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OUTPUT จากโครงการวิจัยที่ได้รับทุนจาก สกว.

1) ผลงานตีพิมพ์ในวารสารวิชาการนานาชาติ

1.1 S. Ananta and T. Tunkasiri, "Synthesis, Formation and Characterization of Lead Titanate Powders", Submitted to Journal of The European Ceramics Society. (manuscript หมายเลข 1 แสดงในภาคผนวก ก.)

1.2 S. Ananta, R. Tipakontitikul and T. Tunkasiri, "Synthesis, Formation and Characterization of Zirconium Titanate Powders", Submitted to Materials Letters. (manuscript หมายเลข 2 แสดงในภาคผนวก ก.)

1.3 S. Ananta and T. Tunkasiri, "Synthesis, Formation and Characterization of Lead Zirconate (PZ) Powders", Submitted to Materials Letters. (manuscript หมายเลข 3 แสดงในภาคผนวก ก.)

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2) การนำผลงานวิจัยไปใช้ประโยชน์

2.1 เชิงพาณิชย์

ในปัจจุบัน ผลการวิจัยที่ได้รับจากโครงการนี้ได้ถูกนำมาใช้โดยตรงในการผลิตผงสาร PZT ขึ้นใช้เองในห้องปฏิบัติการวิจัยวัสดุศาสตร์ ภาควิชาฟิสิกส์ มหาวิทยาลัยเชียงใหม่ ทำให้สามารถประหยัดงบประมาณในการนำเข้าผง PZT จากต่างประเทศได้ประมาณปีละหลายแสนบาท นอกจากนี้ ทาง ศาสตราจารย์ ดร. ทวี ตันฆศิริ ยังได้ทำการติดต่อเจรจากับทางบริษัทผู้ผลิตและจำหน่ายอุปกรณ์พิโซอิเล็กทริกในประเทศไทย ที่ปัจจุบันนี้ยังต้องนำเข้าสาร PZT จากต่างประเทศอยู่ โดยคาดว่าน่าจะมีหลายบริษัทในประเทศไทยที่สนใจ หากมีการเผยแพร่ผลงานวิจัยนี้ให้กว้างขวางยิ่งขึ้น

2.2 **เชิงนโยบาย**

กระบวนการดำเนินการวิจัย และผลการวิจัยที่ได้จากโครงการนี้ได้ถูกนำไปใช้ในการกำหนดแนวนโยบายในการทำงานวิจัย รวมถึงทิศทางในการดำเนินงานวิจัย ของห้องปฏิบัติการวิจัยวัสดุศาสตร์ ภาควิชาฟิสิกส์ มหาวิทยาลัยเชียงใหม่ ที่ชัดเจนขึ้น มีการวางแผนการสร้างงานวิจัยแบบต่อเนื่อง ระยะยาว การวางแผนด้านงบประมาณ ครุภัณฑ์ที่เกี่ยวข้อง และบุคลากรสนับสนุน (โดยเฉพาะอย่างยิ่งการกำหนดแผนการรับนักศึกษาในระดับต่างๆ เข้ามาร่วมทีมวิจัย) ในการพัฒนาวัสดุพิโซอิเล็กทริกที่เป็นรูปธรรมอย่างชัดเจนขึ้นโดยลำดับ

2.3 **เชิงสาธารณะ**

โครงการวิจัยนี้ได้ก่อให้เกิดเครือข่ายความร่วมมือในการวิจัยและพัฒนาวัสดุพิโซอิเล็กทริกในแง่มุมต่างๆ ขึ้น อาทิเช่น

- การจัดตั้งกลุ่มนักวิจัยรุ่นใหม่ในนามห้องปฏิบัติการวิจัยเซรามิกขั้นสูงขึ้น ที่คณะวิทยาศาสตร์ มหาวิทยาลัยเชียงใหม่ เมื่อเดือนเมษายนที่ผ่านมา โดยมีวัตถุประสงค์หลักในการศึกษาวิจัยและพัฒนาเซรามิกขั้นสูง โดยเฉพาะอย่างยิ่งวัสดุในกลุ่ม Smart materials ที่หนึ่งในนั้นก็คือ PZT

- การสร้างเครือข่ายความร่วมมือกับกลุ่มวิจัยของ ผศ.ดร. ศุภสโรช หมื่นสิทธิ์ ภาควิชาฟิสิกส์ คณะวิทยาศาสตร์ มหาวิทยาลัยสงขลานครินทร์ โดยมีการแลกเปลี่ยนนักศึกษาระดับบัณฑิตศึกษาในช่วงภาคฤดูร้อน เพื่อถ่ายทอดเทคโนโลยี การพัฒนาวัสดุพิโซอิเล็กทริกร่วมกัน

- การสร้างเครือข่ายความร่วมมือกับกลุ่มวิจัยของ ดร. อนุสรณ์ นิยมพันธ์ ภาควิชาฟิสิกส์ คณะวิทยาศาสตร์ มหาวิทยาลัยอุบลราชธานี ในการทำวิจัย และพัฒนาการวิเคราะห์พฤติกรรมการก่อเกิดเฟสของสารเพอรอฟสไกต์ ด้วยเทคนิค DTA และเทคนิค XRD

2.4 **เชิงวิชาการ**

- **การพัฒนาการเรียนการสอน**

กระบวนการในการดำเนินงานและผลงานที่ได้จากโครงการวิจัยนี้ได้ถูกนำมาใช้ในการพัฒนาเนื้อหาในการเรียนการสอนของกระบวนวิชา MATS 210723 Ferroelectric Materials และกระบวนวิชา MATS 210703 Fabrication Process of Materials และนอกจากนี้ยังได้นำส่วนของวิธีการวิเคราะห์ผลการทดลอง ไปใช้เป็นกรณีศึกษาประกอบการบรรยายในกระบวนวิชา MATS 210701 Characterisation and Properties of Materials และกระบวนวิชา PHYS 207743 X-ray Crystallography I สำหรับนักศึกษาระดับบัณฑิตศึกษาทั้งในสาขา

วิชาวัสดุศาสตร์ สาขาวิชาฟิสิกส์ และสาขาวิชาฟิสิกส์ประยุกต์ ของภาควิชาฟิสิกส์ คณะวิทยาศาสตร์ มหาวิทยาลัยเชียงใหม่ ตลอดระยะเวลา 2 ปีที่ผ่านมา

- **การสร้างนักวิจัยใหม่**

โครงการวิจัยนี้ได้ช่วยสร้างโอกาสให้แก่นักวิจัยใหม่ซึ่งเป็นนักศึกษาในระดับปริญญาตรี และในระดับบัณฑิตศึกษา ได้ฝึกฝนทักษะในการดำเนินการวิจัยทางวิทยาศาสตร์ ในฐานะของผู้ช่วยวิจัยร่วมกับหัวหน้าโครงการ และเจ้าหน้าที่ในหน่วยงานที่เกี่ยวข้อง นอกจากนี้พวกเขายังได้รับการฝึกฝนประสบการณ์ในการวางแผนงานวิจัย การทำงานร่วมกันเป็นทีม การเขียนบทความทางวิชาการ และการนำเสนอผลงานในที่ประชุมวิชาการต่างๆ ตลอดช่วงระยะเวลา 2 ปีที่ผ่านมาอีกด้วย ซึ่งในปัจจุบันนักศึกษาหลายท่านก็ได้มีโอกาสนำประสบการณ์และแนวทางในการทำวิจัยจากโครงการวิจัยนี้ไปใช้ในการศึกษาต่อในระดับปริญญาชั้นสูง ทั้งในระดับปริญญาโทและเอก ในสถาบันต่างๆ ดังเช่น รายชื่อปรากฏร่วมอยู่ในผลงานทางวิชาการที่ได้นำเสนอเอาไว้แล้วในภาคผนวก

นอกจากนี้ผลการวิจัยที่ได้จากโครงการนี้ยังได้ถูกนำไปใช้เป็นรากฐานในการร่างโครงการวิจัยของคณาจารย์ใหม่ที่พึ่งสำเร็จการศึกษาในระดับปริญญาเอกจากต่างประเทศ และมีความประสงค์ที่จะทำงานวิจัยร่วมกันเป็นทีม เพื่อพัฒนาให้เกิดโครงการวิจัยแบบต่อเนื่องที่เป็นรูปธรรม และนำไปสู่ประโยชน์ในแง่มุมที่กว้างขวางมากยิ่งขึ้น อาทิเช่น โครงการวิจัยของ ดร.รัตติกร ยิ้มนิรัญ ดร.สุกานดา เจียรศิริสมบูรณ์ และ ดร.อานนท์ ชัยพานิช ซึ่งกำลังจะได้รับการสนับสนุนจากทาง สกว. ในปี พ.ศ. 2545 นี้ โดยคณาจารย์เหล่านี้จะใช้เงื่อนไขที่ดีที่สุดที่ได้จากผลการวิจัยในโครงการนี้ในการเตรียมชิ้นงานตัวอย่างเพื่อศึกษาในประเด็นเฉพาะทางของแต่ละโครงการต่อไป

3) อื่นๆ

3.1 การเสนอผลงานในที่ประชุมวิชาการนานาชาติ

1. J. Tontrakoon, A. Udomporn, S. Ananta and T. Tunkasiri, "Effect of Firing Temperatures on Morphology of Mixed Oxide $PbTiO_3$ Powders by Solid State Reaction", J.E.M.S.T. 2001, **15**(suppl.) 125-126.
2. W. Thamjaree, S. Ananta and T. Tunkasiri, "SEM and XRD Studies on PZT Powders Prepared by Using $PbZrO_3$ and $PbTiO_3$ Precursors", J.E.M.S.T. 2001, **15**(suppl.) 131-132.

3. S. Ananta and R. Tipakontitikul, "Lead Zirconate Titanate Powders Derived from A Modified Solid-State Reaction Technique", J.E.M.S.T., 2002, **16**(suppl) 107-108.
4. S. Ananta and T. Tunkasiri, "Synthesis and Characterization of Lead Zirconate Titanate Powders from A Modified Two-Stage Mixed Oxide Route", Accepted as poster presentation, 8th International Conference on Ceramic Processing Science (8th ICCPS), Hamburg, Germany (2002) 2-5 Sept..

   * Paper in preparation and shall be submitted to Journal of The European Ceramics Society during the conference.

3.2 การเสนอผลงานในที่ประชุมวิชาการในประเทศ

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2. วันดี ธรรมจารี และ สุพล อนันตา, "ผลของอุณหภูมิแคลไซน์ต่อพฤติกรรมการเกิดเฟสของเลดติตาเนต" The First Thailand Materials Science and Technology Conference, 19-20 กรกฎาคม 2543. กรุงเทพ, 553-555.
3. S. Ananta, W. Thamjaree and T. Tunkasiri, "Phase Analysis of Calcined Lead Titanate Powders By X-ray Diffraction", 26th Congress on Science and Technology of Thailand, Bangkok, (2543) 315.
4. W. Thamjaree, S. Ananta and T. Tunkasiri, X-Ray Diffraction Approach to The Characterisation of PZT Powders, 26th Congress on Science and Technology of Thailand, Bangkok, (2543) 232.

5. T. Tunkasiri, W. Thamjaree and S. Ananta, Effect of Calcination Temperature on The Phase Formation and Particle Size Distribution of Lead Zirconate Powders, 26th Congress on Science and Technology of Thailand, Bangkok, (2543) 635.

6. W. Thamjaree T. Tunkasiri and S. Ananta, "Characterisation of PZT Powder Prepared by Using Lead Zirconate and Lead Titanate Precursors", 27th Congress on Science and Technology of Thailand, Songkla, (2544) 315.

7. S. Ananta, R. Tipakontitikul and T. Tunkasiri, "Phase Analysis of Calcined Zirconium Titanate Powders by X-ray Diffraction", 27th Congress on Science and Technology of Thailand, Songkla, (2544) 321.

ภาคผนวก

ก) Manuscripts

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Menuscript#1

Synthesis, Formation and Characterisation of Lead Titanate Powders

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Abstract

A perovskite-like phase of lead titanate, $PbTiO_3$ (PT) has been synthesised by a mixed oxide synthetic route. The formation process of lead titanate from the resulting precursors was monitored as a function of calcination temperature, soaking time and heating/cooling rates by thermal analyses and X-ray diffraction techniques. Moreover, particle size distribution, morphology, phase composition and surface area have been determined via laser scattering, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy-dispersive X-ray (EDX) analyses, respectively. It has been found that the unreacted PbO and TiO_2 phases and a monoclinic pyrochlore $PbTi_3O_7$ phase tend to form together with $PbTiO_3$, depending on calcinations conditions. It is seen that single-phase PT powders with a crystallite size of less than 0.5 μm were successfully obtained for a calcinations temperature of 600 °C for 1 h with heating/cooling rates of 30 °C.min^{-1}, without the addition of PbO in excess.

Keywords: Calcination, Milling, PT and Powders-solid state reaction

1. Introduction

Lead titanate ($PbTiO_3$; PT), which exhibits a perovskite-like structure and a Curie temperature of 490 °C, has become one of the most extensively studied ferroelectric materials for decades[1-3]. The growing interest in this material is because of its high Curie temperature, high dielectric constant (~ 2000 at 1 kHz), a large difference between the thickness coupling constant, k_t, and planar coupling constant, k_p, relatively low mechanical quality factor, Q_m, large remanent polarization and large pyroelectric coefficient[2-5]. These characteristics make it a promising candidate for high frequency and high temperature applications[5-6]. Lead titanate when combined with other oxides can form a series of solid solution materials such as $Pb(Zr,Ti)O_3$ (PZT), $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PMNT), and $Pb(Zn,Mg,Nb)O_3$-$PbTiO_3$ (PZMNT)[7-10]. These ferroelectrics are widely used in ultrasonic transducers, microactuators, and electrooptic devices applications[1-3]. Because of these important technological applications, there has been a great deal of interest in the preparation of pure PT powders as well as in the sintering and dielectric properties of PT-based ceramics[11-12]. The stoichiometry of lead titanate is known to be an important factor for ensuring good electrical characteristics[13]. To obtain stoichiometric lead titanate, different preparative methods have been introduced, for example sol-gel, co-precipitation, or hydrothermal treatment, besides the solid state reaction of mixed oxides[14-18]. All these techniques are aimed at reducing the temperature of preparation of the compound even though they are more involved and complicated in approach than the solid-solid reaction method. In all these methods, a calcination at more or less high temperature is needed to get pure crystallized lead titanate. In recent years, only limited attempts have been made to improve the yield of $PbTiO_3$ (PT) by optimising calcination conditions. Whereas purity and reactivity are crucial, attention should also be given to the phase formation characteristics and processing-property relationships of this material, with a view to

enhancing overall understanding. In this study, a solid-state reaction technique has been employed for the manufacturing of lead titanate (PT), analogous to the synthesis of lead magnesium niobate (PMN), lead iron niobate (PFN) and lanthanum magnesium niobate (LMN) previously reported[20-21].

2. Method

2.1 Sample preparation

Laboratory grade purity oxides of lead oxide, PbO and titanium oxide, TiO_2 (Fluka, > 99% purity) were used in this study. The two oxide powders exhibited an average particle size in the range of 3.0 to 5.0 μm. $PbTiO_3$ powder was synthesised by the solid state reaction of these raw materials, according to eqn (1):

$$PbO(s) + TiO_2(s) \rightarrow PbTiO_3(s) \qquad (1)$$

Powder-processing was carried out as shown schematically in Fig. 1. The methods of mixing, drying, grinding, firing and sieving of the products were similar to those employed in the preparation of the perovskite-like $Pb(Mg_{1/3}Nb_{2/3})O_3$, $Pb(Fe_{1/2}Nb_{1/2})O_3$ and $La(Mg_{2/3}Nb_{1/3})O_3$, as described previously[20-21]. Various calcination conditions, *i.e.* temperatures ranging from 400 to 800 °C, soaking times ranging from 1 to 4 h and heating/cooling rates ranging from 3 to 30 $^{\circ}C.min^{-1}$, were selected, in order to investigate the formation of lead titanate.

2.1 Sample characterisation

The reactions of the uncalcined PT powders taking place during heat treatment were investigated by differential thermal analysis (DTA) (NETZSCH-Gerätebau GmbH Thermal Analysis STA 409) using a heating rate of 10 $^{\circ}C.min^{-1}$ in air from room

temperature up to 730 °C. Calcined powders were subsequently examined by room temperature X-ray diffraction (XRD; Philips PW 1729 diffractometer) using CuK_α radiation, to identify the phases formed and optimum calcination conditions for the manufacture of PT powder. The particle size distributions of the calcined powders were determined by laser scattering techniques (MasterSizer, Malvern, UK). Powder morphologies and grain sizes were directly imaged using scanning electron microscopy (SEM; JEOL JSM-840A). The chemical compositions and structures of the phases formed were elucidated by analytical transmission electron microscopy (TEM/STEM; Philip CM20) operated at 200 keV and fitted with an energy-dispersive X-ray (EDX) analyser with an ultra-thin window. EDX spectra were quantified with the virtual standards peaks supplied with the Oxford Instruments eXL software. Powder samples were dispersed in solvent and deposited by pipette on to 3 mm holey carbon grids for observation by TEM. In addition, attempts were made to evaluate the crystal structures of the observed compositions/phases by correlating the XRD and TEM diffraction data.

3. Results and discussion

3.1 Analysis of phases formed

DTA and TGA curves recorded at a heating rate of 10 $^{o}C.min^{-1}$ in air for an equimolar mixture of lead oxide and titanium oxide are shown in Figures 2 and 3. First, the main exothermic peak is observed in the approximate range from 250 to 350 °C. These temperatures have been obtained from the calibration of the sample thermocouple and was found in good agreement with many workers[18-19]. The TGA curve shows that much of the weight loss (28%) occurs upon heating to 300 °C (Fig. 3), and this is associated with the DTA peak and corresponds to the elimination of associated water and volatile products of

organic combustion. The fall in specimen weight over the temperature range from 300 to 350 °C is related to the formation of lead titanate as a result of the reaction between lead oxide and titanium oxide. As shown in Fig. 2, this corresponds to an exothermic peak occurring over the same temperature range in DTA trace of the mixture. At temperature around 480 °C, the DTA curve shows another small exothermic peak. The well known crystallographic-ferroelectric transition temperature of lead titanate at 490 °C[2-3] is within the temperature range of this DTA peak and lends credibility to the suggestion that lead titanate has already been formed before 730 °C, the maximum temperature attained by the mixture in the DTA study. The lower value of the Curie temperature observed may be due to the difference in the densities[18]. Little further weight loss is observed at temperatures above 350 °C, indicating the completion of all the reaction involving a weight loss. No further weight loss is observed with increasing temperature for the precursor at temperatures above 400 °C. These data, together with those in literatures[18-19], were used to define the ranges of temperatures (400 to 800 °C), soaking time (1 to 4 h) and heating/cooling rates (3 to 30 $^{\circ}C.min^{-1}$) for the XRD investigation.

All calcined powders were examined by XRD in order to investigate the phase development (Figs. 4-6). The results of X-ray diffraction measurement supported the above conclusion that $PbTiO_3$ is formed at approximately 400-500 °C. As shown in Fig. 4, fine PT crystallites were developed in the powder at a calcinations temperature as low as 400 °C, inconsistent with the upper temperature of TG-DTA study. In general, the strongest reflections apparent in the majority of the XRD patterns indicate the formation of the lead titanate, $PbTiO_3$. These can be matched with JCPDS file number 06-0452 for the tetragonal phase, in space group *P4/mnm* with cell parameters a = 389.93 pm and c = 415.32 pm. Depending on the calcinations conditions, at least three minor phases were identified, *i.e.* PbO (▼), TiO_2 (*), and $PbTi_3O_7$ (●). The additional reflections of these

minor phases can be correlated with JCPDS files numbers 5-0570, 21-1272 and 21-0949, respectively. This study shows that minor amount of the unreacted PbO and TiO_2 phases tend to co-exist along with the lead titanate phase, after calcinations in the range 400 to 500 °C in agreement with other work[22]. A pyrochlore phase of lead titanium oxide, $PbTi_3O_7$ earlier reported by Tartaj *et al.*[11] has been found in the samples calcined for long soaking times or employing slow heating/cooling rates. A pyrochlore phase has a monoclinic structure with cell parameter a = 107.32 pm, b = 381.2 pm, c = 657.8 pm and $\beta = 98.08^{\circ}$. By increasing the calcination temperature from 400 to 800 °C, the yield of the tetragonal PT phase increase significantly until at 600 °C, a single phase of $PbTiO_3$ is formed (Fig. 4). Crystalline tetragonal PT is the only detectable phase in the powder when it is calcined at 600 to 800 °C. The optimum calcinations temperature for the formation of a high purity PT phase was found to be about 600 °C.

Relative intensities (areas) however did not vary significantly with soaking times, indicating full crystallisation to have occurred at relatively shorter calcination times. In this work, the single phase of perovskite PT (yield of 100% within the limitations of the XRD technique) was found to be possible only in powders, calcined at their optimum temperatures with soaking time less than 4 hours. This is probably due to the effectiveness of vibro-milling and a carefully optimised reaction to form single-phase precursor powders. From XRD results (Fig. 5), it is obviously that the prolong soaking time can lead to the appearance of TiO_2 residual and a pyrochlore $PbTi_3O_7$ which is most likely to be due solely to PbO evaporation.

