล่าวจะเป็นข้อมูลสำคัญที่สามารถนำไปประยุกต์ใช้ต่อไปได้จริงในอุตสาหกรรมเซรามิกได้ในอนาคตได้

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Output จากโครงการวิจัยที่ได้รับทุนจาก สกอ. และ สกว.

1. ผลงานตีพิมพ์ในวารสารวิชาการนานาชาติ

- 1.1 A. Watcharapasorn, S. Jiansirisomboon, T. Tunkasiri, Sintering of Fe-doped $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ at $< 1000\text{ }^{\circ}\text{C}$, Materials Letters 61 (2007) 2986-2989. Impact factor = 1.625.
- 1.2 A. Watcharapasorn, S. Jiansirisomboon, Grain growth kinetics in Dy-doped BNT ceramics, Ceramics International 34 (2008) 769-772. Impact factor = 1.360.

2. การนำผลงานไปใช้ประโยชน์

- 2.1 สามารถสร้างงานวิจัยใหม่ที่น่าสนใจและช่วยให้เกิดการพัฒนาการวิจัยด้านวัสดุเฟอร์โรอิเล็กทริกเซรามิกในประเทศไทยได้
- 2.2 สามารถใช้งานวิจัยนี้เป็นส่วนหนึ่งของการเรียนการสอนในสาขาวิชาวัสดุศาสตร์ ภาควิชาฟิสิกส์ คณะวิทยาศาสตร์ มหาวิทยาลัยเชียงใหม่
- 2.3 สามารถผลิตผลงานวิจัยเพื่อนำเสนอและแลกเปลี่ยนผลงานวิจัยในการประชุมวิชาการในระดับชาติและนานาชาติได้
- 2.4 สามารถผลิตบัณฑิตในระดับปริญญาตรี เป็นจำนวน 4 คน ภายในระยะเวลาสองปีที่ผ่านมาในโครงการ
- 2.5 การสร้างเครือข่ายและความร่วมมือในการทำวิจัยกับคณาจารย์และนักวิจัยภายในสถาบันและหน่วยงานต่างๆนอกสถาบันได้

3. การนำผลงานไปใช้ประโยชน์ด้านอื่นๆ

- 3.1 ได้นำเสนอในการประชุมวิชาการนาโนเทคโนโลยีแห่งประเทศไทย ครั้งที่ 1 เรื่อง วัสดุนาโน แก๊ส ทัศนศาสตร์ อุปกรณ์ และการประยุกต์ใช้ ณ โรงแรมเซ็นทรัลพลาซ่า ดะวัน จัหวัดเชียงใหม่ 14-16 สิงหาคม 2550

Anucha Watcharapasorn and Sukanda Jiansirisomboon ในหัวข้อเรื่อง Effects of Al_2O_3 Nano-particle Addition on Electrical and Mechanical Properties of PLZT Ceramics.

- 3.2 ได้นำเสนอในการประชุมวิชาการ International Conference on Smart Materials: Smart/Intelligent Materials and Nanotechnology and 2nd International Workshop on Functional Materials and Nanomaterials, Chiang Mai, Thailand, 22-25 April 2008

A. Watcharapasorn and S. Jiansirisomboon ในหัวข้อเรื่อง Dielectric and Piezoelectric Properties of Zr-doped Bismuth Sodium Titanate Ceramics

ภาคผนวก



Sintering of Fe-doped $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ at $<1000^\circ\text{C}$

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Abstract

Fe-doped $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ ceramics with Fe-ion content varied from 0 to 0.15 at.% were successfully prepared by conventional solid state reaction method. The sintering temperature used was between 850 and 1000 °C. X-ray diffraction patterns showed that all produced ceramics were single phase with a rhombohedral structure. SEM micrographs of the ceramics showed a dramatic change in densification behavior as a result of Fe-ion doping. At 850 °C, the undoped BNT ceramic had a very porous structure. As the Fe-ion concentration increased, the ceramics showed denser microstructures and, for the sample containing 0.15 at.% Fe, a very dense grain structure with almost no porosity was obtained. This microstructural observation agreed well with the measured density whose value increased with increasing Fe content. The relative density of at least 95% was achieved in 0.15 at.% Fe-doped BNT ceramics even when it was sintered at 850 °C. Increasing the sintering temperature only had an effect of increasing the grain size of this sample without appreciably affecting its density. The results of this investigation showed that addition of Fe_2O_3 in BNT could help improve the densification process and significantly reduced the sintering temperature of BNT ceramics.