The effect of heating/cooling rates on phase formation was found to be quite significant (Fig. 6). It is seen that faster heating/cooling rates leads to low lead losses and consequently avoids the formation of pyrochlore. The observation that faster heating/cooling rates are required for lead-based ferroelectrics is also consistent with other

investigators[23-24]. It is also of interest to point out that these considerations should form part of a future study of the fast-firing behavior of PT formation.

Therefore, XRD results clearly show that, in general, the used of a simple ball-milling technique together with the optimum calcinations conditions in the preparation of PT powders does effectively enhance the perovskite phase yield without the addition of PbO in excess[25].

3.2 Particle size analysis

Figure 7 shows the particle size distribution of PT powders after calcinations at 600 °C for 1 h with heating/cooling rates of 30 °C.min^{-1} measured by laser scattering technique. Two types of measurement were carried out: (i) measurement without ultrasonic dispersion; and (ii) measurement with a 10 min of ultrasonic dispersion. Apparently, the ultrasonic aims to disperse those soft particle agglomerates in the powder. As shown in Fig. 7, there is a remarkable difference between the without-ultrasonication measurement (average size range: ~ 0.40 to 3.00 μm, Fig. 7(a)) and the with-ultrasonication measurement (average size range: ~ 0.04 to 1.00 μm, Fig. 7(b)). Therefore, the particle agglomerates in this powder are soft and dispersible by ultrasonication. This will offer an apparent advantage towards achieving a high sintered density and homogeneous microstructure for PT ceramic at a reduced sintering temperature.

3.3 Microstructural analysis

Figure 8 shows the morphological evolution of all samples as a function of the calcination temperatures. The average crystallite size after calcined at 400 °C was estimated from SEM to be ~ 0.3 μm (Fig. 8(a)), increasing slightly to ~ 0.4 μm at 600 °C (Fig. 8(b)), in good agreement with the particle size distribution determined previously

(Fig. 7(b)), increasing significantly to ~ 0.8 μm at 700 °C (Fig. 8(c)) and reaching a value of ~ 1.2 μm at 800 °C (Fig. 8(d)). The degree of bridging between crystallites increased for calcinations temperature above 600 °C; considerable local densification was observed in samples heated at 700 °C. At 800 ° C, it is found that the PT particles of irregular size and shape have developed sharp edges. Although the two unreacted phases (PbO and TiO_2) were observed in X-ray diffraction analysis, but from the SEM micrograph it was difficult to distinguish these two phases because of the identical particle morphology. A bright field TEM image of discrete particles of the PT powder calcined at 600 °C for 1 h with heating/cooling rates of 30 °C.min^{-1} is shown in Fig. 9, indicating the particle sizes and shapes at higher magnification. The observed morphology reveals the considerable variation in sizes and shapes of the particles. The particle diameter was found to be about 0.1 – 0.5 μm in this TEM micrograph. In general, EDX analysis using a 20 nm probe from a large number of particles of this calcined powder confirmed the composition to be $PbTiO_3$ in agreement with the XRD analysis.

4. Conclusion

Fine powders of perovskite-type compound lead titanate have been successfully prepared via a simple ball-milling technique which show a high level of reproducibility. Evidence has been obtained for a 100% yield of tetragonal $PbTiO_3$ at a calcinations temperature of 600 °C for 1 h with heating/cooling rates of 30 °C.min^{-1}, without the addition of PbO in excess. The preparative method involved the use of laboratory-grade precursors, low milling and drying times of powders, moderately low calcinations temperature and time together with fast heating/cooling rates.

Acknowledgements

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FIGURE CAPTIONS

Fig. 1 Preparation route for the $PbTiO_3$ powder

Fig. 2 A DTA curve for the $PbTiO_3$ powder

Fig. 3 A TGA curve for the $PbTiO_3$ powder

Fig. 4 Powder XRD patterns of the calcined powders at various calcination temperatures for 1 h with heating/cooling rates of 20 $^{o}C.min^{-1}$

Fig. 5 Powder XRD patterns of the calcined powders at 600 ^{o}C with heating/cooling rates of 20 $^{o}C.min^{-1}$ for various soaking times

Fig. 6 Powder XRD patterns of the calcined powders at 600 ^{o}C for 1 h with various heating/cooling rates

Fig. 7 The particle size distribution curve of the calcined PT powder (a) the without- and (b) with-ultrasonication measurements

Fig. 8 SEM micrographs of the $PbTiO_3$ powders calcined at (a) 400 ^{o}C, (b) 600 ^{o}C, (c) 700 ^{o}C and (d) 800 ^{o}C

Fig. 9 TEM micrograph of the calcined $PbTiO_3$ powder

Fig. 1 Ananta Tunkasiri

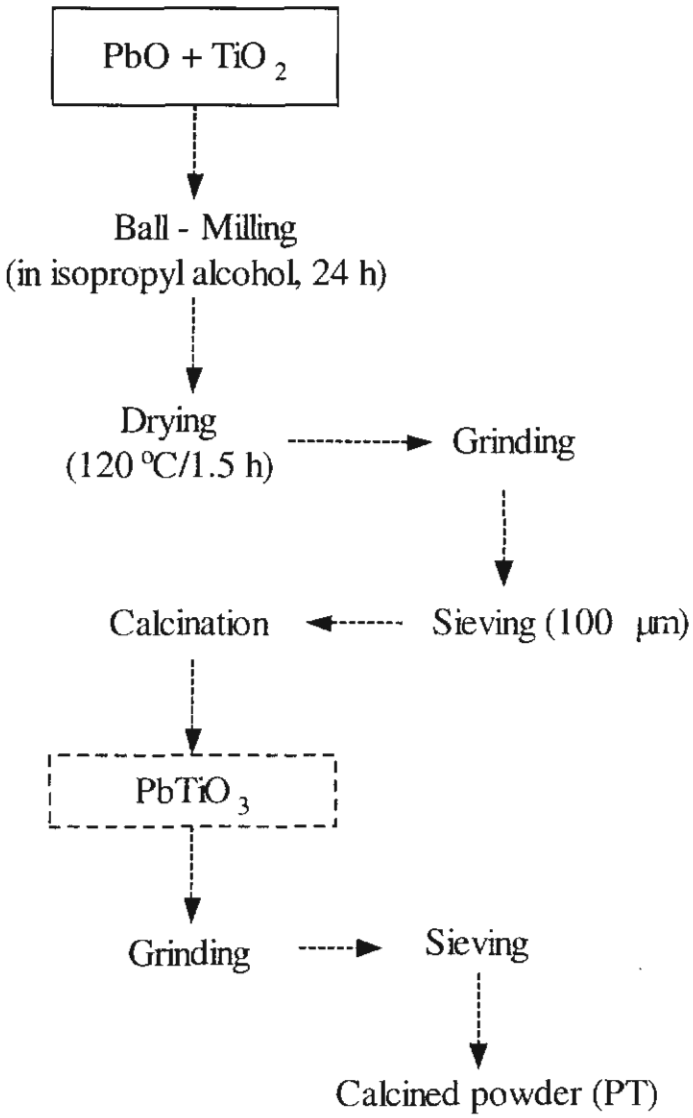


Fig. 2 Aranta & Tunkasiri

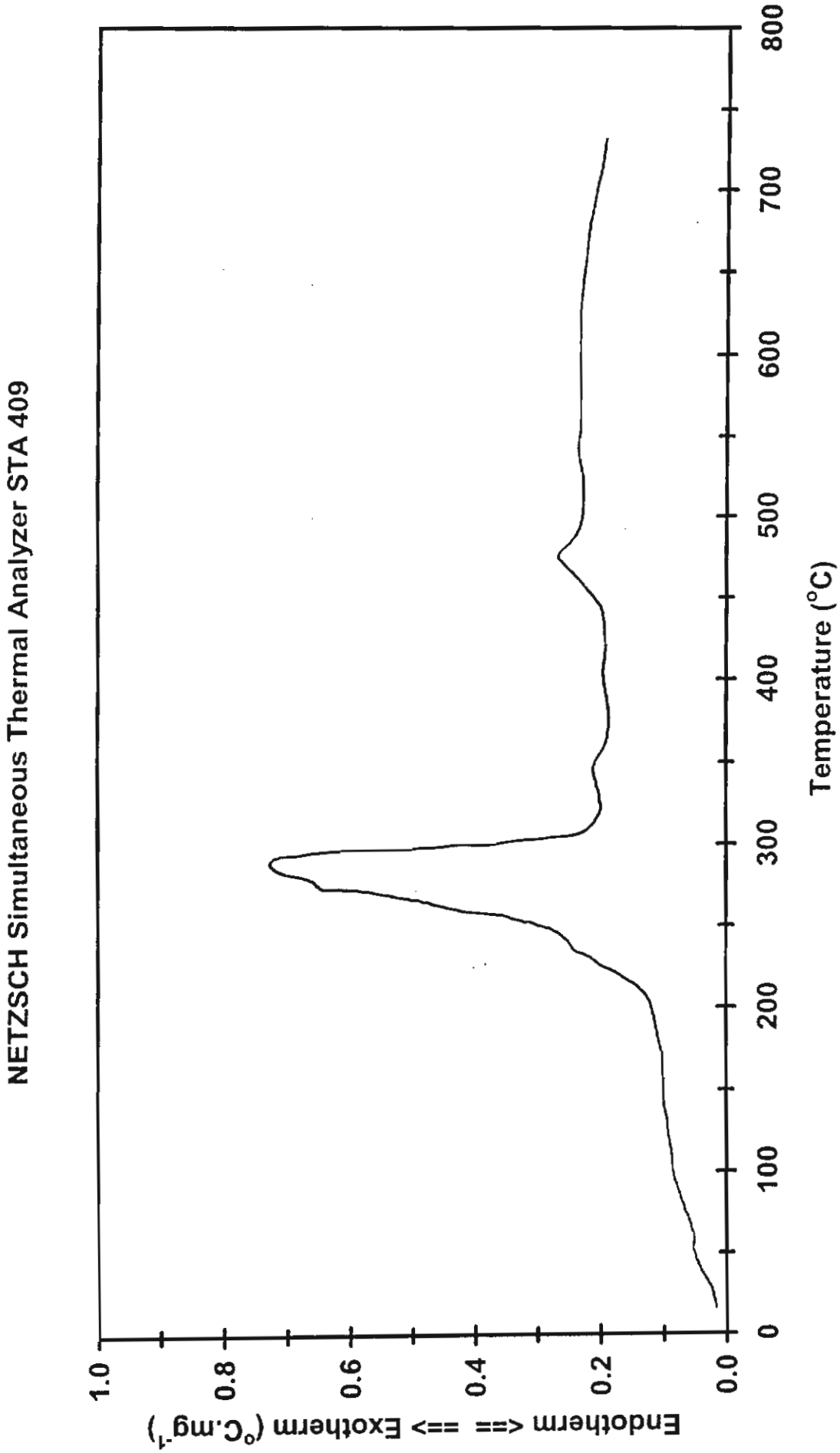


Fig.3 Ananta & Tonkasiri

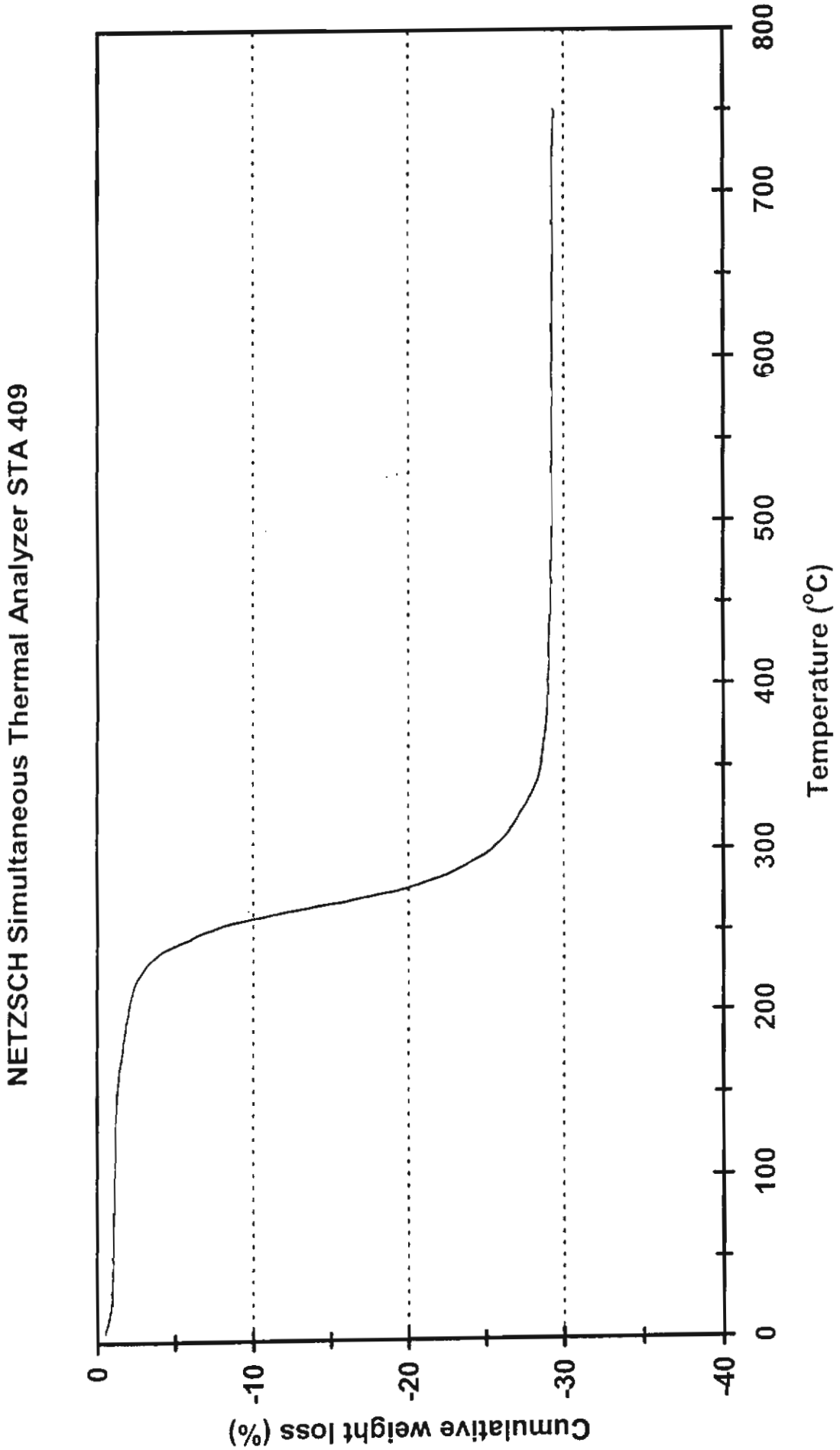


Fig. 4 Ananta & Lonkasiri

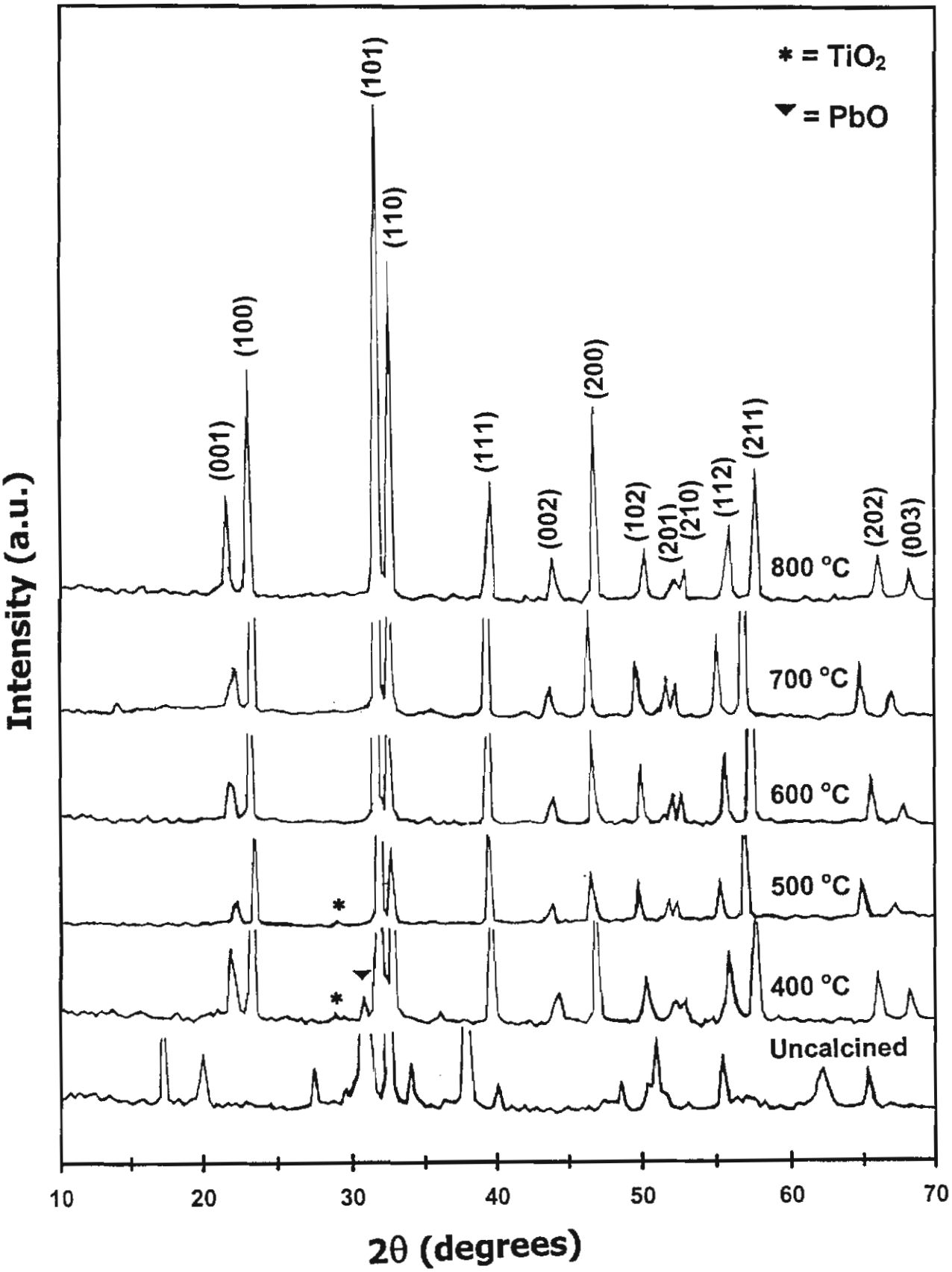
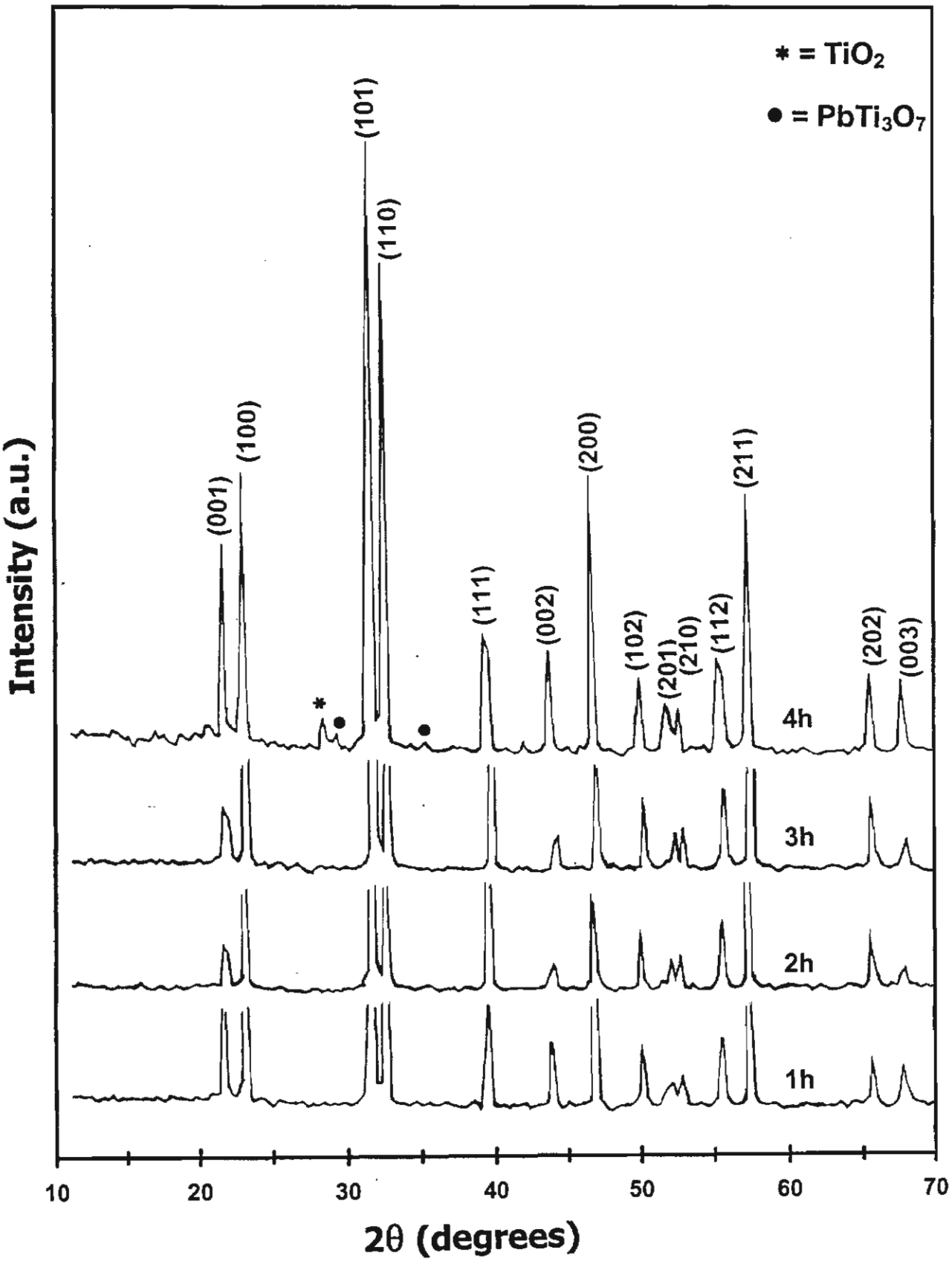
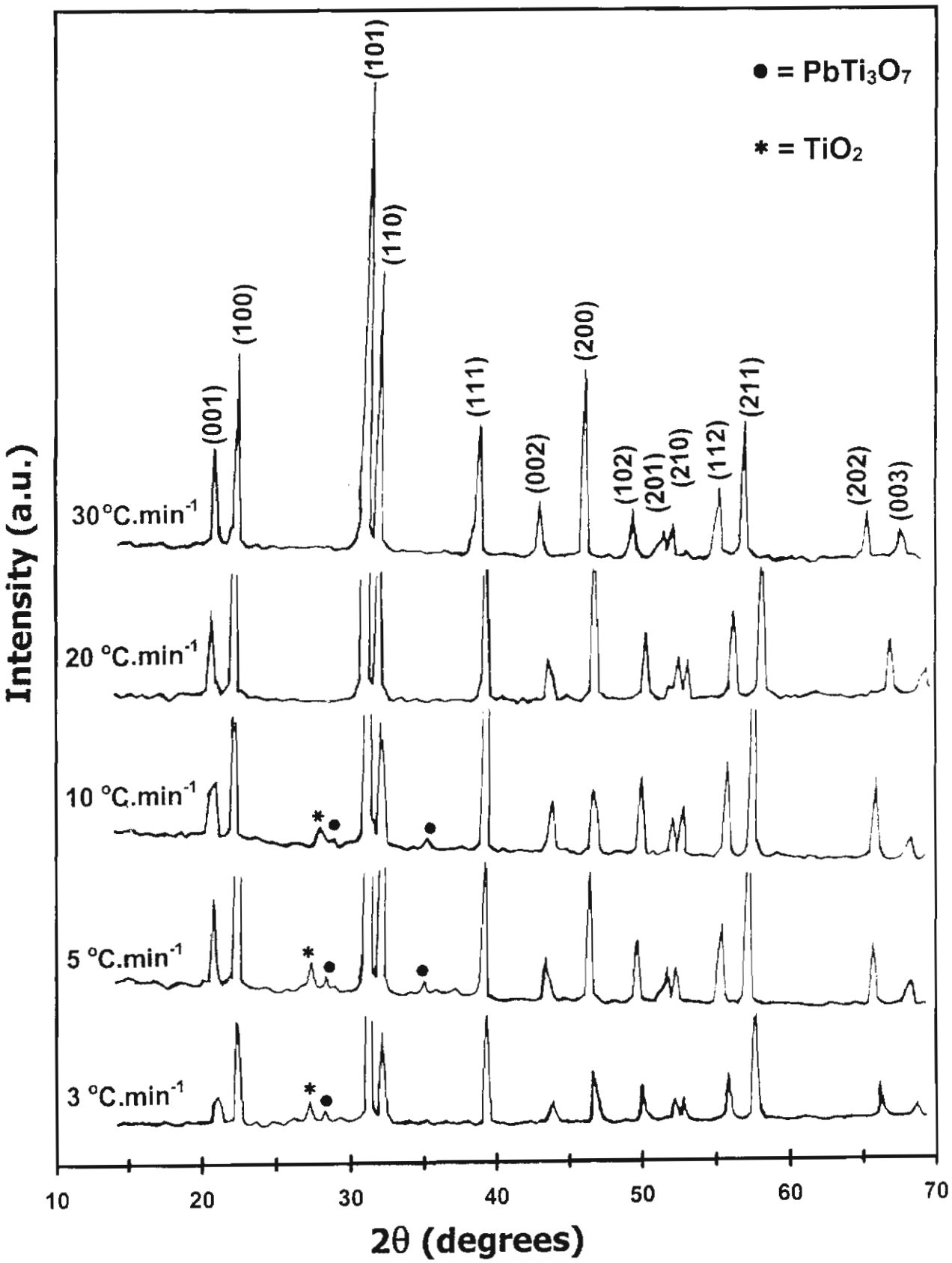


Fig.5 Anatase formation

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* = TiO2
(001)
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30°C.min-1
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5 °C.min-1
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2θ (degrees)

Fig. 7(a) Amanita punkasiri

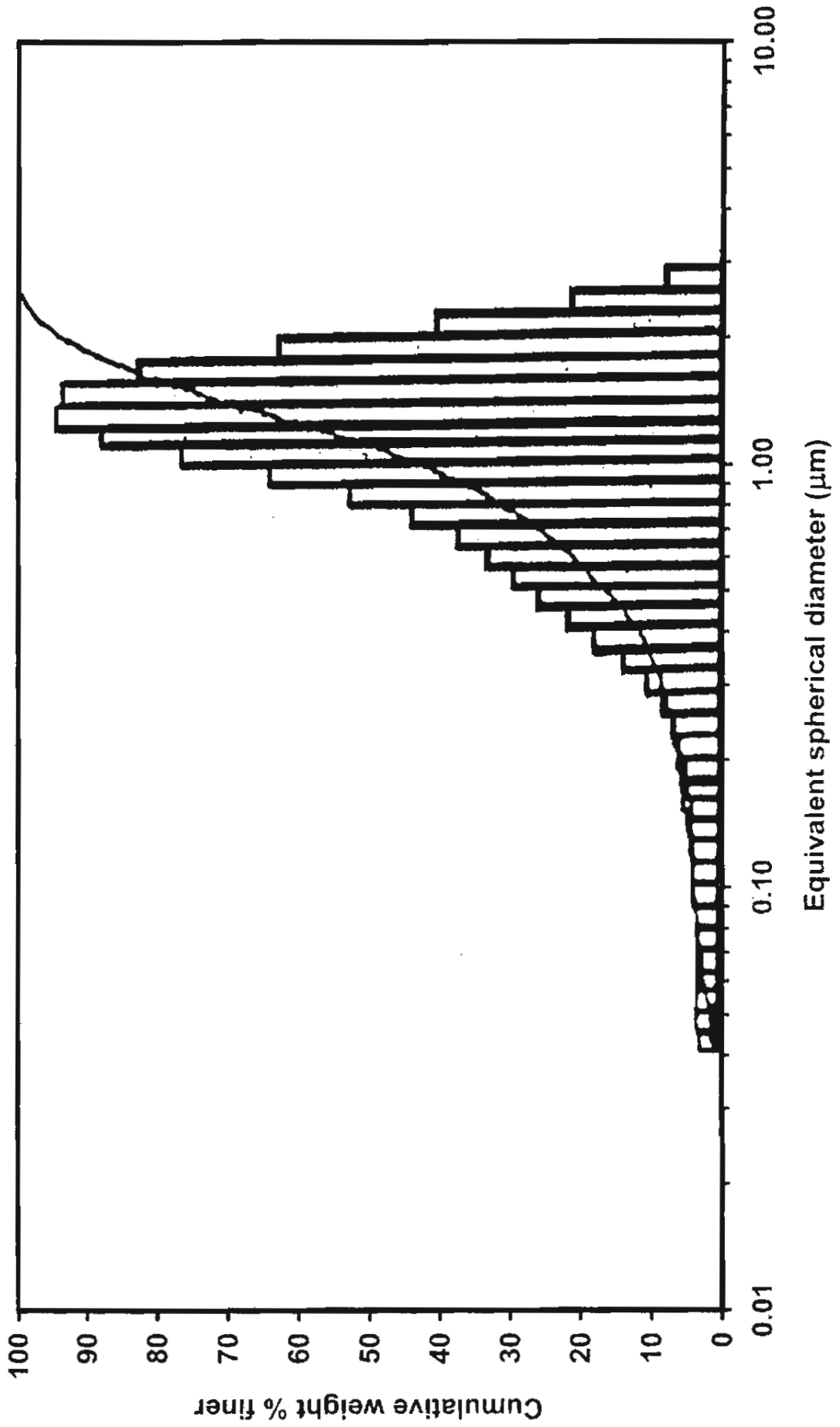


Fig. 7(b) Amartay Tankasiri

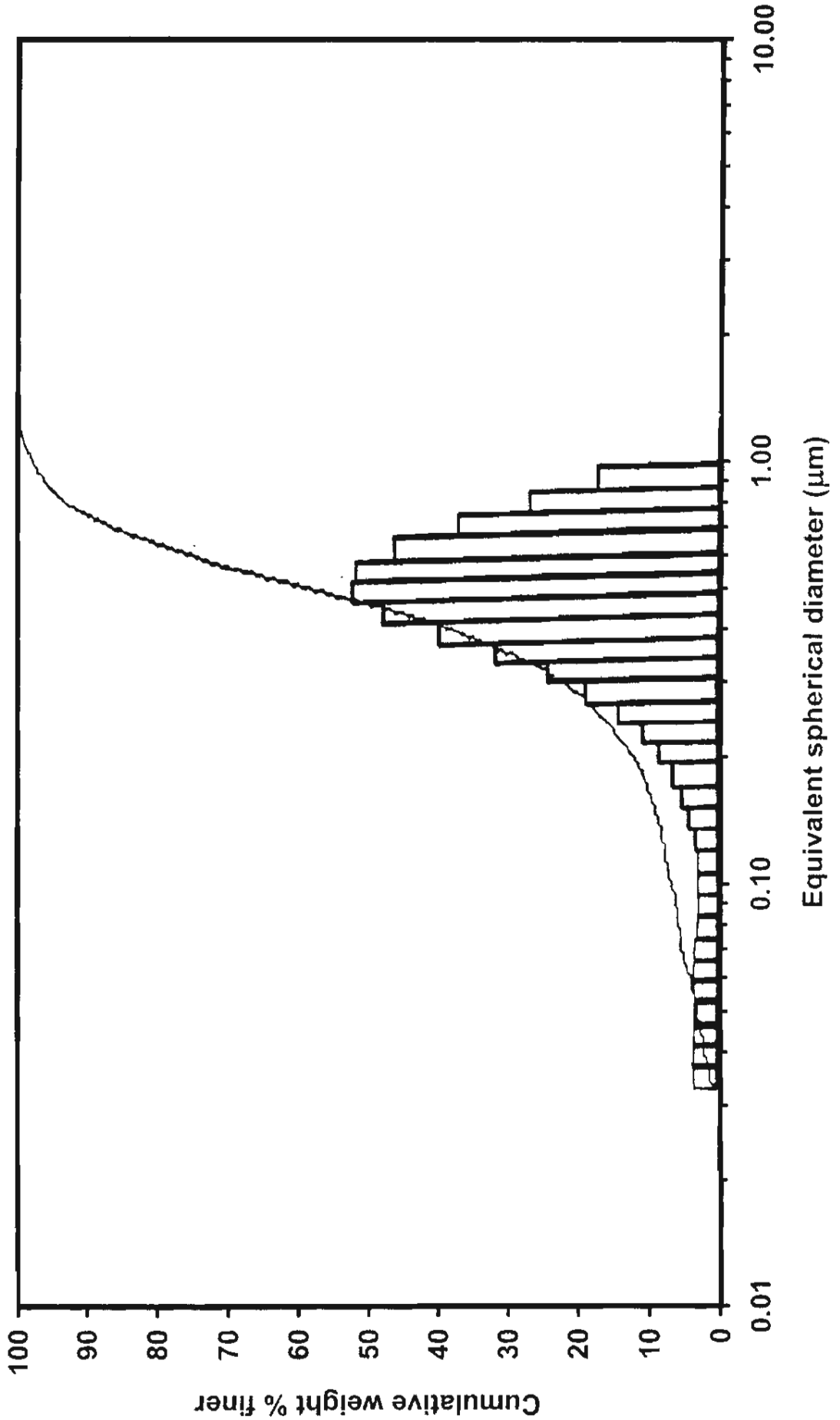
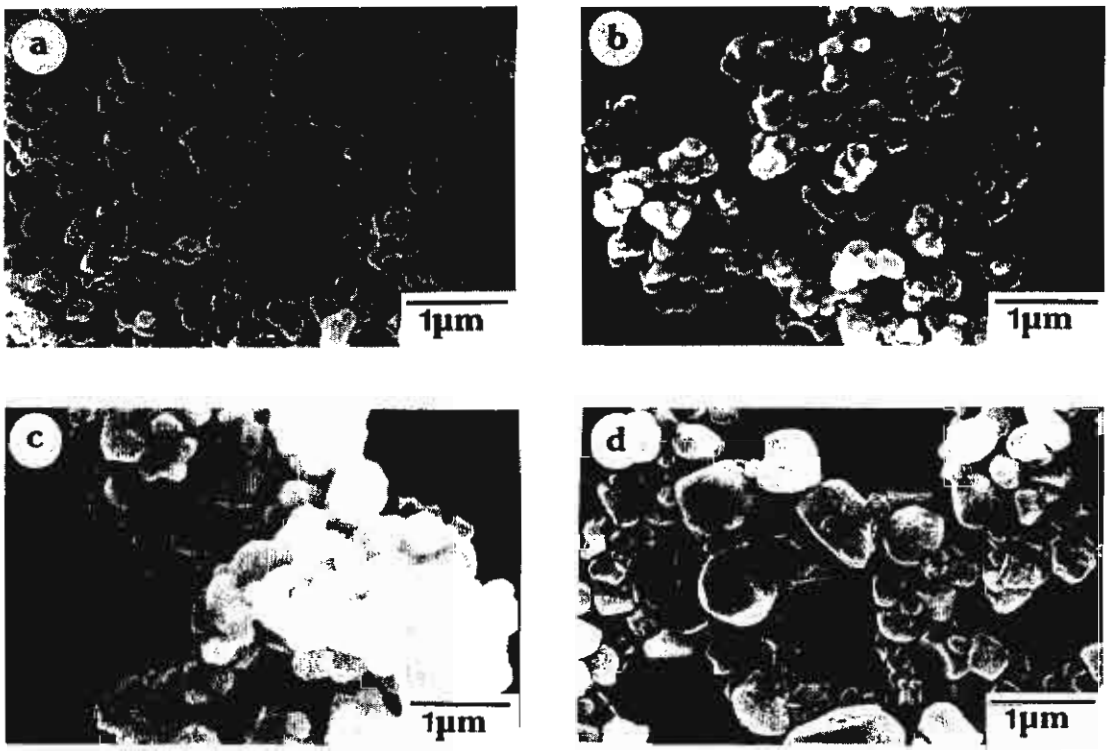


Fig. 8 Ananta + Tunkasiri



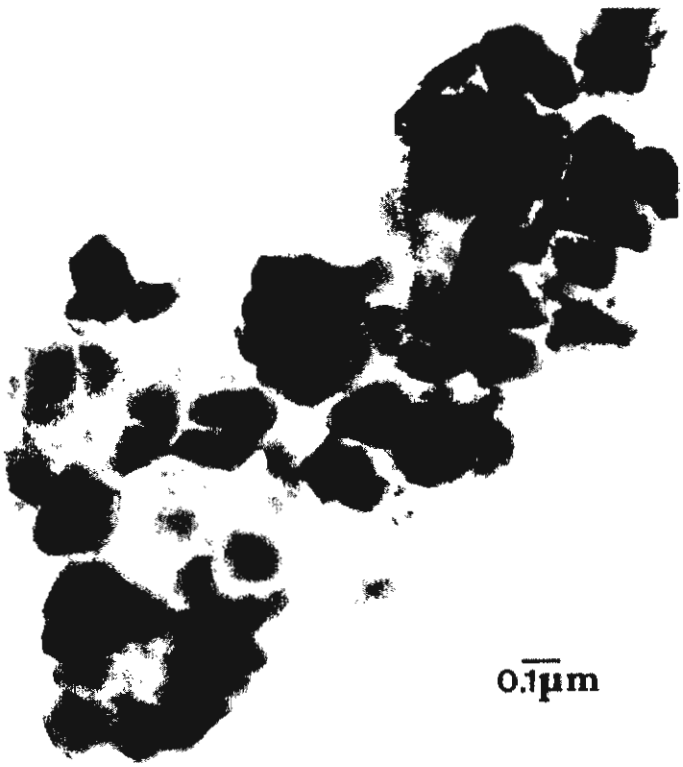


Fig. 9 Ananta + Tunkasiri

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Menuscript#2

Synthesis, Formation and Characterisation of Lead Zirconate Powders

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Abstract

Lead zirconate ($PbZrO_3$) powders have been prepared and characterised by TG-DTA, XRD, SEM, EDX and laser diffraction techniques. The effect of calcinations temperature, dwell time and heating/cooling rates on phase formation, morphology and particle size distribution of the powders are examined. The calcination temperature and heating/cooling rates have been found to have a pronounced effect on the phase formation and particles size of the calcined $PbZrO_3$ powders. It has been found that the unreacted precursor of PbO and ZrO_2 tend to form together with $PbZrO_3$, depending on calcination conditions. It is seen that optimisation of calcination conditions can lead to a single-phase $PbZrO_3$ in an orthorhombic phase. The resulting powders consist of agglomerated particles of 0.3 to 1.0 μm in size, which are rounded in morphology.

Keywords: Lead zirconate; $PbZrO_3$; Powders-solid state reaction; Perovskite; Phase development; X-ray diffraction

1. Introduction

Lead zirconate, $PbZrO_3$ (PZ) is a typical antiferroelectric (AFE) material at room temperature, with a Curie temperature of 230 °C [1]. It has an orthorhombic symmetry with a structure similar to that of classical ferroelectric of orthorhombic barium titanate ($BaTiO_3$) [2]. The dipoles due to a displacement of the Zr^{4+} ions from the geometric centre of the surrounding six O^{2-} ions in the material are alternately directed in opposite senses so that the spontaneous polarization is zero [3]. It is reported that the antiferroelectric to ferroelectric transition can be induced when subjected to a strong electric field [4]. This materials is a potential candidate used in energy storage applications for DC fields, owing to its AFE nature [5]. It can be used as low loss linear capacitor at a low electric field because the AFE phase achieves free of remanant polarization. Recently, the double hysteresis behavior of this material makes it attractive for the microelectronic, microelectromechanical system (MEMs) as well as for actuator applications [6-8]. Lead zirconate when combined with other oxides can form a series of solid solutions materials such as $Pb(Zr,Ti)O_3$, $PbZrO_3$-$Pb(Mg_{1/3}Nb_{2/3})O_3$, $PbZrO_3$-$PbTiO_3$-$Pb(Fe_{1/5}Nb_{1/5}Sb_{3/5})O_3$, and $PbZrO_3$-$BaZrO_3$, which find tremendous applications in the electroceramic industries [8-10]. In all these applications, the stoichiometry and homogeneity of materials are known to be the important factor for ensuring the performance of devices [6,7]. To obtain stoichiometric and better homogeneity lead zirconate, different preparation methods have been introduced, for example sol-gel [11], co-precipitation [12], hydrothermal [13], citrate combustion [14] and precipitation of molecular precursors [15,16]. All these techniques are aimed at reducing the formation temperature of PZ to ~ 700 °C to avoid the PbO loss, even though they are more involved and complicated in approach than the solid state reaction method. As is well known, PbO volatilisation hinders the formation process and makes control of the composition of the powder difficult [17,18]. Therefore, a decrease in

the processing temperature of PZ may result in an improvement in the final properties of the ceramic part. However, much of the work concerning the $PbZrO_3$ over the past few years has been directed towards determining preferred orientation and electrical properties of the PZ thin films [19-22]. So far, the majority of the studies in PZ powders, were focused on monitoring the influence of calcination temperature, but only limited attempts have been made to improve the yield of $PbZrO_3$ by optimising calcination conditions. Whereas purity, reactivity, degree of mixing, calcination temperature and time, and heating/cooling rates are crucial, attention should also be given to the phase formation characteristics of this material, with a view to enhancing overall understanding. It was our interest to explore a simple mixed oxide synthetic route for the production of PZT powders. In this context, a systematic study of the reaction between lead oxide and zirconium oxide is of interest. The phase formation, morphology and particle size of the powder calcined at various conditions will be studied and discussed.