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Keywords: Bismuth sodium titanate; Sintering; Microstructure; Ceramics; Defects

1. Introduction

In ceramic processing, the use of low sintering temperature is often desired. Apart from energy cost consideration, the lower the sintering temperature, the closer stoichiometric or nominal composition the produced ceramics will have. This is because at high temperature the presence of intrinsic point defects as well as the loss of volatile compounds usually occur.

Consequently, various techniques have been utilized in order to lower the sintering temperature and improve the densification process of ceramics. These include the use of non-conventional sintering processes such as spark plasma sintering [1] and microwave sintering [2]. Other processes such as multi-step sintering and heating [3,4] and reactive sintering [5] were also employed. These methods, though found very effective in producing high-density ceramics, involve a rather complicated experimental set up and/or need longer processing time than conventional single-step firing process. An alternative method

is to fabricate ceramics by utilizing fine particles in sub-micrometer or nanometer range that are produced by high-energy ball milling or some chemical routes [1,6]. The former has some risk of contamination from milling media while the latter still faces the problem of mass production capability.

One method that has been utilized the most to lower the sintering temperature is to use sintering aid which can be in the form of a single compound (e.g. B_2O_3 , LiF, LiCO_3 , MnO_2 , CaF_2) or mixture of these compounds [7–13], glassy phase (e.g. $\text{PbO} + \text{SiO}_2$) [14] and complex oxides (e.g. $\text{Pb}(\text{Yb}_{1/2}\text{Nb}_{1/2})\text{O}_3$ – PbTiO_3 – PbZrO_3 system) [15]. The purpose of these sintering aids is to provide a low melting point material where liquid phase can form along the grain boundaries of the ceramics and, hence, help promote atomic diffusion. However, it is often found that the presence of the low melting temperature phase along grain boundaries degrade the properties of materials.

Apart from these methods, one can add a small amount of aliovalent dopant that substitutes ions in the lattice sites in ionic compounds to produce point defect such as vacancies that can help promote diffusion during sintering. Notable for this effect is the oxygen vacancies whose number can be increased by

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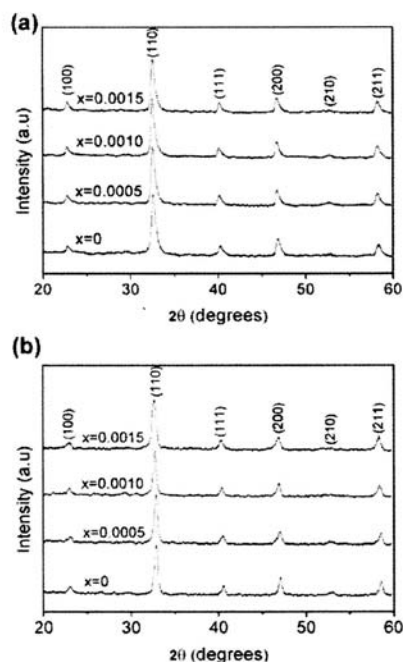


Fig. 1. X-ray diffraction patterns of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{Ti}_{1-x}\text{Fe}_x\text{O}_{3-0.5x}$: (a) calcined powders and (b) ceramics sintered at 1000 °C.

introducing an acceptor dopant to substitute for cations [16,17]. Based on this defect chemistry, this paper attempts to investigate the effect of doping Fe ions into $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT) compound, which is currently considered as a potential lead-free ferroelectric material [18–20]. The phase formation, microstructure and density of Fe-doped BNT ceramics in relation with sintering temperature are presented and discussed.

2. Experimental procedure

Fe-doped $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ powders were prepared from binary oxides and carbonate, i.e. Bi_2O_3 (>98%, Fluka), Na_2CO_3 (99.5%, Carlo Erba), TiO_2 (>99%, Riedel-de Haën) and Fe_2O_3 (99.9%, Fluka). The amount of Fe_2O_3 varied from 0 to 0.075 mol%. This corresponds to the nominal composition, $\text{Bi}_{0.5}\text{Na}_{0.5}\text{Ti}_{1-x}\text{Fe}_x\text{O}_{3-0.5x}$, where x varied from 0 to 0.0015. The powder mixtures were ball milled in ethanol using zirconia milling media for 24 h, calcined at 800 °C for 2 h, and checked for phase purity using a powder X-ray diffractometer (XRD, JEOL JDX-8030). The calcined powders were re-ground using agate mortar and pestle, sieved, pressed into small pellets and sintered at temperature ranging between 850 and 1000 °C for 2 h and re-checked for phase purity using X-ray diffraction technique. The sintered ceramics were characterized for their

densities using Archimedes method and the surface morphologies were studied using a scanning electron microscope (JEOL JSM-5910LV).

3. Results and discussion

X-ray diffraction patterns of undoped and Fe-doped BNT powders are shown in Fig. 1(a). The materials were single phase with a rhombohedral structure, in agreement with the patterns reported in the literature [21,22]. The relative peak intensities in all samples were virtually the same which suggested that the presence of small amount of Fe ions in BNT lattice did not cause any significant change in crystal structure. Investigation of peak position indicated a very small peak shift to lower angle for all reflections. Assuming the rhombohedral symmetry and using the peak positions of (200) reflections, the lattice constants of all samples were approximated and listed in Table 1. X-ray diffraction patterns of undoped and Fe-doped BNT ceramics sintered at various temperatures were virtually the same as their corresponding powder patterns. Fig. 1(b) showed X-ray diffraction patterns of the ceramic samples sintered at 1000 °C.

SEM micrographs of undoped and Fe-doped BNT ceramics sintered at 850 °C are shown in Fig. 2. It can be noticed that, in undoped BNT ceramics, the surface morphologies showed a very porous structure. As the amount of Fe concentration in BNT lattice increased, the structure became more dense and a well developed grain morphology with almost no porosity was finally obtained in BNT ceramics doped with 0.15 at.% Fe. Increasing the sintering temperature had the effect of enhancing the densification in low-density samples while for the 0.15 at.% Fe-doped BNT ceramics, the only observed effect was a slight increase in grain size.

The resulting microstructures of these ceramics were in good agreement with their measured densities. From Fig. 3, the undoped BNT ceramics possessed lowest density among all samples. At 850 °C, the sample was so porous that its density could not be measured using the Archimedes method. Increasing the sintering temperature caused the sample to be better densified and therefore to possess higher density. As the amount of Fe increased, the density of the ceramics increased and became less dependent on sintering temperature. Eventually, the samples with highest Fe concentration had about the same density regardless of their sintering temperature. The highest measured density corresponded to about 95% of the theoretical value. Based on these results, the Fe-doped BNT ceramics apparently could be sintered at a much lower temperature than typical sintering temperatures, which ranged between 1050 and 1200 °C [21–24].

This densification behavior may be explained in terms of defect chemistry and the creation of oxygen vacancies. As it has been known theoretically and experimentally that the number of vacancies generally increase with increasing temperature and therefore, allows better atomic diffusion during the sintering process. At a lower temperature, the number of these vacancies is reduced and the ability for atoms to diffuse is also less. The creation of vacancies by using dopant is therefore thought to have some benefit in sintering process. For the

Table 1
Peak position of (200) reflections and determined lattice constants

	BNT	0.05 at.% Fe	0.10 at.% Fe	0.15 at.% Fe
Position of (200) reflection (°)	46.801	46.761	46.701	46.739
Lattice constant (Å)	3.8792	3.8823	3.8870	3.8840

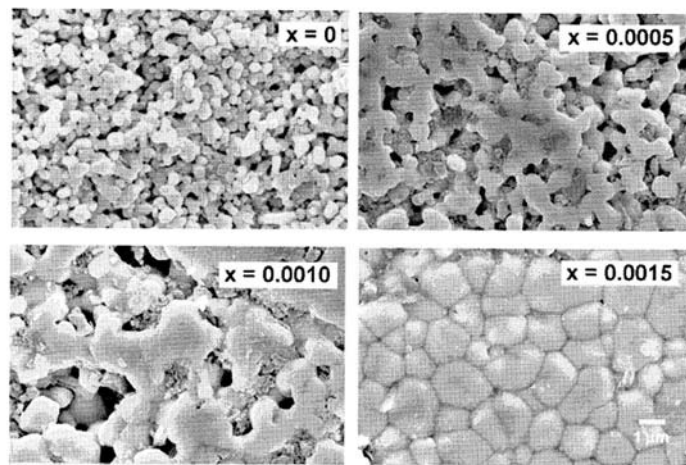


Fig. 2. SEM micrographs of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{Ti}_{1-x}\text{Fe}_{2x}\text{O}_{3-0.5x}$ ceramics sintered at 850 °C.