2. Experimental procedure

Laboratory grade purity oxides of lead oxide, PbO and zirconium oxide, ZrO_2 (Fluka, 99.0 % purity) were used in this study. The two oxide powders exhibited an average particle size in the range of 5.0 to 10.0 μm. $PbZrO_3$ powder was synthesised by the solid state reaction of thoroughly ground mixtures of PbO and ZrO_2 powders taken in the required stoichiometric ratio. The milling operation was carried out for 24 h in isopropanal. High purity zirconia balls with diameter of 10 mm were used as the milling media. After drying at 120 °C, various calcination conditions, *i.e.* temperatures ranging from 600 to 800 °C, dwell times ranging from 2 to 4 h and heating/cooling rates ranging from 5 to 20 °C/min, were applied, in order to investigate the formation of zirconium

titanate. The reactions of the uncalcined PT powders taking place during heat treatment were investigated by thermogravimetry analysis (TGA) and differential thermal analysis (DTA) using a heating rate of 10 °C/min in air from room temperature up to 900 °C. Calcined powders were subsequently examined by room temperature X-ray diffraction (XRD; Philips PW 1729 diffractometer) using CuK_α radiation, to identify the phases formed and optimum calcination conditions for the manufacture of PZ powder. The particle size distribution of the samples were determined by laser diffraction technique (Mastersizer, Malvern, U.K.). Powder morphologies and grain sizes were directly imaged using scanning electron microscopy (SEM; JEOL JSM-840A). The chemical compositions of the phases formed were elucidated by an energy-dispersive X-ray (EDX) analyser with an ultra-thin window. EDX spectra were quantified with the virtual standards peaks supplied with the Oxford Instruments eXL software.

3. Results and discussion

Figure 1 shows the TG-DTA curves obtained for a powder mixed in the stoichiometric proportions of $PbZrO_3$ heated from room temperature to 900 °C at a rate of 10 °C/min in air. Two exothermic peaks with maxima at 260 °C and 720 °C, and two endothermic peaks centered at *ca.* 305 °C and 800 °C were observed in this profile. These temperatures having been obtained from the calibration of the sample thermocouple. It is to be noted that there is no obvious interpretation of the first exothermic peaks, whilst the first endothermic peak at ~ 305 °C could be attributed to the elimination of residual water and organic substances from the sample, which was manifested by a weight loss in TG curve (~ 30%) at the corresponding temperature range. A small exothermic peak at ~ 720 °C, which had no associated weight loss manifestation in the TG curve, corresponded to the crystallization of the perovskite $PbZrO_3$ phase, in consistent with Li *et al.* [23]. The

second endotherm effect (~ 810 °C), which had associated gradually weight loss in the TG curve could be attributed to the decomposition of the $PbZrO_3$ and possibly the melting of some lead. These data were used to define the range of temperatures for XRD investigation to between 600 and 800 °C.

All calcined powders were examined by XRD in order to investigate the phase development (Figs. 2-4). The results of X-ray diffraction measurement supported the above conclusion that $PbZrO_3$ is formed at approximately 700 °C. As shown in Fig. 2, fine PZ crystallites were developed in the powder at a calcinations temperature as low as 700 °C, inconsistent with the TG-DTA study. In general, the strongest reflections apparent in the majority of the XRD patterns indicate the formation of lead zirconate phase, $PbZrO_3$, which could be matched with JCPDS file no. 35-739. To a first approximation, this major phase has orthorhombic structure, space group *P2cb* (no. 32), with cell parameter a = 823 pm, b = 1177 pm and c = 588 pm. Depending on the calcination conditions, at least two unreacted precursors were identified, *i.e.* PbO (∇) and ZrO_2 (•). The additional reflections of these minor phases can be correlated with JCPDS files numbers 5-0570 and 21-0949, respectively. This study shows that minor amount of the unreacted PbO and ZrO_2 phases tend to co-exist along with the lead zirconate phase, after calcinations below 750 °C.

By increasing the calcination temperature from 700 to 800 °C, the yield of the orthorhombic PZ phase increase significantly until at 750 °C, a single phase of $PbZrO_3$ is formed (Fig. 2). Lead zirconate synthesized by Li *et al.* [23] via an acetate precursor also showed a similar result for the formation of the perovskite PZ phase. In this study, crystalline PZ is the only detectable phase in the powder when it is calcined at 750 to 800 °C. The optimum calcinations temperature for the formation of a high purity PZ phase was found to be about 750 °C. The effects of soaking time and heating/cooling rates on phase formation were found to be quite insignificant (Figs. 3 and 4). It is seen that full

crystallization of the perovskite $PbZrO_3$ phase can occurred at relatively fast heating/cooing rates. In this work, the single phase of perovskite PZ (yield of 100% within the limitations of the XRD technique) was found to be possible in all powders calcined at their optimum temperatures with soaking time of at least 4 h. Therefore, XRD results clearly show that, in general, the used of a simple mixed oxide technique together with the optimum calcination conditions in the preparation of PZ powders does effectively enhance the perovskite phase yield without the addition of PbO in excess [18]. The experimental work carried out here suggests that the optimal calcination conditions for single phase $PbZrO_3$ is 750 °C for 1 h with heating/cooling rates as fast as 20 °C/min.

Figure 5 shows the particle size distribution curves of uncalcined and calcined PZ powders at various temperatures, which indicate appreciable size fractions at approximately 0.7, 1.2, 1.7 and 2.0 μm diameters, respectively. The morphological evolution during calcination was investigated by scanning electron microscopy (SEM). Micrographs of PZ powders calcined at various temperatures from 700 to 800 °C are shown in Fig. 6. In general, the particles are agglomerated and basically irregular in shape, with a substantial variation in particle size, particularly in samples calcined at high temperatures. Observed diameters range from ~ 0.2 to 0.7 μm, 0.2 to 0.8 μm, 0.3 to 1.0 μm and 0.5 to 1.5 μm for the PZ powders calcined at 0 °C, 700 °C, 750 °C and 800 °C, respectively, in good agreement with the particle size distribution previously determined (Fig. 5). The results indicate that averaged particle size and degree of agglomeration tend to increase with calcination temperature. Moreover, the grain shape tends toward greater sphericity at higher temperatures. Energy dispersive X-ray (EDX) analysis showed the calcined compositions of the powder calcined at 750 °C for 1 h with heating/cooling rates of 20 °C/min to be $PbZrO_3$, in agreement with XRD results.

One of the great attractions of the mixed oxide approach towards synthesizing perovskite powders is its simplicity and low manufacturing cost. Furthermore, solid-state reactions of this kind lend themselves to straightforward diagnosis by several physical techniques, e.g. TG-DTA, XRD, SEM and EDX. The synthesis used here for PZ powders represents a considerable advance, in term of simplicity, flexibility, time and cost, over a sol-gel and co-precipitation synthesis recently advocated [11,12].

4. Conclusions

The effect of calcination conditions on the phase formation and particle size of lead zirconate ($PbZrO_3$) powders has been investigated. It was demonstrated that the purity and the particle size of PZ phase increased continuously with calcination temperature. This study showed that it is possible to obtain chemically uniform submicrometer powders of PZ by employing a simple mixed oxide synthetic route together with the optimum calcination conditions. Evidence has been obtained for a 100 % yield of an orthorhombic $PbZrO_3$ at a calcination temperature 750 ^{o}C for 1 h with heating/cooling rates of 20 ^{o}C/min.

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Figure captions

Fig. 1 TG-DTA curves for the mixture of PbO-ZrO_2 powder.

Fig. 2 XRD patterns of PZ powder calcined at various temperatures for 1 h with heating/cooling rates of 20 °C/min.

Fig. 3 XRD patterns of PZ powder calcined at 750 °C with heating/cooling rates of 20 °C/min for various dwell times.

Fig. 4 XRD patterns of PZ powder calcined at 750 °C for 1 h with various heating/cooling rates

Fig. 5 Particle size distribution curves of the PZ powder calcined at (a) 0 °C, (b) 700 °C, (c) 750 °C and (d) 800 °C.

Fig. 6 SEM micrographs of the PZ powders calcined at (a) 0 °C, (b) 700 °C, (c) 750 °C and (d) 800 °C.