system under investigation, the defect equation could be written as the following:



It has to be noted that the above defect reaction only assumed ionic defect compensation. In addition, it was assumed that Fe ions preferentially substituted Ti sites. The latter assumption was based on the fact that the ionic radius of Fe ion ($r_{\text{Fe}^{3+}} = 0.69 \text{ \AA}$) was much closer to the ionic radius of Ti ion ($r_{\text{Ti}^{4+}} = 0.61 \text{ \AA}$) than those of Bi ion ($r_{\text{Bi}^{3+}} \sim 1.38 \text{ \AA}$) and Na ion ($r_{\text{Na}^{+}} = 1.39 \text{ \AA}$). Furthermore, the ratio of cationic radius to anionic radius ($r_{\text{O}^{2-}} = 1.40 \text{ \AA}$) would exclude the Fe ion from residing at the Bi or Na site due to the instability of the structure [17]. Based on the nominal charge of Fe^{3+} , the amount of oxygen vacancies could be approximated from this equation and it obviously increased with increasing amount of Fe^{3+} ions substituting Ti^{4+} sites.

Although exact mechanisms involved in the sintering behavior of Fe-doped BNT ceramics still needs further investigation, this study

clearly showed that the addition of small amount of Fe_2O_3 in $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ during synthesis based on the defect Eq. (1) could significantly improve the densification of the ceramics and the sintering temperature as low as 850 °C could be used to sinter this ceramic to a near theoretical value.

4. Conclusions

Fe-doped $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ ceramics were successfully prepared using the conventional method with the starting compositions based on defect chemistry consideration. SEM micrographs of the undoped BNT ceramics sintered at 850 °C showed a rather porous structure. Increasing the amount of Fe ions in BNT lattice caused the BNT ceramics to be better densified, and in the sample containing 0.15 at.% Fe, a very dense grain morphology with nearly no porosity was obtained. The well developed grain structure in 0.15 at.% Fe-doped BNT ceramics also agreed with its measured density which was found to be at least 95% of the theoretical value. This experiment clearly showed that the presence of Fe^{3+} acceptor ions which induced the oxygen vacancies in BNT lattice helped promote the densification process and dramatically reduced the sintering temperature used in BNT ceramic processing.

Acknowledgements

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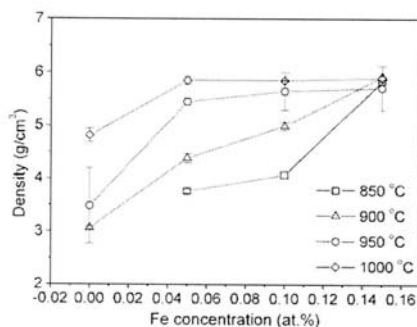


Fig. 3. Density variation of Fe-doped BNT ceramics as a function of Fe concentration and sintering temperature.

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Grain growth kinetics in Dy-doped $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ ceramics

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Abstract

Dysprosium-doped bismuth sodium titanate ceramics were prepared using the conventional mixed-oxide method. The amount of dysprosium used was varied from 0 to 2 at.%. The mixed powders were calcined at 800 °C and checked for phase purity using X-ray diffraction technique. The calcined powders were then cold-pressed into pellets and sintered at 1050 °C for the time ranging from 2 to 48 h. The ceramics were checked for phases and microstructures using an X-ray diffractometer and a scanning electron microscope, respectively. The analysis showed that undoped BNT ceramics sintered at longer time exhibited a significant grain growth with non-uniform grain size distribution and shape. The Dy-doped BNT however showed a much more limited grain growth behavior, resulting in smaller grain size and more equiaxed grain shape. It was also found that all Dy-doped BNT ceramics sintered at 48 h possessed lower porosity than those sintered for shorter time.

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Keywords: A. Grain growth; A. Sintering; B. Electron microscopy; B. Defects

1. Introduction

Bismuth sodium titanate ($\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ or BNT) is currently considered as a potential lead-free ferroelectric material [1–3]. Although this material has been investigated in terms of variation in their dielectric and piezoelectric properties due to various dopants [4–6] and the formation of solid solution with other compounds [7–9], the studies on grain growth behavior of pure and doped BNT has not been studied much.

Yi et al. [10] has investigated the microstructure of lanthanum-doped BNT and it was found that the substitution of La^{3+} ions in the A-site (Bi^{3+} or Na^+ ions), inducing A-site vacancies, resulted in grain growth inhibition as well as improvement of densification. Based on the study of aliovalent doping in BaTiO_3 by Desu and Payne [11] and Rahaman and Manalert [12], similar reduction in grain boundary mobility was observed regardless of whether the dopants were donors or acceptors if their concentration was above the threshold values. The effects of these dopants were attributed to the segregation of cation vacancies as well as acceptor solutes at the grain boundaries in which the space-charge region was induced and this limited the movement of grain boundaries [12].

Furthermore, Yi et al. [10] found that the inhibition of grain growth was much more effective when La^{3+} ions substituted the A-site of BNT, inducing the B-site vacancies. The substitution at A-site of BNT by Pb^{2+} ions was also found to have the same effect as other previously mentioned dopants [8].

Besides La^{3+} and Pb^{2+} , the dysprosium ion was also used to dope BaTiO_3 and it was found that it also caused a reduction in grain growth. Unlike La^{3+} and Pb^{2+} , Dy ion could substitute either A-site or B-site [13,14] and this seemed to suggest a complex role in densification and grain growth behavior of ceramics. In this study, Dy-doped BNT ceramics are prepared and their grain growth behavior is investigated in order to provide some insight in terms of dopant substitution and its effects on grain morphology.

2. Experimental procedure

The Dy-doped BNT powders were prepared from the mixed powder of Bi_2O_3 (>98%, Fluka), Na_2CO_3 (99.5%, Carlo Erba), TiO_2 (>99%, Riedel-de Haën) and Dy_2O_3 (99.9%, Cerac). The amount of Dy_2O_3 used was calculated according to the chemical formula $(\text{Bi}_{0.5}\text{Na}_{0.5})_{1-1.5x}\text{Dy}_x\text{TiO}_3$, where $x = 0.005, 0.010, 0.015$ and 0.020 . The starting powder mixtures were ball milled for 24 h, calcined at 800 °C for 2 h, and checked for phase purity using a powder X-ray diffractometer (Siemens D500). The calcined powders were then ball milled for another

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24 h and pressed into small pellets, which were subsequently sintered at 1050 °C for 2, 10, 24 and 48 h in a presence of BNT powder. X-ray diffraction analysis was performed on these samples to re-check for phase purity. The ceramic samples were then polished and thermally etched at 950 °C for 15 min prior to microstructural investigation using a scanning electron microscope (JEOL JSM-5910LV). The grain size was measured from the SEM micrographs using a mean linear intercept method.

3. Results and discussion

X-ray diffraction patterns of Dy-doped BNT ceramics sintered at 1050 °C for 2 and 48 h are shown in Fig. 1. The results showed that all ceramic samples were virtually single phase with rhombohedral structure. The peak splitting due to rhombohedral symmetry was difficult to observed in this compound since peak overlapping occurred and it was known that its lattice dimension was nearly cubic [1]. As the Dy concentration increased, there was a slight shift of peaks to greater 2θ angle corresponding to smaller lattice size. This seemed to indicate that the substitution of smaller Dy^{3+} ion ($r_{\text{Dy}^{3+}} \sim 1.2 \text{ \AA}$) in larger Bi^{3+} ion ($r_{\text{Bi}^{3+}} \sim 1.38 \text{ \AA}$) or Na^+ ion ($r_{\text{Na}^+} \sim 1.39 \text{ \AA}$) occurred during synthesis.

SEM micrographs of Dy-doped BNT ceramics sintered at 1050 °C for 2 h are shown in Fig. 2. The micrographs showed that the grain size generally decreased when Dy content was increased. The grain size values ranged from about 3.2 μm in pure BNT to about 0.8 μm in 2.0 at.% Dy-doped BNT. For these ceramics, a rather wide grain size distribution could be observed from the figure and in this study, the standard deviation (S.D.) from grain size measurement was used to represent the distribution. The S.D. for pure BNT was about 1.3 while that for 2.0 at.% Dy-doped sample was about 0.3. The grain size as well as the standard deviation for these two samples were also plotted and are shown in Fig. 4 (note that all samples had a range of grain size with their corresponding S.D.'s but were omitted from Fig. 4 for clarity in comparison). The general trend was that the standard deviation decreased with increasing Dy content. This indicated that not only was the grain size reduced but the grain size distribution also decreased,

suggesting a more uniform grain size in the samples containing high Dy concentration.