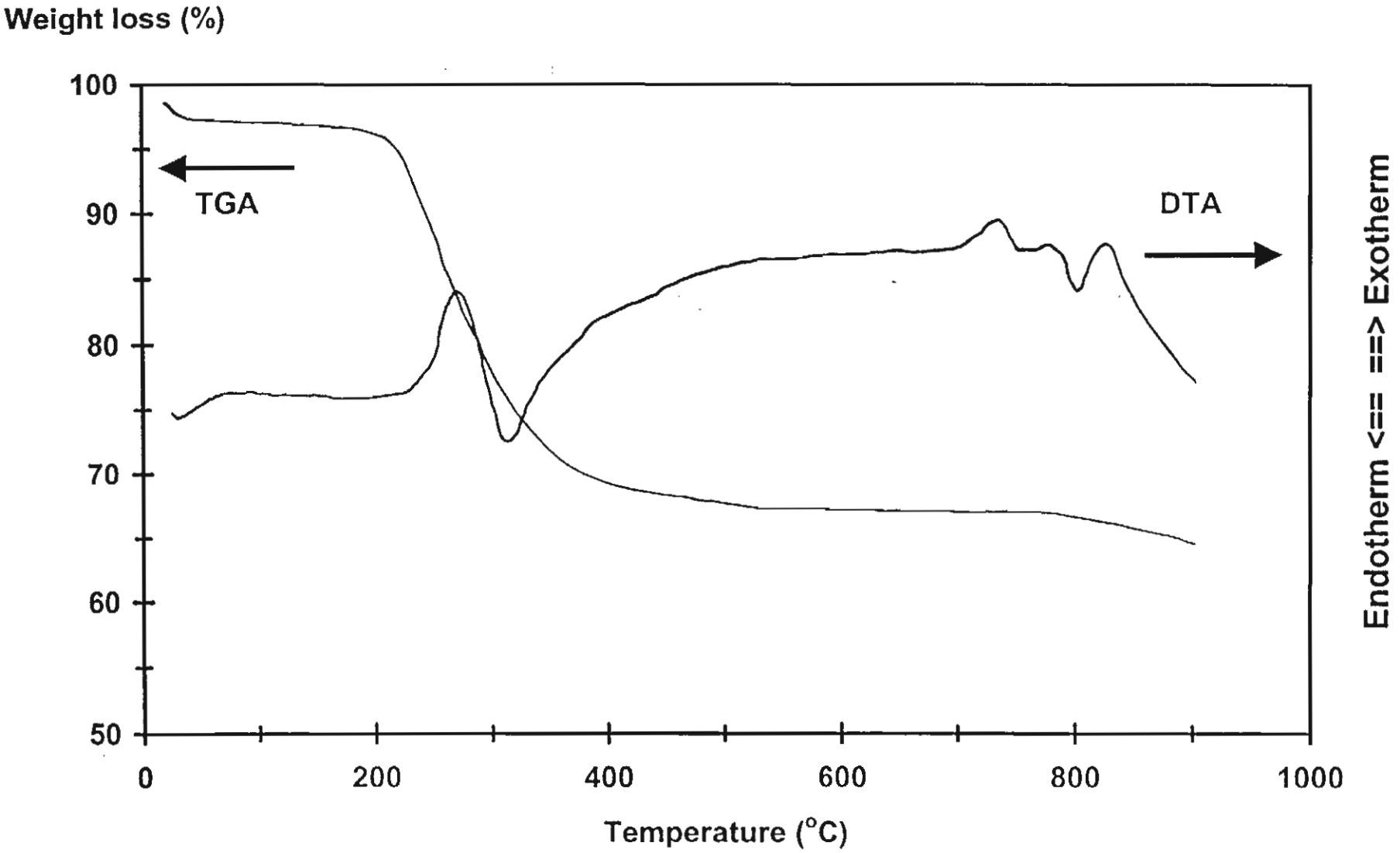


Fig. 1 Ananta + Tunkasiri

Fig.2 Ananta et al

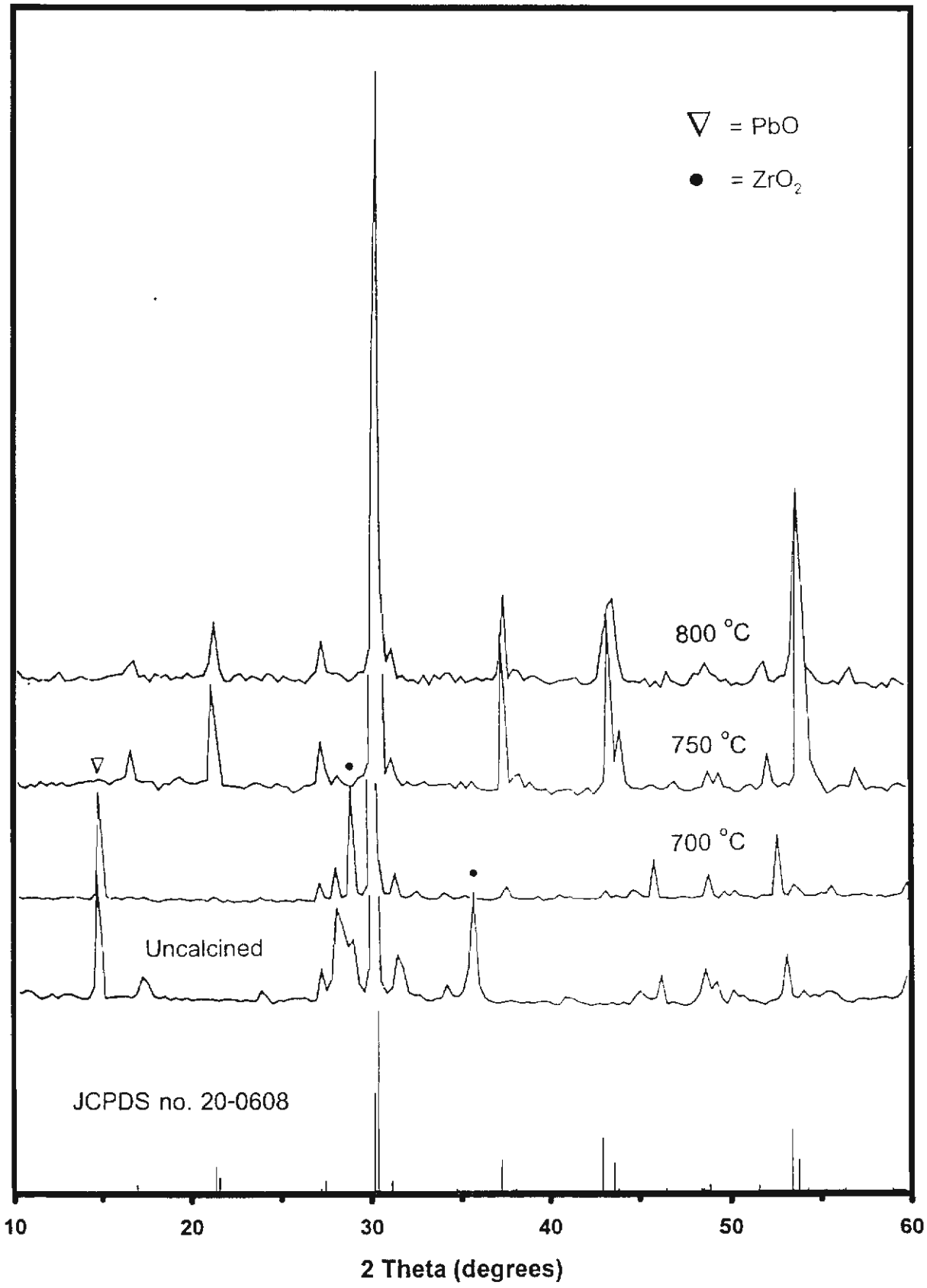


Fig.3 Ananta & Tonkosi'ri

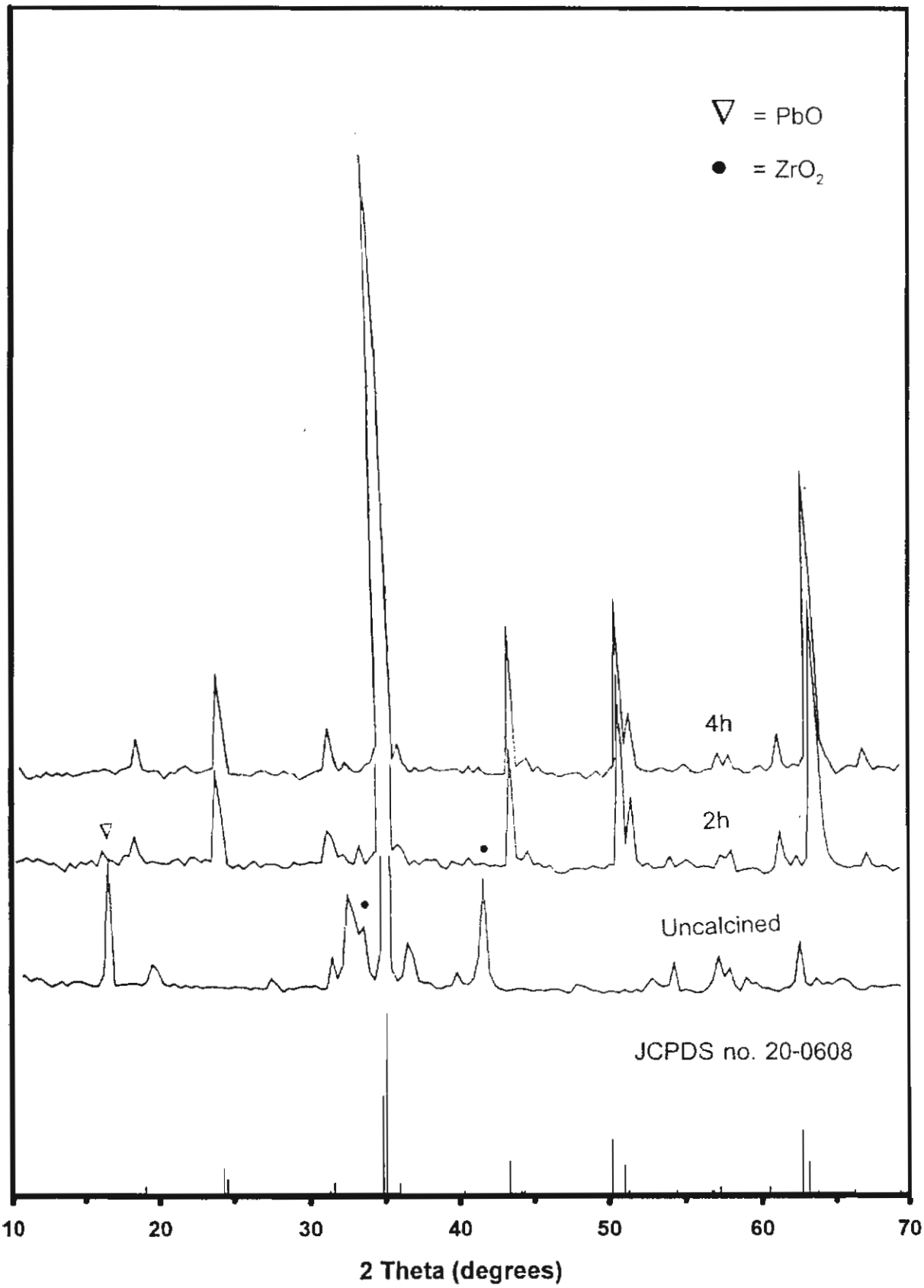


Fig.4 Ananta + Tunkasiri

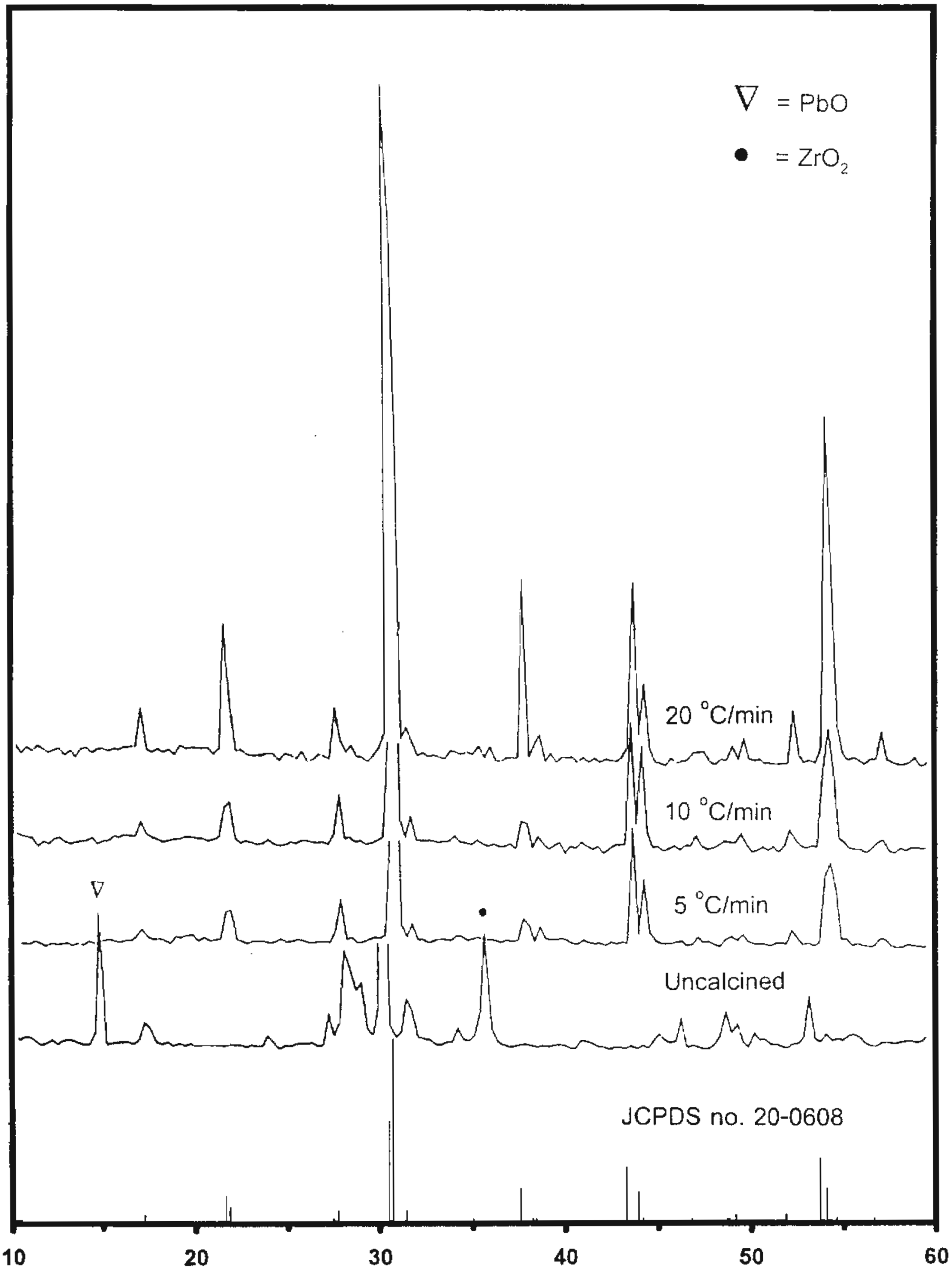


Fig.5 Ananta + Tunkasiri

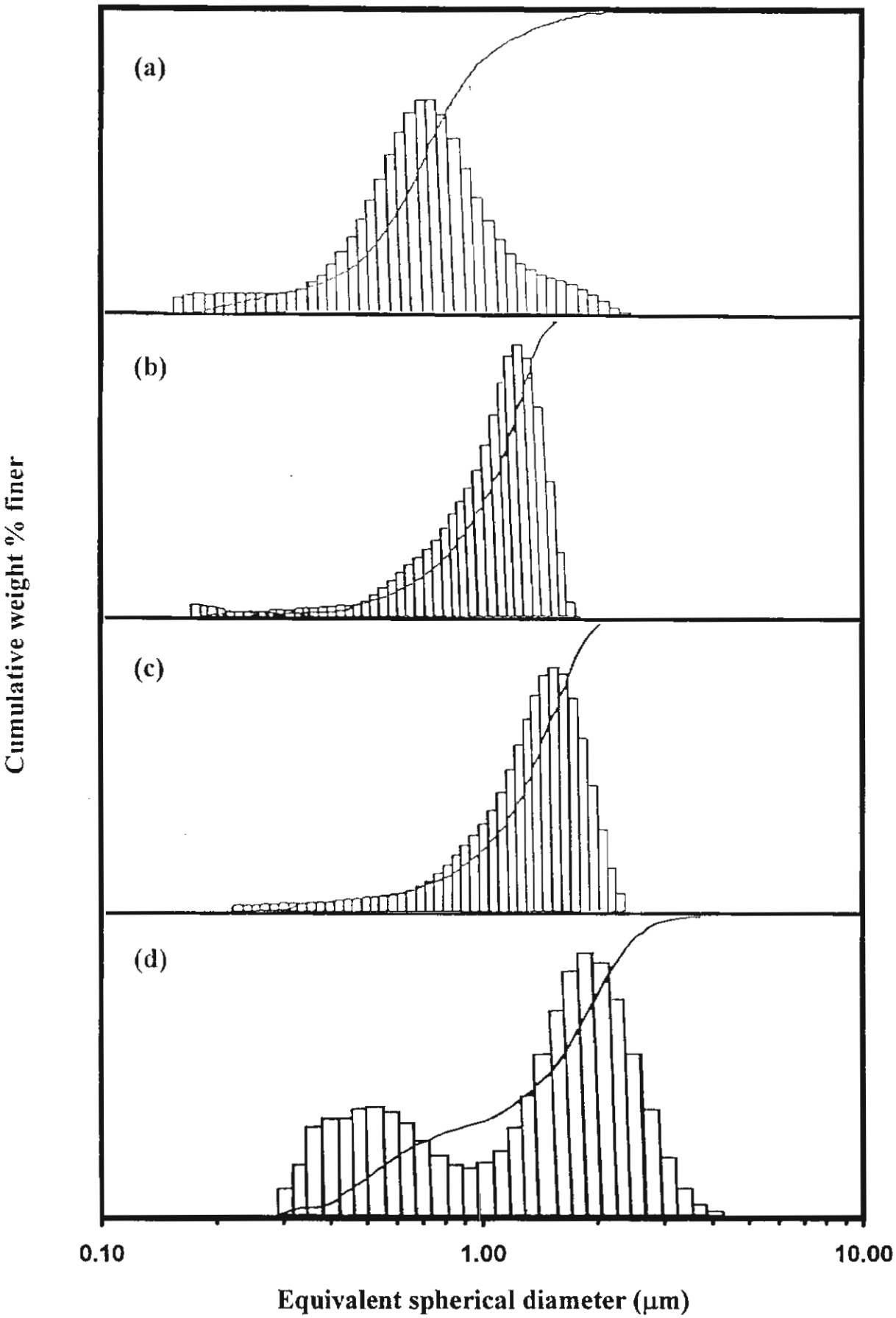
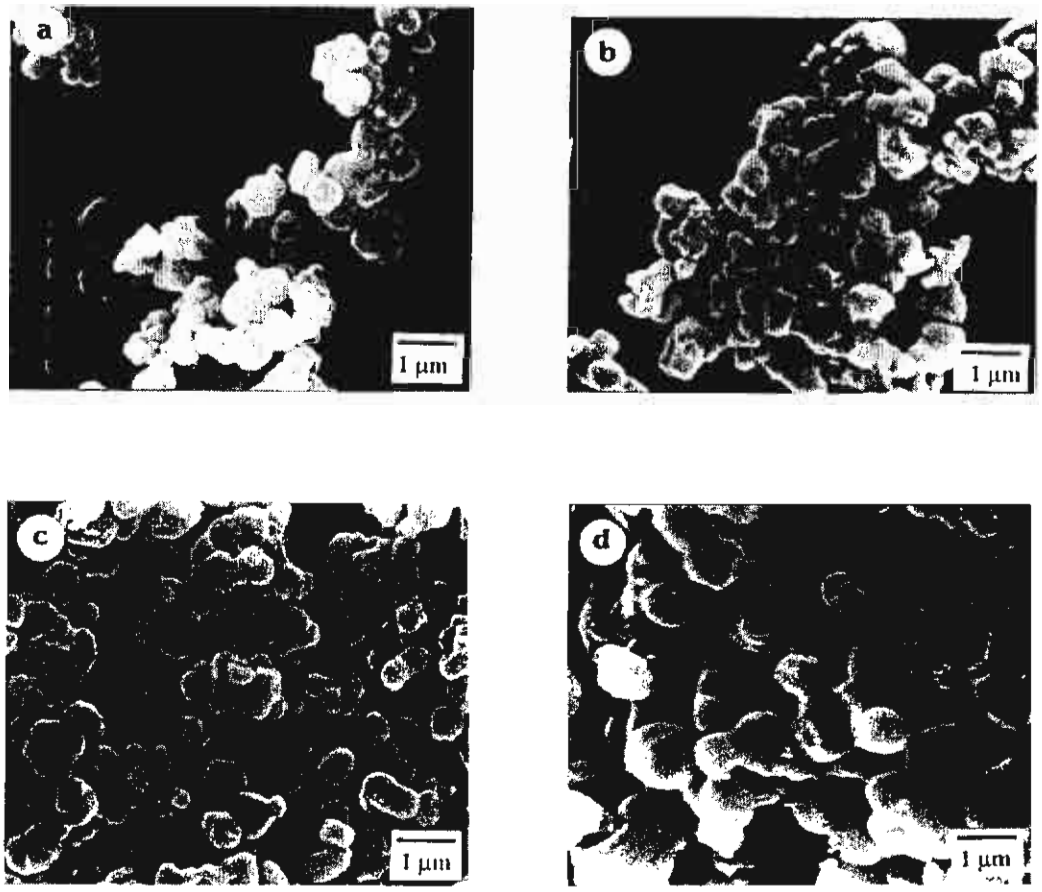


Fig.6 Ananta & Tamhane



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Synthesis, Formation and Characterisation of Zirconium Titanate (ZT) Powders

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Abstract

Zirconium titanate ($ZrTiO_4$) powders have been prepared and characterised by DTA, XRD, SEM and EDX techniques. The effect of calcinations temperature, dwell time and heating/cooling rates on phase formation, morphology and particle size distribution of the powders are examined. The calcination temperature and dwell time have been found to have a pronounced effect on the phase formation and particles size of the calcined ZT powders. It has been found that the minor phases of ZrO_2 and TiO_2 tend to form together with $ZrTiO_4$, depending on calcination conditions. It is seen that optimisation of calcination conditions can lead to a single-phase $ZrTiO_4$ in an orthorhombic phase.

Keywords: Zirconium Titanate; $ZrTiO_4$; Powder synthesis; Oxides; Calcination; X-ray diffraction

1. Introduction

Zirconium titanate-based compositions are extensively used as dielectric resonators for microwave telecommunications [1-3]. They also are of interest for a wide range of applications including catalysis, humidity sensors, high-temperature pigments and composites [4-8]. It is known that all forms of $ZrTiO_4$ (ZT) have the orthorhombic structure [9]. Above 1200 °C, the high temperature phase of $ZrTiO_4$ was related to that of α–PbO_2, having random distributions of cations in available octahedral sites. On cooling within the temperature range 1200-1100 °C, a disorder-order transition has been observed; the reported phase transition is characterized by (1) a decrease in the length of the the *b* axis [10], (2) ordered arrangement of metal ions gives rise to a doubled axis along the *a* direction [11], and the reconstructive transition requiring a large scale rearrangement of the cations in the lattice [12].

The stoichiometry of zirconium titanate is known to be an important factor for ensuring good properties [2-5]. In order to obtain fined grained, high quality and stoichiometric zirconium titanate powders at low processing temperatures, various chemical routes, for example hydrolysis of alkoxides [13], sol-gel [14], Pechini [15], and co-precipitation [16] have been developed as alternative to the conventional solid state reaction of mixed oxides [17]. All these techniques are aimed at reducing the temperature of preparation of the compound even though they are more involved and complicated in approach than the mixed oxide route. Generally, the mixed oxide method involves the heating of a mixture of zirconium oxide and titanium oxide above 1200 –1600 °C during long heating times [17], and has been employed intensively in the last decade [18-20]. The optimisation of calcinations conditions, however, have not received detailed attention, and the effects of applied dwell time and heating/cooling rates have not yet been studied extensively to our knowledge. It was our interest to explore a simple mixed oxide

synthetic route for the production of ZT powders. In this context, a systematic study of the reaction between zirconium oxide and titanium oxide is of interest. The phase formation, morphology and particle size of the powder calcined at various conditions will be studied and discussed.

2. Experimental procedure

Laboratory grade purity oxides of zirconium oxide, ZrO_2 (baddeleyite) and titanium oxide, TiO_2 (anatase) (Fluka, 99.9% purity) were used in this study. The two oxide powders exhibited an average particle size in the range of 3.0 to 5.0 μm. $ZrTiO_4$ powder was synthesised by the solid state reaction of thoroughly ground mixtures of ZrO_2 and TiO_2 powders taken in the required stoichiometric ratio. The milling operation was carried out for 24 h in isopropanal. High purity zirconia balls with diameter of 10 mm were used as the milling media. After drying at 120 °C, various calcination conditions, *i.e.* temperatures ranging from 1100 to 1350 °C, dwell times ranging from 0.5 to 6 h and heating/cooling rates ranging from 2 to 20 °C/min., were applied, in order to investigate the formation of zirconium titanate. The reactions of the uncalcined PT powders taking place during heat treatment were investigated by differential thermal analysis (DTA) (NETZSCH-Gerätebau GmbH Thermal Analysis STA 409) using a heating rate of 10 °C/min. in air from room temperature up to 1400 °C. Calcined powders were subsequently examined by room temperature X-ray diffraction (XRD; Philips PW 1729 diffractometer) using CuK_α radiation, to identify the phases formed and optimum calcination conditions for the manufacture of ZT powder. Powder morphologies and grain sizes were directly imaged using scanning electron microscopy (SEM; JEOL JSM-840A). The chemical compositions of the phases formed were elucidated by an energy-dispersive X-ray (EDX)

analyser with an ultra-thin window. EDX spectra were quantified with the virtual standards peaks supplied with the Oxford Instruments eXL software.

3. Results and discussion

A DTA curve obtained for a powder mixed in the stoichiometric proportions of $ZrTiO_4$ is shown in Fig. 1. Two exothermic peaks with maxima at 1150 °C and 1240 °C, and two endothermic peaks centered at *ca.* 1200 °C and 1270 °C were observed in this profile. These temperatures having been obtained from the calibration of the sample thermocouple. It is to be noted that there is no obvious interpretation of the peaks, although it is likely to correspond to a phase transition reported by a number of workers [10-12]. These data were used to define the range of temperatures for XRD investigation to between 1100 and 1350 °C.

Powder XRD patterns of the calcined ZT powders are given in Figs. 2-4. In general, the strongest reflections apparent in the majority of the XRD patterns indicate the formation of zirconium titanate phase, $ZrTiO_4$, which could be matched with JCPDS file no. 34-415. To a first approximation, this major phase has orthorhombic structure, space group *Pnab* (no. 60), with cell parameter a = 503 pm, b = 549 pm and c = 480 pm. It is also of interest to point that no evidence has been obtained for the existence of the α–PbO_2–like orthorhombic phase (space group *Pcnb*) reported by Newnham [9]. Depending on the calcinations conditions, at least four minor phases were identified, *i.e.* monoclinic-ZrO_2 (*), tetragonal-ZrO_2 (∇), anatase-TiO_2 (•) and rutile-TiO_2 (+). The additional reflections of these minor phases can be correlated with JCPDS files numbers 37-1484, 17-923, 21-1272 and 21-1276, respectively. Precursor ZrO_2 has a baddeleyite-type structure with monoclinic unit cell (a = 5.31 Å, b = 5.21 Å, c = 5.14 Å and β = 99.22°), space group $P2_1/a$ (no. 14), whereas tetragonal symmetry (a = 3.78 Å and c = 9.51 Å) is

associated with anatase-TiO_2 precursor, space group $I4_1/amd$ (no. 141). Both minor phases of ZrO_2 (∇) and TiO_2 (•) have tetragonal symmetry with unit cell parameters: a = 5.12 Å and c = 5.25 Å, space group $P4m2$ (no. 115), and a = 3.78 Å and c = 9.51 Å, space group $P4_2/mnm$ (no.136), respectively. It is well established that there are a number of polymorphic forms of ZrO_2 and TiO_2 stable at different temperature and pressures. In the work reported here, monoclinic/tetragonal transformations of ZrO_2 and the anatase/rutile transformation of TiO_2 have been found. Monoclinic zirconia (*) is detected from the original mixture up to 1200 °C, whereas partial conversion to tetragonal zirconia (∇) was observed after heating at 1100 °C, which is associated to the DTA exothermic effect previously observed in Fig. 1. It is seen that completed conversion of anatase-TiO_2 (•) precursor to rutile (+) was found after calcined at 1100 °C, in agreement with other work [21]. No evidence of Ti_2ZrO was found, nor was there any indication of the orthorhombic phase of $Zr_5Ti_7O_{24}$ [22] being present.

This study shows that minor amount of the ZrO_2 and TiO_2 phases tend to co-exist along with the zirconium titanate $ZrTiO_4$ phase, after calcinations in the range 1100 to 1200 °C. By increasing the calcination temperature, the yield of $ZrTiO_4$ phase increases significantly until 1300 °C, whereafter higher temperatures do not enhance the yield (Fig. 2). Apart from the calcination temperature, the effect of dwell time was also found to be quite significant (Fig. 3). It is seen that the single phase of $ZrTiO_4$ (yield of 100% within the limitations of the XRD technique) was found to be possible only in powders, calcined at 1300 °C with dwell time of 4 h or more. In the present study, an attempt was also made to calcine ZT powders under various heating/cooling rates (Fig. 4). In this connection, it is obviously that the yield of $ZrTiO_4$ phase did not vary significantly with different temperature changing rates and fast heating/cooling rates of up to 20 °C/min. can be used

for the preparation of single phase ZT powders. It may be concluded that, over a wide range of calcinations conditions, single phase $ZrTiO_4$ cannot be straightforwardly formed via a solid state mixed oxide synthetic route. The experimental work carried out here suggests that the optimal calcination conditions for single phase $ZrTiO_4$ is 1300 °C for 4 h with heating/cooling rates as fast as 20 °C/min.

The morphological evolution during calcination was investigated by scanning electron microscopy (SEM). Micrographs of ZT powders calcined at various temperatures from 1100 to 1300 °C are shown in Fig. 5. In general, the particles are agglomerated and basically irregular in shape, with a substantial variation in particle size, particularly in samples calcined at high temperatures. The particle diameter was found to be about 0.2-2.5 μm in these SEM micrographs. The results indicate that averaged particle size and degree of agglomeration tend to increase with calcination temperature. Moreover, the grain shape tends towards greater sphericity at higher temperatures. Energy dispersive X-ray (EDX) analysis showed the calcined compositions of the powder calcined at 1300 ° C for 4 h with heating/cooling rates of 20 ° C/min. to be $ZrTiO_4$, in agreement with XRD results.

4. Conclusions

Single-phase of zirconium titanate powders may be produced by employing a solid state reaction process using oxides as starting materials. Evidence has been obtained for a 100% yield of an orthorhombic $ZrTiO_4$ at a calcination temperature of 1300 °C for 4 h with heating/cooling rates of 20 °C/min. The resulting ZT powders consist of agglomerated particles of 0.2 to 2.5 μm in size, which are rounded in morphology.

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Figure captions

Fig. 1 A DTA curve for the mixture of ZrO_2-TiO_2 powder.

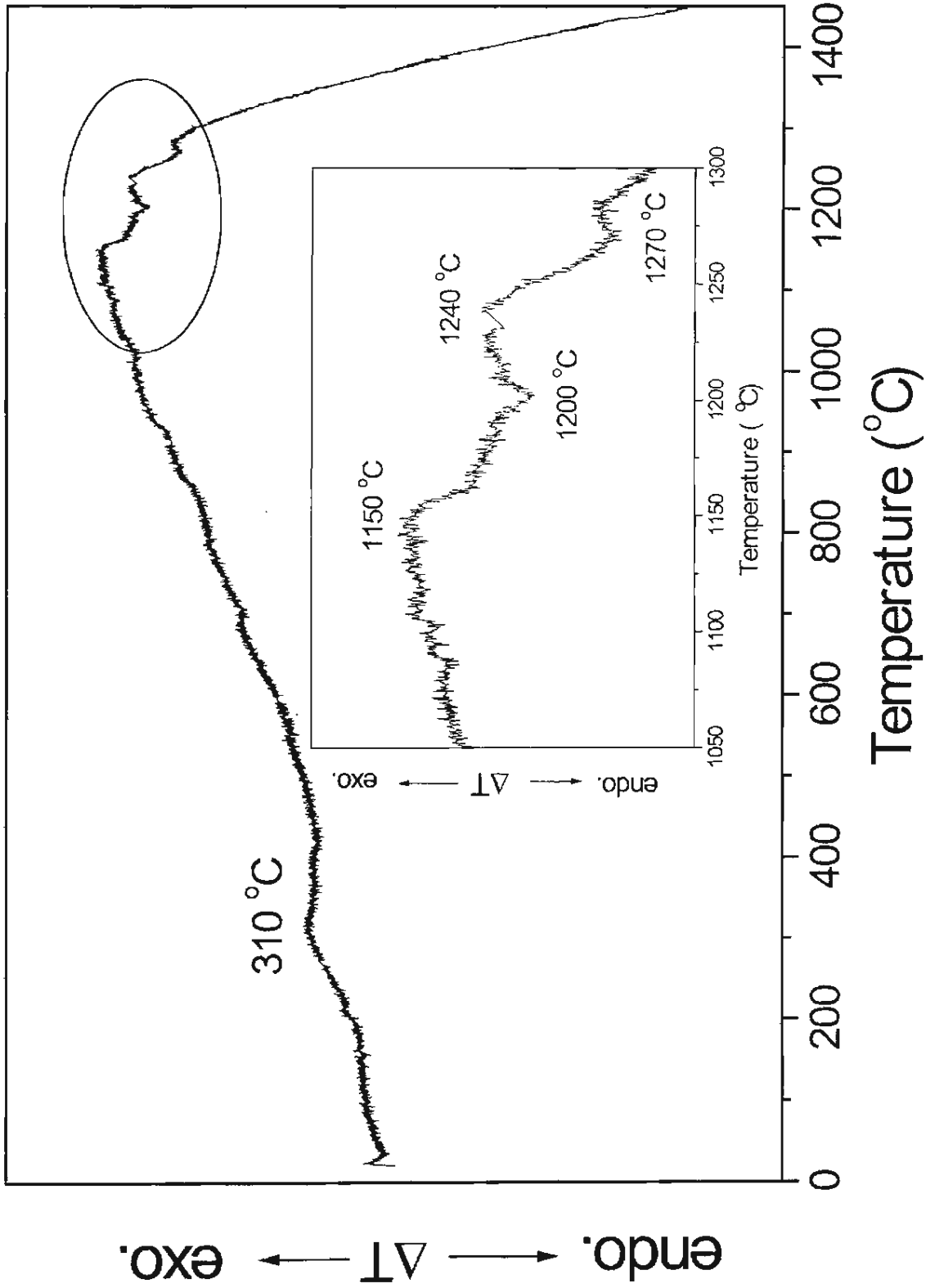
Fig. 2 XRD patterns of ZT powder calcined at various temperatures for 4 h with heating/cooling rates of 20 °C/min.