It could also be seen from Fig. 2 that the porosity increased with increasing Dy concentration. This observation was in agreement with the slightly higher measured density of pure BNT compared to Dy-doped BNT ceramics. Nevertheless, all samples were found to have densities of at least about 95% of their theoretical values. The effect of Dy ions in a reduction of grain size but with a somewhat non-uniform grain size distribution was observed by Yamaji et al. for BaTiO_3 system [15]. The authors attributed this observation to the original particle size prior to sintering and they also found that a use of fine starting BaTiO_3 powder having the size in nanometer range could produced Dy-doped BaTiO_3 ceramics having small grains with narrower size distribution [16]. Since the average starting particle size for powders used in this study was about 0.3 μm , these were probably not small enough to allow uniform distribution of Dy ions.

After increasing the sintering time to 10, 24 and 48 h, the grain sizes of all samples increased. SEM micrographs of ceramic samples sintered for 48 h are shown in Fig. 3. In pure BNT and lowly doped samples, the grain size increased such that some grains grew faster than other grains which resulted in the presence of very large grains as well as very small grains and, hence, a wider grain size distribution. From grain size measurement, it was found that the pure BNT ceramic sintered for 48 h contained grains as small as 0.7 μm and grains as large as 14.2 μm . At such long sintering time, the effect of grain growth inhibition was more pronounced for 2.0% Dy-doped BNT ceramics and, hence, resulting in narrower grain size distribution. The 2.0% Dy-doped BNT ceramics sintered for 48 h contained grains having minimum size of $\sim 0.5 \mu\text{m}$ and maximum size of $\sim 8.7 \mu\text{m}$. It could also be noticed from Fig. 3 that all Dy-doped samples showed denser microstructures when sintered at longer time.

The effects of sintering time on grain size and grain size distribution for all pure and Dy-doped BNT ceramics investigated are summarized in Fig. 4. It could be seen that regardless of sintering time, the 2.0 at.% Dy-doped samples had the smallest grain size compared to the rest of samples. The

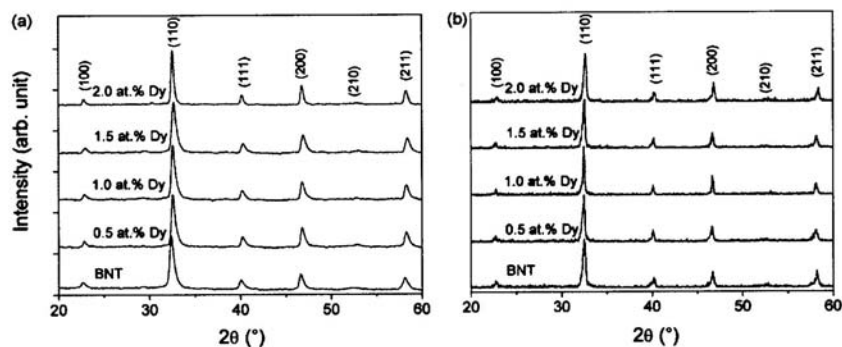


Fig. 1. XRD patterns of Dy-doped BNT ceramics sintered at 1050 °C for (a) 2 h and (b) 48 h.