Fig. 3 XRD patterns of ZT powder calcined at 1300 °C with heating/cooling rates of 20 °C/min for various dwell times.

Fig. 4 XRD patterns of ZT powder calcined at 1300 °C for 4 h with various heating/cooling rates

Fig. 5 SEM micrographs of the ZT powders calcined at (a) 1100 °C, (b) 1175 °C, (c) 1200 °C and (d) 1300 °C

Fig.: Ananta et al.



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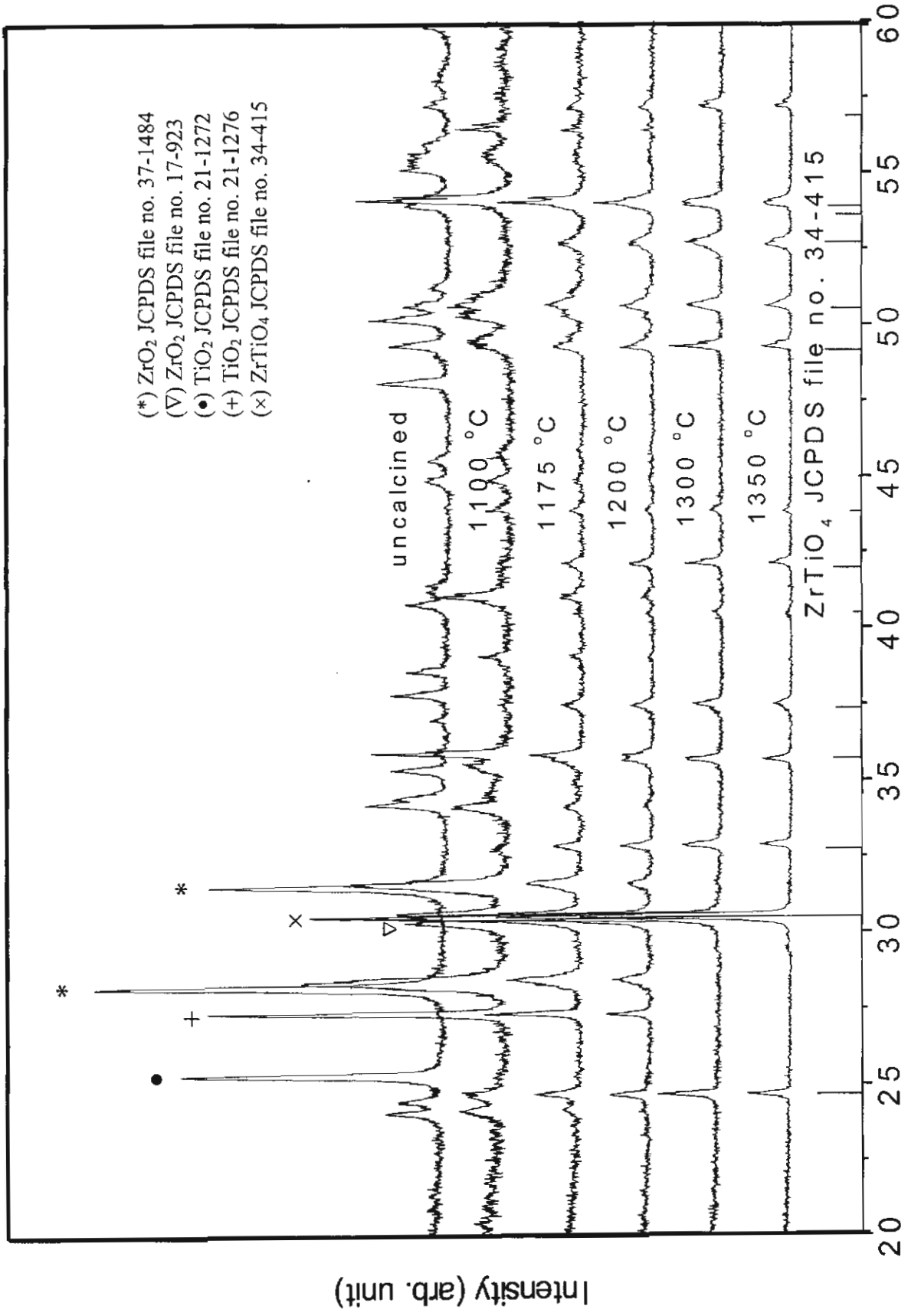

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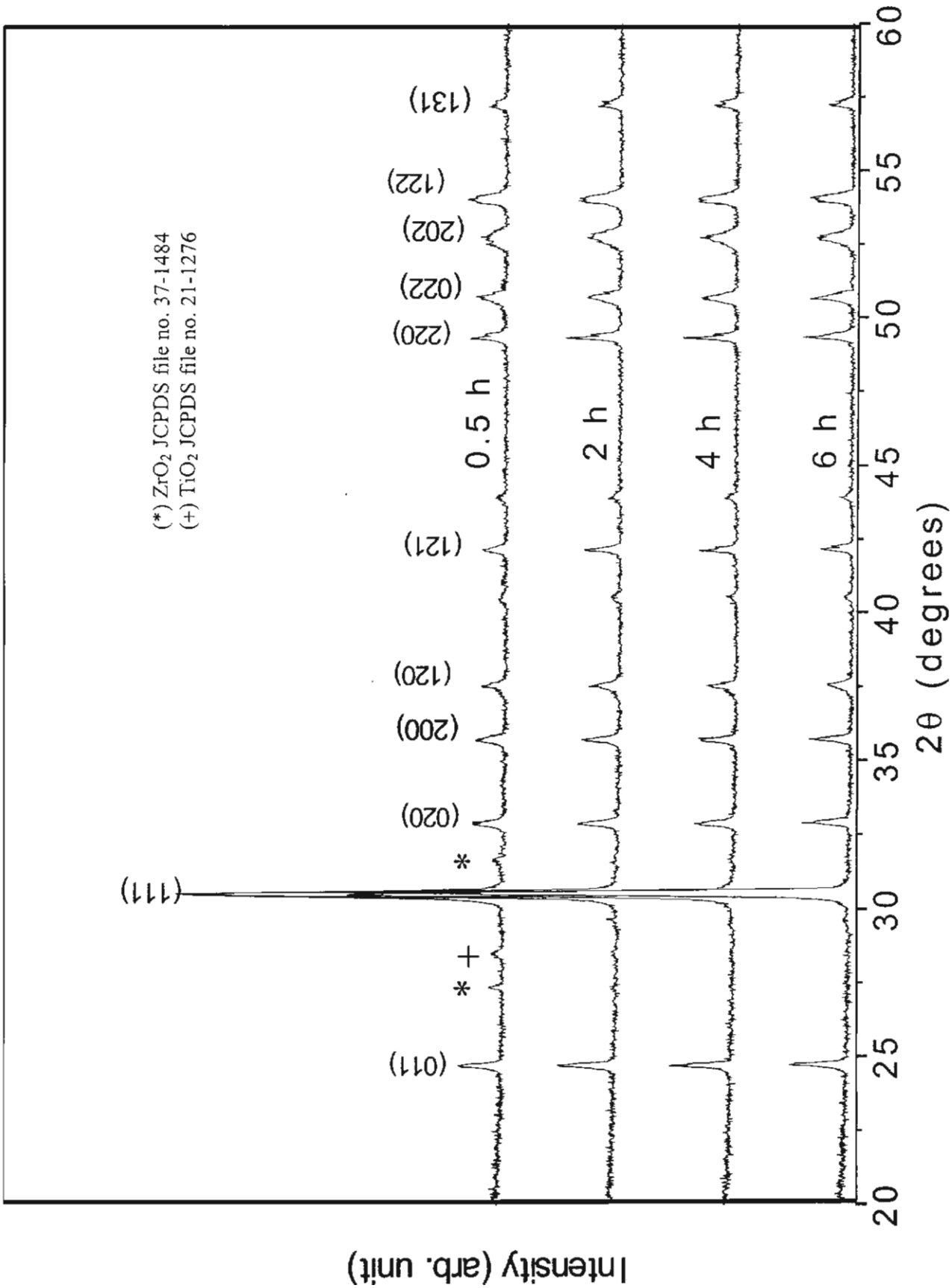

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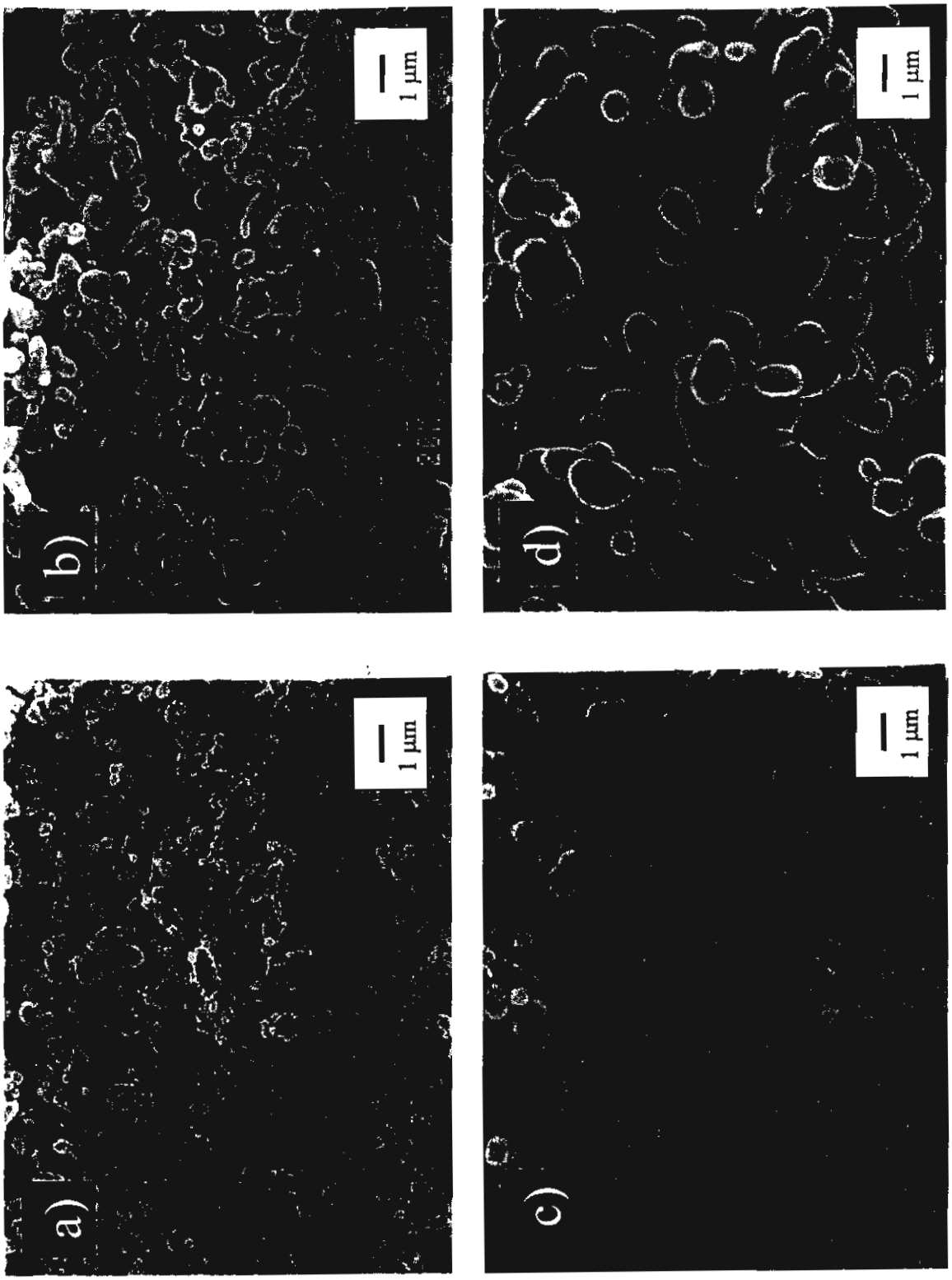

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A Modified Two-Stage Mixed Oxide Synthetic Route to Lead Zirconate Titanate Powders

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Abstract

An approach to synthesis lead zirconate titanate [$Pb(Zr_{1-x}Ti_x)O_3$; PZT] powders with a modified two-stage mixed oxide synthetic route has been developed. To ensure a single-phase perovskite formation, an intermediate phase of zirconium titanate ($ZrTiO_4$) was employed as starting precursor. The formation of perovskite phase in the calcined PZT powder has been investigated as a function of calcination temperature and time by DTA and XRD techniques. The particle size distribution of calcined powders was determined by laser diffraction, with the morphology, phase composition and crystal structure determined via SEM and EDX techniques. It has been found that the unreacted PbO and $ZrTiO_4$ phases tend to form together with PZT, with the latter appearing in both tetragonal and rhombohedral phases, depending on calcination conditions. It is seen that optimisation of calcination conditions can lead to a 100 % yield of PZT in a tetragonal phase.

Keywords: Lead zirconate titanate; PZT powder; Perovskite; Calcination; Phase formation

1. Introduction

Lead zirconate titanate, $Pb(Zr_{1-x}Ti_x)O_3$ or PZT, is one of the most widely used piezoelectric materials with a perovskite structure. The compositions close to the morphotropic phase boundary (MPB) have been extensively exploited in commercial[1,2]. The excellent piezoelectric and electrostrictive properties make it a promising material for sonar, modulator, ferroelectric memory, optoelectronic, piezoelectric and electrostrictive actuator, and electromechanical transducer applications[3,4]. In connection with these applications, the ideal material would provide high coupling coefficient and relative permittivity over the operational temperature, together with a low ageing rate. However, a practical limitation to the utilization of these materials in device applications has been the lack of a simple, reproducible fabrication technique for a pure perovskite phase with consistent composition and properties. The main hindrance to the commercial exploitation of lead-based complex perovskites arises from processing difficulties, concerned with the high volatility of lead oxide and the formation of pyrochlore phase[5,6]. To compensate for the lead loss, excess lead oxide precursor has been widely used with contradicted results[7,8]. However, excess PbO must be avoided in perovskite materials; the PbO excess either precipitates into the grain boundaries[9,10], damaging the electrical properties, or shifts the PZT composition toward the titanium-lean side, because TiO_2 has higher solubility than ZrO_2 in the PbO liquid phase.

There has been a great deal of interest in the preparation of single-phase PZT powders as well as in the sintering and piezoelectric properties of PZT-based ceramics. The mixed oxide synthetic route is probably one of the most fundamental, practical routine methods which has been used, and it has been developed and modified in both scientific research and industrial mass production for many years[11,12]. In general, PZT powders prepared by a mixed oxide route have spatial fluctuations in their compositions. The extent

of the fluctuation depends on the characteristics of the starting powders as well as on the processing schedule. The reaction sequence through which PZT are formed by solid state reactions has been investigated by many workers but with varying conclusions[13-16]. When the calcinations is performed in one step, *i.e.* starting from the three individual oxide, the problem of PbO vaporization limits the calcinations temperature and as a consequence prolongs the calcinations. It has been shown that increases homogeneity, which enhances the final properties of the PZT solid solution, can be achieved by carrying out the calcinations in two steps[17,18]. Mori *et al.*[13] were the first to study the mechanisms of a two-step reaction, initiated by the constituent oxides reacting to form a solid solution of lead titanate ($PbTiO_3$) and zirconium oxide, which later homogenized to form the PZT phase. On the other hand, Speri[14] proposed a three step reaction sequence which was further substantiated by Hanky and Biggers[15]. The formation of PZT via a homogenisation process, commencing at 700 °C, by interdiffusion of Zr^{4+} and Ti^{4+} within and between the PZT phases formed at the original PbO/ZrO_2 and $PbTiO_3/ZrO_2$ interfaces was proposed by Chandratreya *et al.*[16]. However, this sequence does not agree with the two stage process proposed by Mori *et al.*[13]. Similar problem of pyrochlore formation have been encountered in the preparation of lead magnesium niobate (PMN) powders, where the use of the B-site precursor $MgNb_2O_6$ has been proposed by Swart and Shrout[17] as an effective way of producing PMN powder in high yield. More recently, Babushkin *et al.*[18] subsequently combined the approach of Swart and Shrout with that of Mori *et al.* by investigating a two-stage synthesis with $Zr_{0.52}Ti_{0.48}O_2$ as a precursor. The essentially pyrochlore-free powders obtained could be attributed to its high reactivity with PbO. Whereas some workers have been prompted to investigate synthetic route different from the mixed oxide approach, e.g. sol-gel[19], hydrothermal[20], co-precipitation[21], and combustion[22], the overall aim of the work described here is to refine the two-stage mixed oxide method further. An attempt has been

made to synthesis and investigate the PZT powders by employing an intermediate phase of zirconium titanate ($ZrTiO_4$) as a key precursor. The following elements are investigated in this connection: (a) development of a modified mixed oxide synthetic route; (b) reproducibility of the method and (c) the ability to use laboratory grade chemical.

2. Experimental procedure

$Pb(Zr_{0.5}Ti_{0.5})O_3$ was synthesised by the solid state reaction of appropriate amounts of laboratory grade lead oxide, PbO, zirconium oxide, ZrO_2 and titanium oxide, TiO_2 (Fluka, > 99 % purity). The three oxide powders exhibited an average particle size in the range of 5.0 to 10.0 μm. The following reaction sequences are proposed for the formation of PZT:

$$ZrO_2(s) + TiO_2(s) \rightarrow ZrTiO_4(s) \quad (1)$$

$$2PbO(s) + ZrTiO_4(s) \rightarrow 2Pb(Zr_{0.5}Ti_{0.5})O_3(s) \quad (2)$$

Powder-processing was carried out as shown schematically in Fig. 1. The methods of mixing, drying, grinding, firing and sieving of the products were similar to those employed in the preparation of the perovskite-like $Pb(Mg_{1/3}Nb_{2/3})O_3$, $Pb(Fe_{1/2}Nb_{1/2})O_3$ and $La(Mg_{2/3}Nb_{1/3})O_3$ powders as described previously[23,24]. Various calcination conditions, *i.e.* temperatures ranging from 700 to 950 °C, soaking times ranging from 1 to 4 h and heating/cooling rates ranging from 2 to 10 °C.min^{-1}, were selected, in order to investigate the formation of lead zirconate titanate. The reactions of the uncalcined PZT powders taking place during heat treatment were investigated by differential thermal analysis (DTA) (NETZSCH-Gerätebau GmbH Thermal Analysis STA 409) using a heating rate of 10 °C.min^{-1} in air from room temperature up to 1000 °C. Calcined powders were subsequently examined by room temperature X-ray diffraction (XRD; Philips PW 1729

diffractometer) using CuK_α radiation, to identify the phases formed and optimum calcination conditions for the manufacture of PZT powder. The particle size distributions of the calcined powders were determined by laser scattering techniques (MasterSizer, Malvern, UK). Powder morphologies and grain sizes were directly imaged using scanning electron microscopy (SEM; JEOL JSM-840A). The chemical compositions of the phases formed were elucidated by an energy-dispersive X-ray (EDX) analyser with an ultra-thin window. EDX spectra were quantified with the virtual standards peaks supplied with the Oxford Instruments eXL software.

3. Results and discussion

A DTA curve obtained for a powder mixed in the stoichiometric proportions of $Pb(Zr_{0.5}Ti_{0.5})O_3$ is shown in Fig. 2. In the temperature range 200° – 400 °C, the sample shows several large exothermic peaks in the DTA curve. These DTA peaks can be attribute to the decomposition of the organic species from the milling process. The different temperature, intensities, and shapes of the thermal peaks probably are related to the different natures of the organic species and consequently, caused by the removal of species differently bounded in the network. In the temperature range 700° – 1000 °C, both exothermic and endothermic peaks are observed in the DTA curve. The enlarge zone of this DTA curve showed that the exothermic peak centered at ~ 780 °C, may result from perovskite phase crystallization, and the last endothermic peak centeed at ~ 840 °C, may be caused by the decomposition of lead oxide. These temperatures have been obtained from the calibration of the sample thermocouple and were used to define the ranges of temperatures (700 to 950 °C), soaking time (1 to 4 h) and heating/cooling rates (2 to 10 $^{\circ}C.min^{-1}$) for the XRD investigation.

Powder XRD patterns of the calcined powders are given in Figs. 3-8, with the corresponding JCPDS patterns also shown. The optimum calcination temperature for the formation of a high purity PZT phase was found to be about 760 °C, *i.e.* slightly lower than the exothermic temperature in Fig. 2. In general, the strongest reflections apparent in the majority of the XRD patterns indicate the formation of two lead zirconate titanate phases. These can be matched with JCPDS file numbers 50-0346 and 73-2022 for the tetragonal $Pb(Zr_{0.44}Ti_{0.56})O_3$ and rhombohedral $Pb(Zr_{0.52}Ti_{0.48})O_3$ (Fig. 4), respectively. As is well known, the variations in composition may lead to a diffuse MPB between the tetragonal and rhombohedral PZT phases[25]. The most obvious different between the patterns for tetragonal and rhombohedral PZT phases concerns the presence of a splitting of (002)/(200) peak at two-theta ~ 45° for the former phase (Fig. 5).