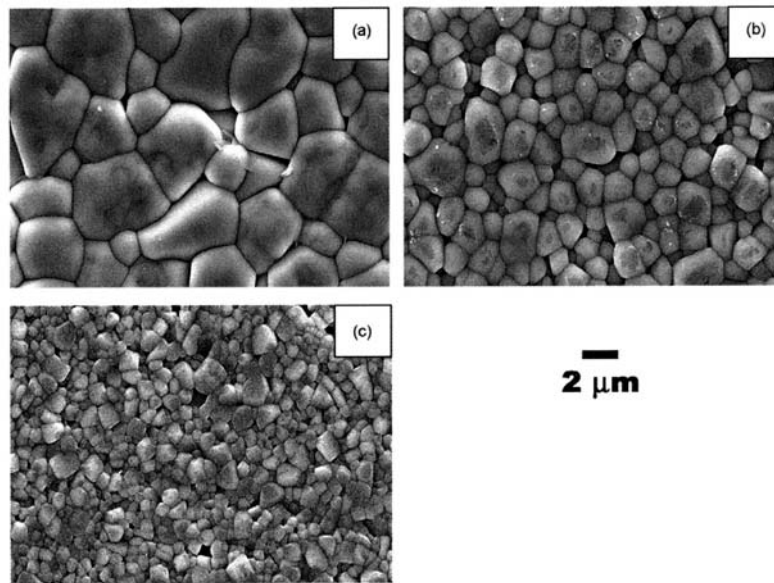


Fig. 2. SEM micrographs of Dy-doped BNT ceramics sintered at 1050 °C for 2 h: (a) 0 at.%, (b) 1.0 at.% and (c) 2.0 at.%.

error bars for samples sintered as 2 and 48 h indicated the standard deviation from grain size measurement. These rather large standard deviations indicated that, for all samples, the grain growth was not truly uniform. Therefore, the study on the rate of increase in grain size in order to determine the effect of Dy ions on grain boundary mobility was difficult. Comparing to

the work by Yi et al. [10], it seemed that doping BNT with La ions were more effective in producing ceramics with uniform grain size and hence, grain growth kinetics based on grain growth law could be studied in details.

From this study, it has been shown that addition of Dy ions into BNT lattice could inhibit grain growth but the

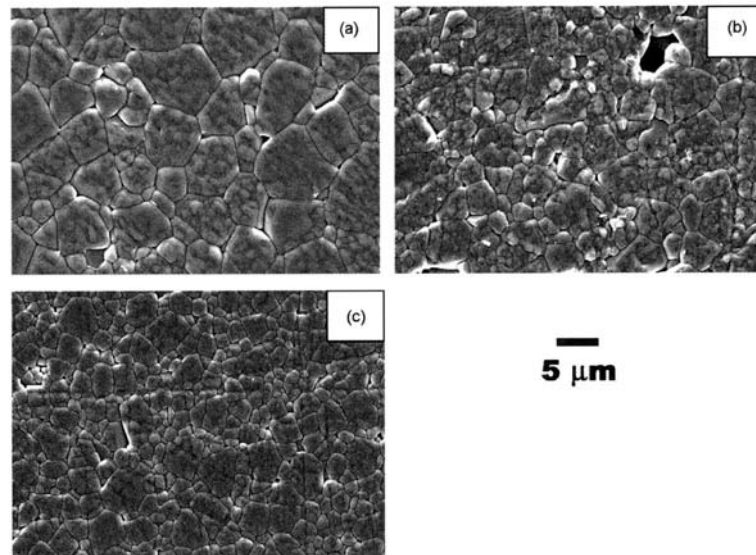


Fig. 3. SEM micrographs of Dy-doped BNT ceramics sintered at 1050 °C for 48 h: (a) 0 at.%, (b) 1.0 at.% and (c) 2.0 at.%.

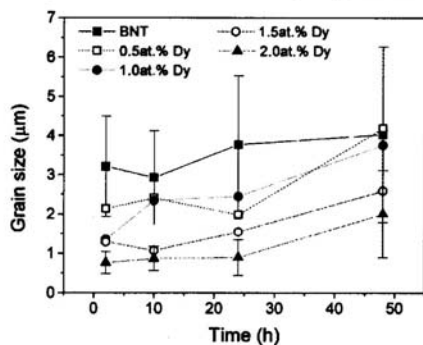


Fig. 4. The change in grain size as a function of sintering time for Dy-doped BNT ceramics. The error bars for pure BNT and 2.0 at.% Dy-doped sample corresponded to the standard deviation from grain size measurement.

distribution of Dy ions was not uniform and for longer sintering time, some of the grains grew faster and consumed smaller grains. The final microstructures for all samples therefore consisted of a range of grain size although a narrower grain size distribution was observed in BNT ceramics doped with higher Dy concentration.

4. Conclusions

Dy-doped BNT ceramics having nominal compositions $(\text{Bi}_{0.5}\text{Na}_{0.5})_{1-1.5x}\text{Dy}_x\text{TiO}_3$, where $x = 0.005, 0.010, 0.015$ and 0.020 , were successfully prepared by solid state reaction. X-ray analysis of ceramics sintered at 1050°C for various time up to 48 h showed that the materials were virtually single phase with small shift in peak positions to the right which indicated that the smaller Dy ions substituted the larger A-site ions. Based on microstructural investigation, increasing sintering time caused grains of BNT ceramics to grow inhomogeneously and result in a wide grain size distribution. Addition of Dy ions into BNT lattice resulted in grain growth inhibition for all sintering time especially for the samples containing 2.0 at.% Dy. However, the observed grain size variation in Dy-doped BNT ceramics indicated a rather non-uniform distribution of Dy ions in the powder mixture during material synthesis. It is expected that further increase in Dy concentration and/or using nano-sized starting powders could produce Dy-doped BNT ceramics with more uniform grain size.

Acknowledgements

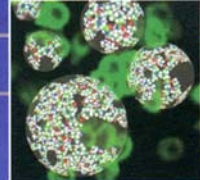
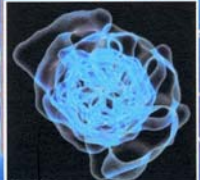
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Effects of Al₂O₃ Nano-particle Addition on Electrical and Mechanical Properties of PLZT Ceramics

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ABSTRACT

PLZT (9/65/35) ceramics with addition of 0-2 vol% γ -Al₂O₃ nano-particles (~40 nm) were sintered at various temperature ranging from 1100-1250 °C. X-ray diffraction analysis of these ceramics indicated that they were single phase with cubic structure. At sintering temperature of 1100 and 1150 °C, the density of PLZT/Al₂O₃ ceramics decreased with increasing Al₂O₃ content. At higher sintering temperatures, the ceramics were densified to at least 95% of their theoretical densities regardless of Al₂O₃ content. The samples sintered at 1200 °C were used for mechanical and electrical property measurements. It was found that the Knoop and Vickers hardness values were improved with addition of Al₂O₃ nano-particles up to 1.0 vol% at which the Young's modulus was also optimized. The fracture toughness was also found to be improved with increasing amount of Al₂O₃ especially at higher applied mechanical load. The dielectric constant and dielectric loss at 1 kHz of 0.5 vol% Al₂O₃ added PLZT ceramics were found to be about 4000 and 0.04, respectively. These values were comparable to those of pure PLZT. The ferroelectric measurements of PLZT/Al₂O₃ ceramics indicated that all samples showed similar hysteresis behavior with comparable values of remanent polarization and coercive field. These results suggested that small addition of Al₂O₃ nano-particles could improve mechanical properties while maintain good electrical properties of PLZT ceramics.

Key words: PLZT, Al₂O₃ nano-particles, Mechanical, Dielectric, Ferroelectric properties

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Dielectric and Piezoelectric Properties of Zr-doped Bismuth Sodium Titanate Ceramics

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$\text{Bi}_{0.5}\text{Na}_{0.5}\text{Ti}_{1-x}\text{Zr}_x\text{O}_3$, where $x = 0, 0.05, 0.10, 0.15$ and 0.20 , were prepared by solid state reaction between stoichiometric mixture of Bi_2O_3 , Na_2CO_3 , TiO_2 and ZrO_2 powders. The mixture was calcined at 800°C for 2 h and checked for phase purity using X-ray diffraction analysis. The calcined powders were pressed into pellets and sintered at 1100°C for 2 h to form dense ceramics. These ceramics were re-checked for second phases using X-ray diffraction analysis. It was found that single phase solid solution could be produced, indicating that high solid solubility limit is possible for this system. The approximate relative density of all sintered samples was found to be at least 95% of theoretical value. Microstructural investigation using a scanning electron microscope of fractured surface showed that the fracture mode changed from intergranular to intragranular mode when Zr concentration increased. The grain size of these ceramics was found to slightly increase with Zr content. Dielectric properties of Zr-doped BNT ceramics showed more diffused behavior with addition of Zr. However, the piezoelectric properties seemed to be degraded possibly due to the aging effect typically found in isovalent-ion substituted solid solutions. These behaviors were discussed and compared to the more common systems such as PZT and $\text{Ba}(\text{Zr,Ti})\text{O}_3$.