It is seen that, with the exception of powder calcined at 950 °C, the rhombohedral PZT phase is always present in the product. Moreover, some additional weak reflections are found in the XRD patterns (marked by ▾ and *), which correlate with the precursors PbO and $ZrTiO_4$, respectively. The relative amounts of the two majority PZT phases, *i.e.* tetragonal and rhombohedral, which are present in each calcined powder, may in principle, be calculated from the intensities of the most intense X-ray reflections:

$$\text{wt\% tetragonal phase} = \left(\frac{I_T}{I_T + I_R} \right) \times 100 \qquad (3)$$

This equation is analogous to the well known equation [17] widely employed in connection with the fabrication of complex perovskite materials. It should be seen as a first approximation since its applicability requires comparable maximum intensities of the peaks of tetragonal and rhombohedral phases. Here I_T and I_R refer to the intensities of the {200} tetragonal and {020} rhombohedral peaks. For the purpose of estimating the concentrations of the phases present, Eq. (3) has been applied to the powder XRD patterns

obtained as given in Fig. 6. This study shows that minor amount of the unreacted PbO and $ZrTiO_4$ phases tend to co-exist along with the PZT phase, after scanning calcinations in the temperature range 700 to 740 °C. Upon calcination at 760°, the phases of PbO and $ZrTiO_4$ have been found completely disappear, and crystalline PZT of both tetragonal and rhombohedral is the only detectable phases in the powder. By increasing the calcination temperature from 760 to 950 °C, the yield of the tetragonal PZT phase increase significantly until at 950 °C, a single phase of tetragonal PZT is formed (Fig. 7). Neither lead titanate ($PbTiO_3$) or lead zirconate ($PbZrO_3$) earlier reported by Chakrabarti and Maiti[26] has been found in this study. It is also of interest to point out that no evidence has been obtained for the existence of pyrochlore phase $Pb_2Ti_2O_7$ reported by Babushkin *et al.*[27].

Relative intensities (areas) however did not vary significantly with soaking times, indicating full crystallisation to have occurred at relatively shorter calcination times. In this work, the single phase of perovskite PZT (yield of 100% within the limitations of the XRD technique) was found to be possible only in powders, calcined at their optimum temperatures with short soaking time of only 2 hours. This is probably due to the effectiveness of a carefully optimised reaction to form single-phase zirconium titanate precursor powders (Fig. 8). The effect of heating/cooling rates on phase formation was found to be quite significant (Fig. 9). It is seen that the optimum heating/cooling rates for the formation of a high purity PZT phase was found to be at 5 °C.min^{-1}.

Therefore, XRD results clearly show that, in general, the methodology presented in this work provide a simple method for preparing perovskite PZT powders via a solid state mixed oxide synthetic route without the addition of PbO in excess[7,8].

Figure 10 shows the particle size distribution of PZT powder after calcination at 760 °C for 2 h with heating/cooling rates of 5 °C.min^{-1}, indicating a uniform frequency distribution curve with an appreciable size fraction at about 1.2 μm within the range 0.2 to 5.0 μm. The morphological changes in the PZT powders formed by a two-stage mixed oxide are illustrated in Fig. 11 as a function of formation temperature. After calcinations at 720 to 800 ° C, the powders have similar morphology. They had spherical secondary particles composed of submicrometer-sized primary particulates. This structure is similar to that of $BaTiO_3$ powders synthesised by previous researchers[28]. The primary particles have sizes of ~ 0.05 – 0.20 μm, and the agglomerates measure ~ 1.0 – 80.0 μm. At 700 °C, three phases (PbO, $ZrTiO_4$ and PZT) were observed in X-ray diffraction analysis (Fig. 3), but from the SEM micrograph it was difficult to distinguish these three phases because of the lumpy particle morphology, indicating significant growth interaction in the multiphase composition. This granule characteristic will offer an apparent advantage towards achieving a high sintered density and homogeneous microstructure for PZT ceramic at a reduced sintering temperature.

4. Conclusions

A modified, two-stage mixed oxide synthetic route for preparing high purity PZT powders has been developed, which show a high level of reproducibility. By using a combination of XRD and SEM techniques, the effect of the calcination condition on phase transformation and particle size of PZT was examined. The firing condition has been found to have a pronounced effect on the formation of PZT phase and its particle size. The mixture of both tetragonal and rhombohedral phases with various sizes of irregular shaped particles was observed at low temperature while the tetragonal PZT phase with equisized clusters and hard agglomerates was found at high temperature.

Acknowledgements

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FIGURE CAPTIONS

Fig. 1 Preparation route for the PZT powder.

Fig. 2 A DTA curve for the mixture of PbO-$ZrTiO_4$ powder.

Fig. 3 Powder XRD patterns of the calcined powders at various calcinations temperatures for 2 h with heating/cooling rates of 30 $^{o}C.min^{-1}$.

Fig. 4 Computerised JCPDS data-matching confirms the formation of both tetragonal and rhombohedral PZT phases in the calcined powder.

Fig. 5 Enlarged XRD peaks for the tetragonal (T) and rhombohedral (R) phases as a function of calcinations temperatures.

Fig. 6 Calculated PZT phases as a function of calcinations conditions.

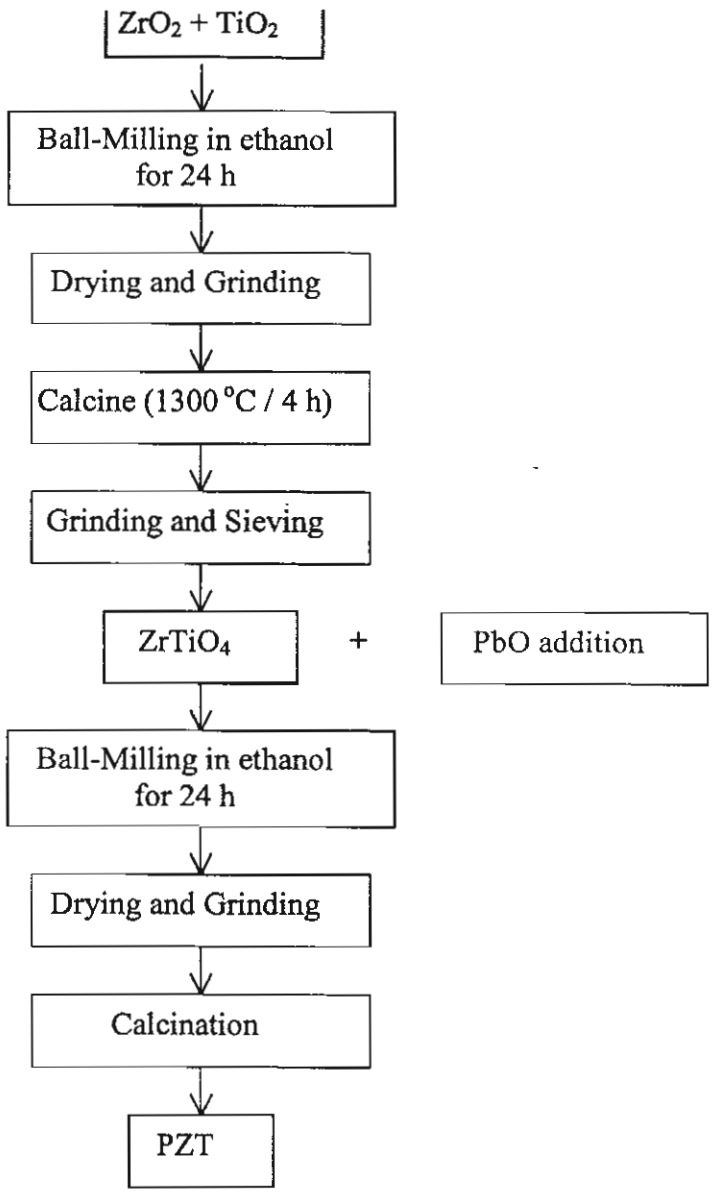
Fig. 7 Computerised JCPDS data-matching confirms the formation of the single-phase tetragonal PZT.

Fig. 8 Powder XRD patterns of the calcined powders at 760 ^{o}C with heating/cooling rates of 5 $^{o}C.min^{-1}$ for (a) 1h (b) 2h and (c) 4h.

Fig. 9 Powder XRD patterns of the calcined powders at 760 ^{o}C for 2 h with heating/cooling rates of (a) 2 ^{o}C/min (b) 5 ^{o}C/min and (c) 10 ^{o}C/min.

Fig. 10 The particle size distribution curve of the calcined PZT powder.

Fig. 11 SEM micrographs of the PZT powders calcined at (a) 720 ^{o}C, (b) 740 ^{o}C, (c) 780 ^{o}C and (d) 800 ^{o}C.



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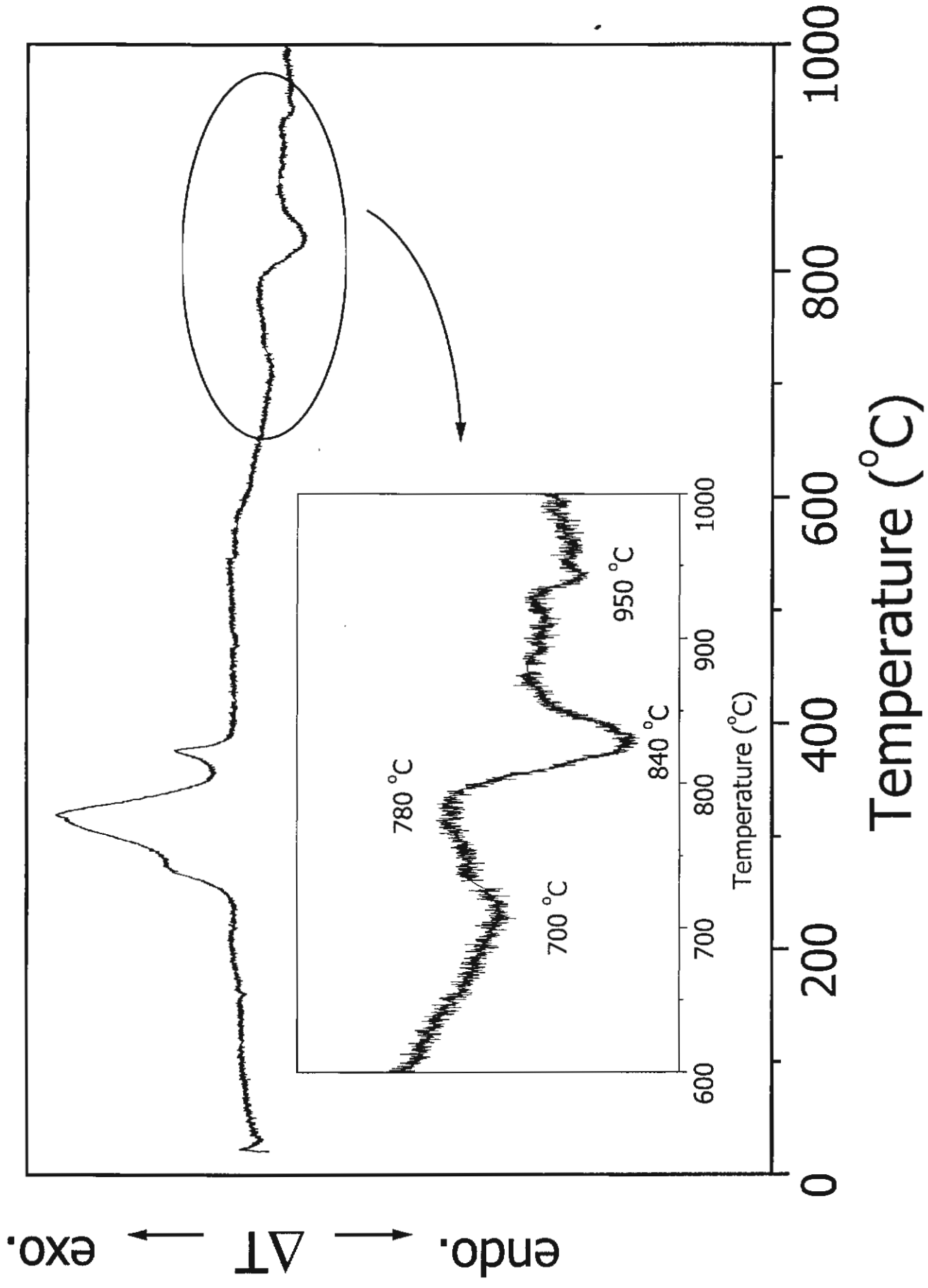

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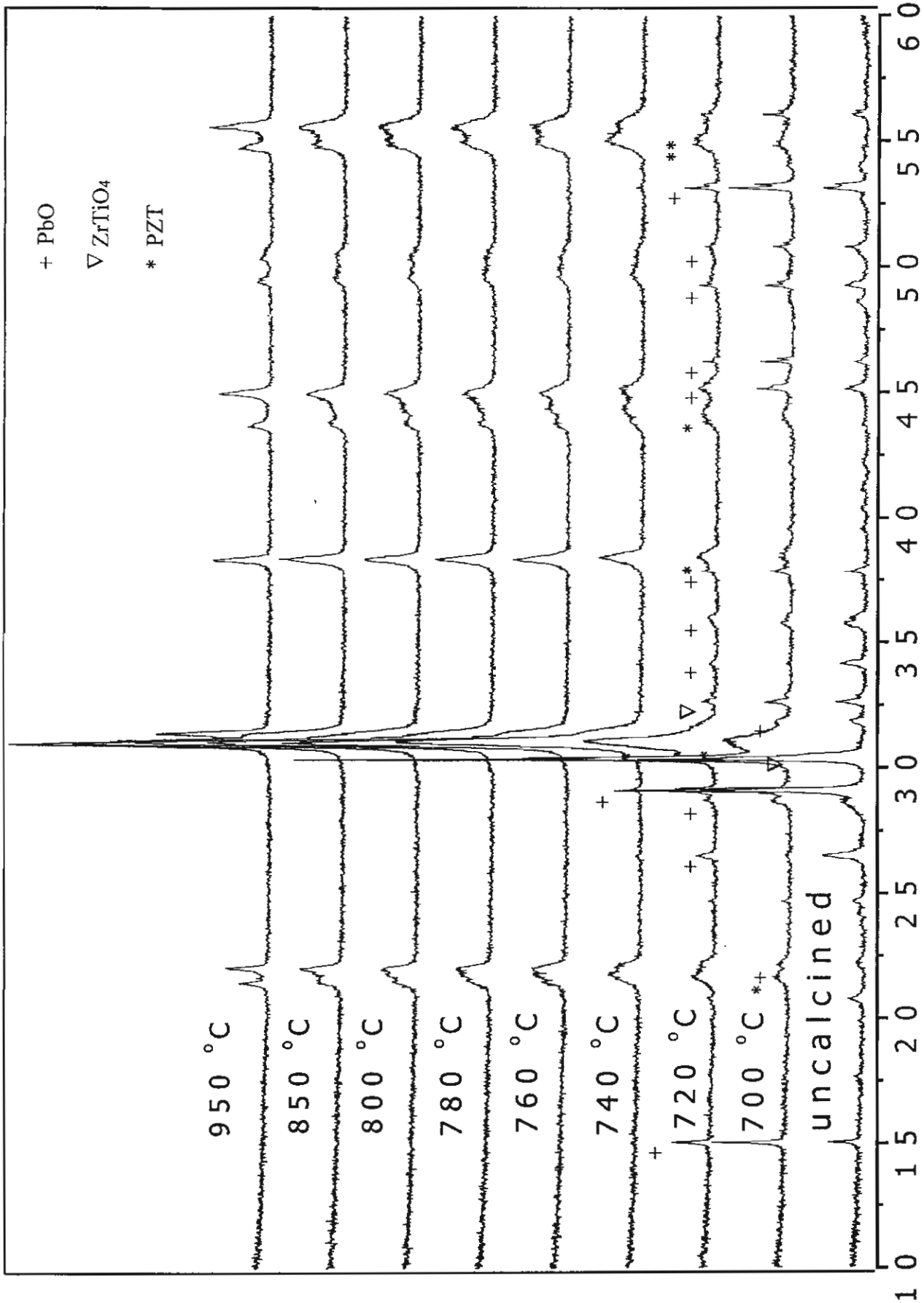

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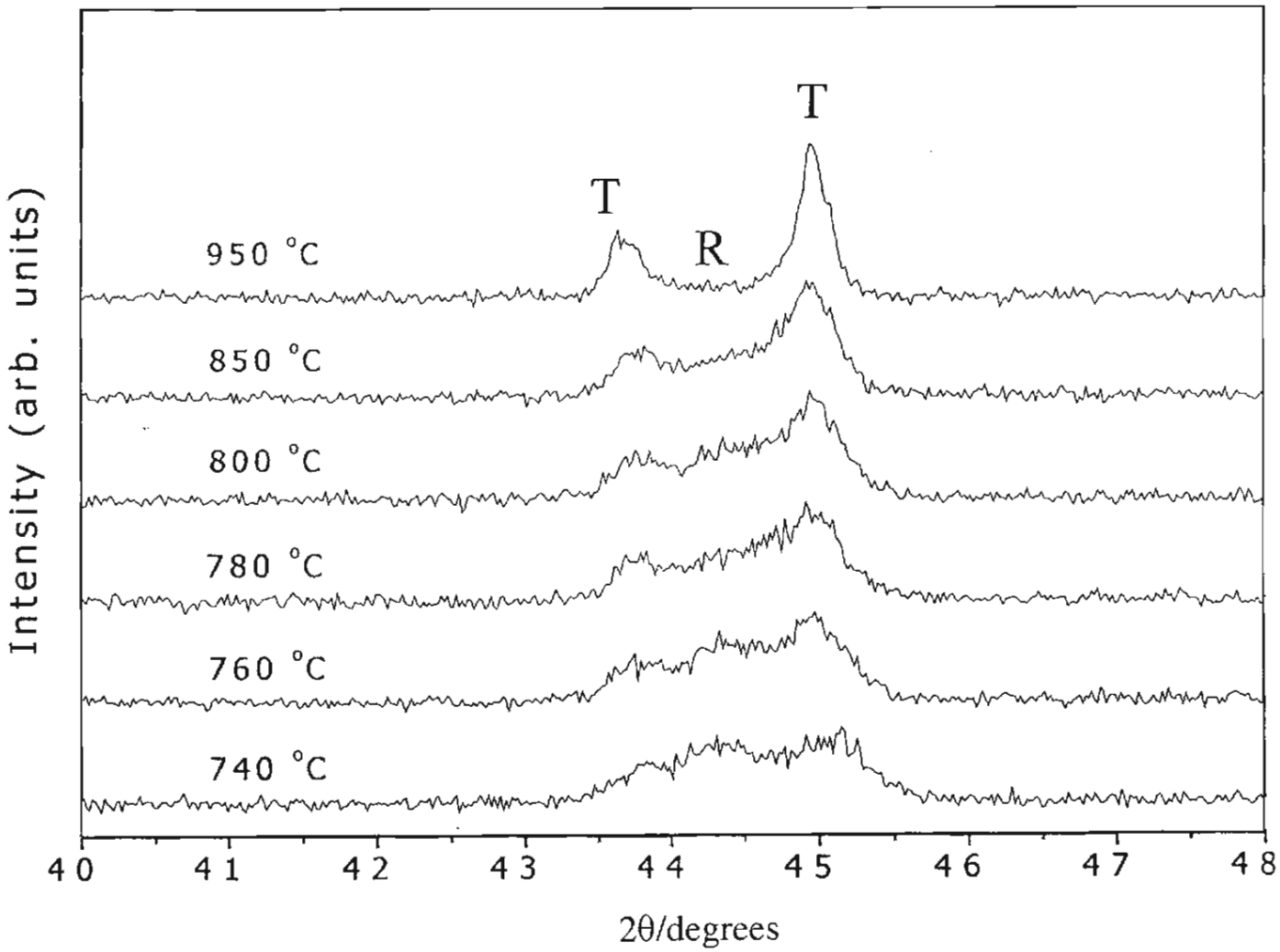

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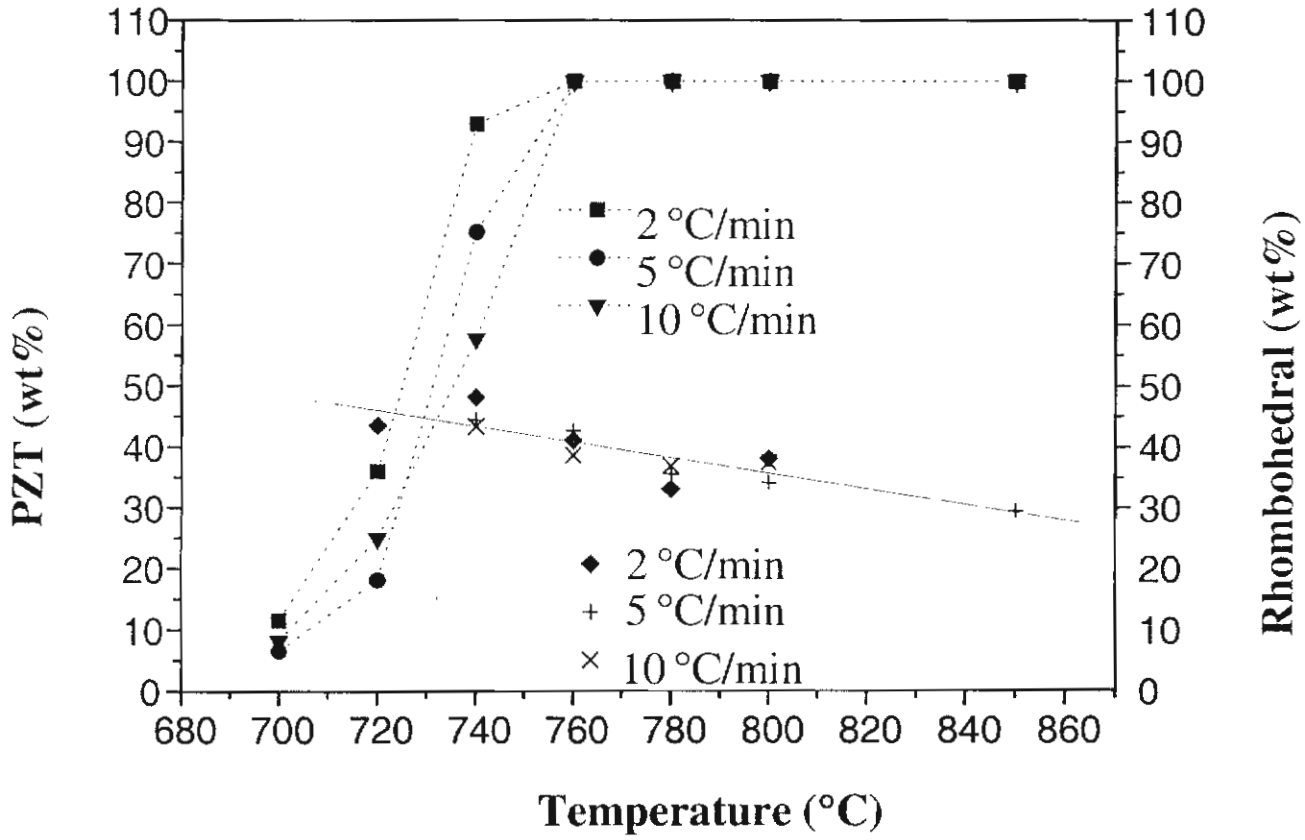

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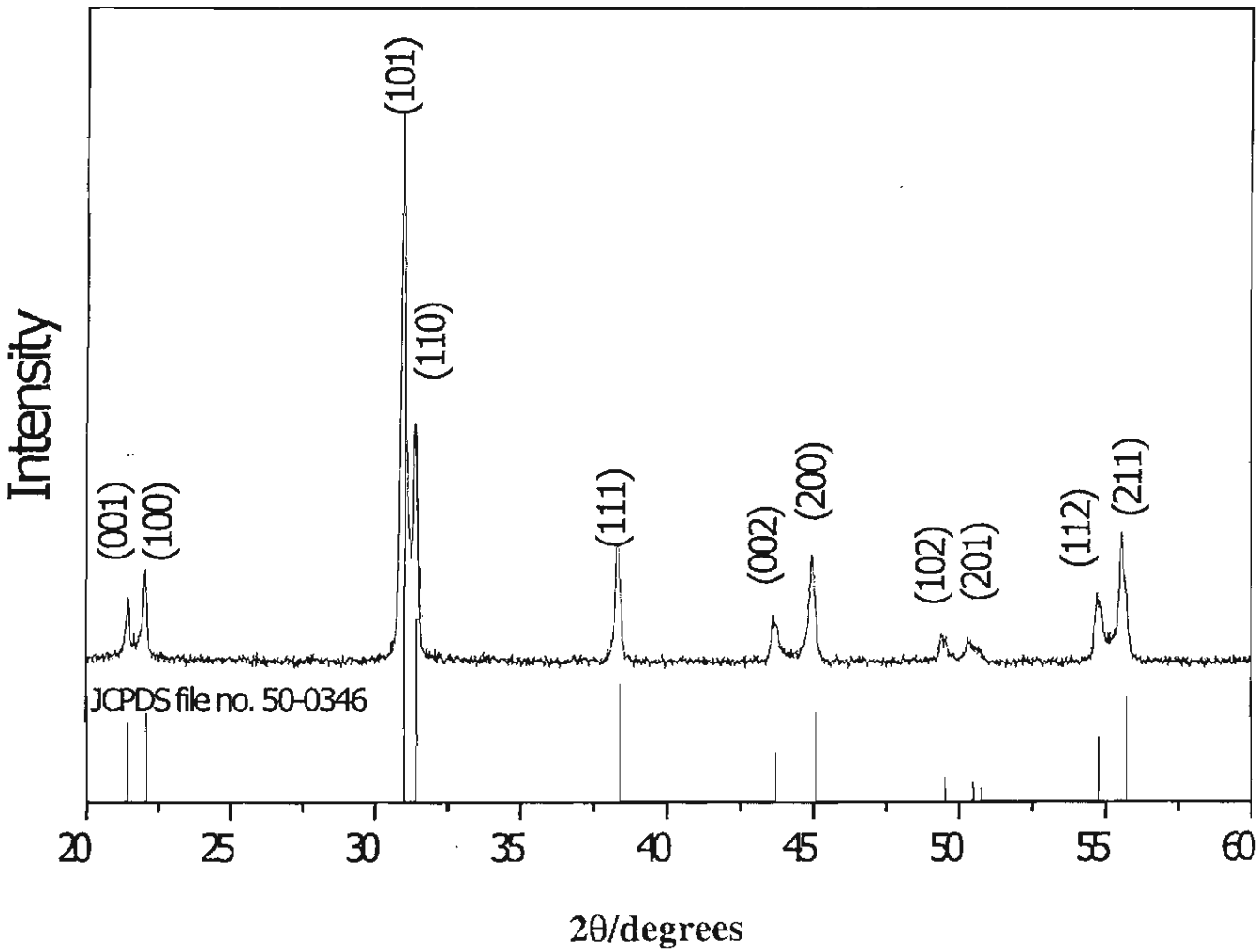

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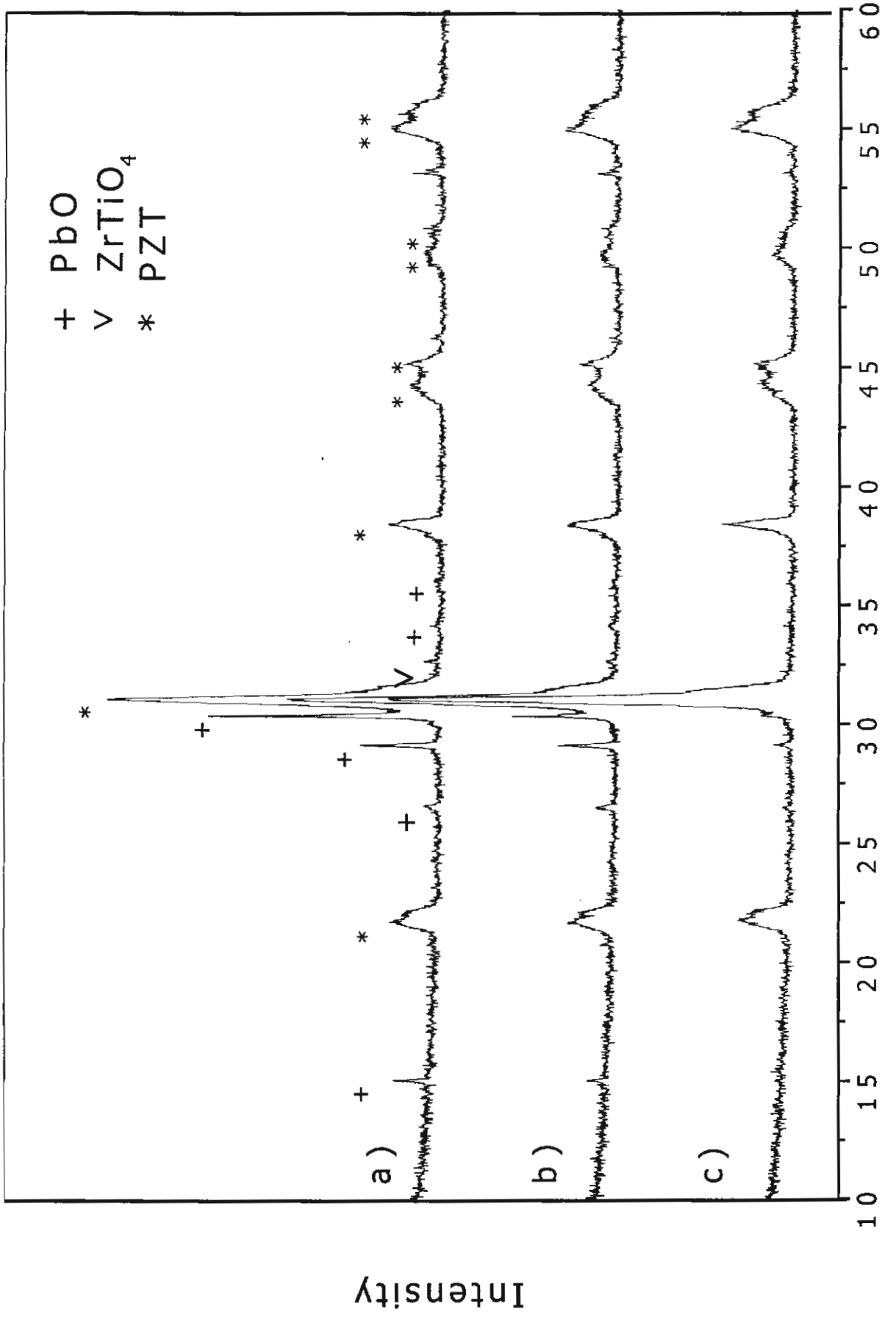


Fig. 9 Ananta et al.

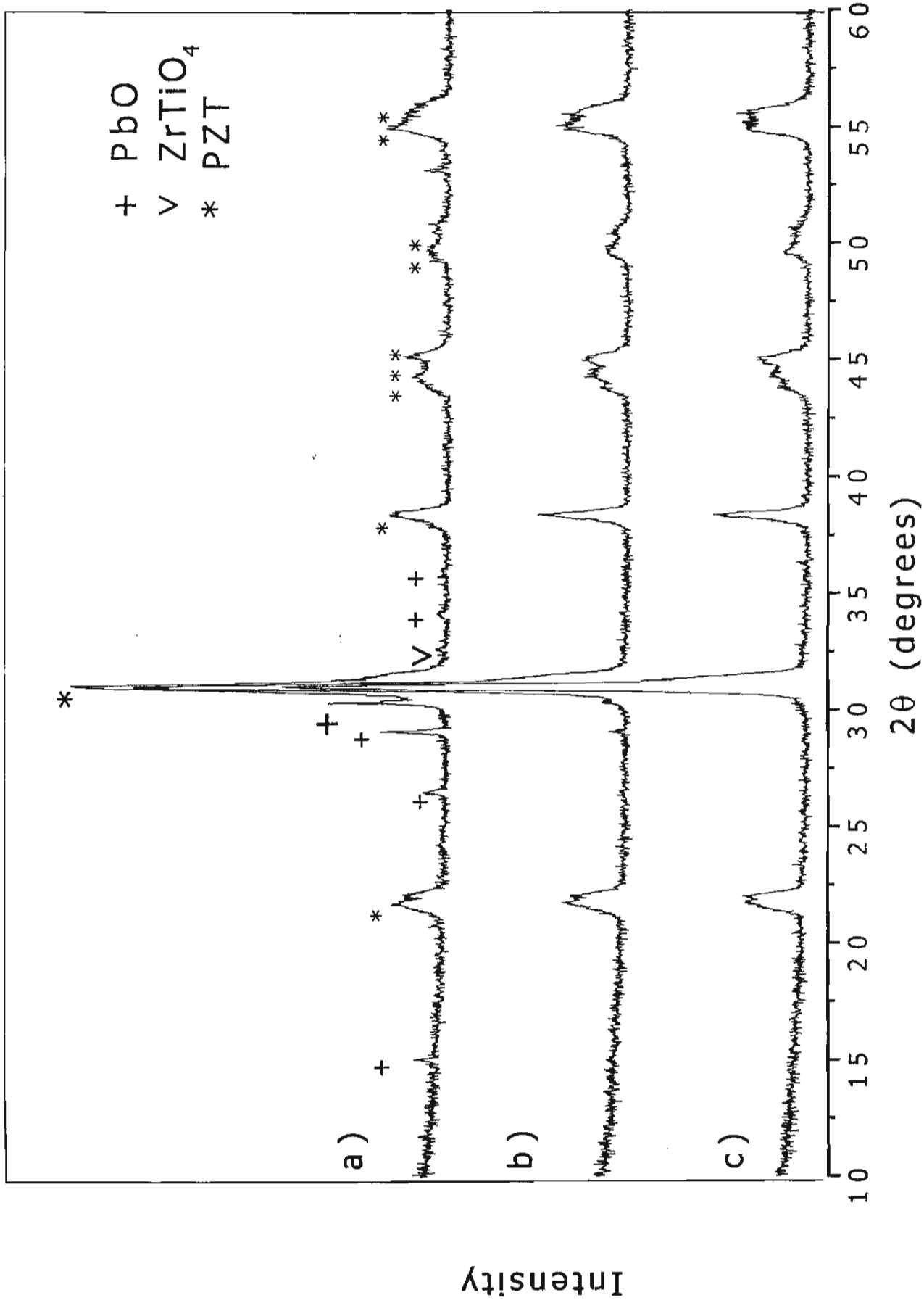


Fig. 10 Aranto et al.

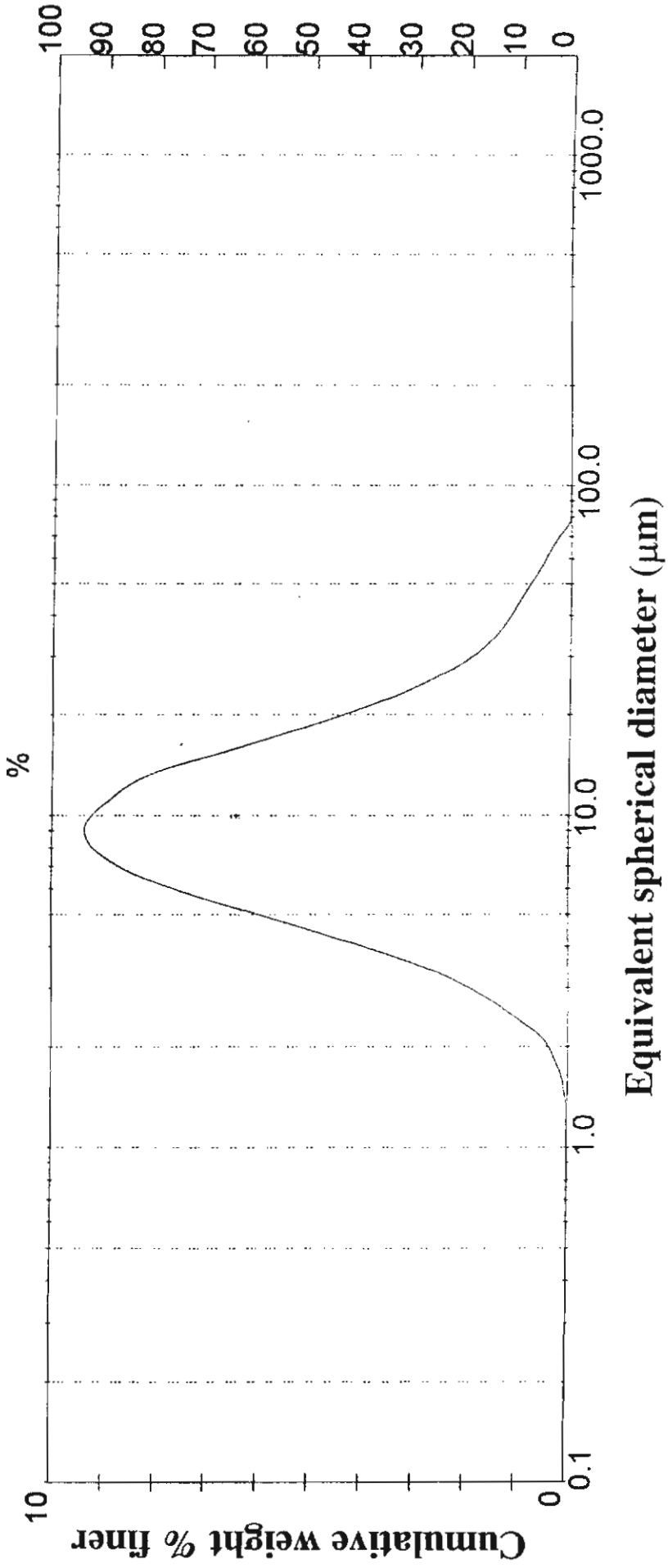
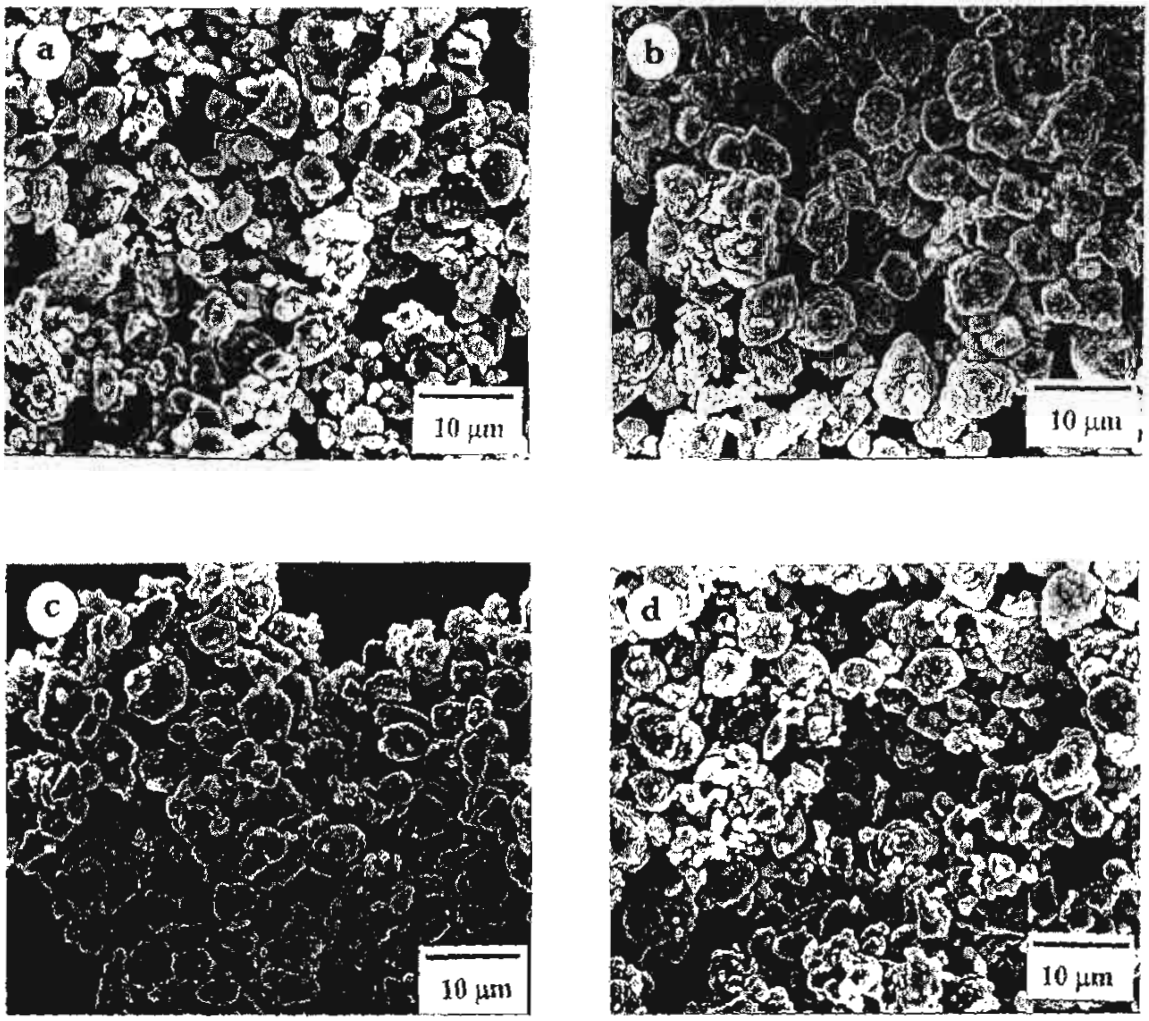


Fig. 11 Ananta et al.



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Poster Presentation

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Effect of Firing Temperatures on Morphology of Mixed Oxide $PbTiO_3$ Powders by Solid State Reaction

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Lead titanate (PT: $PbTiO_3$) is a perovskite-like structured ferroelectric material, with Pb^{2+} cations positioned in the A-site and Ti^{4+} cations occupying B-site.[1] It has been one of the most popular choice for many sensor, actuator, electronic and microelectronic applications, because of its high Curie temperature, high pyroelectric coefficient and high spontaneous polarisation.[2] However the difficulty in obtaining a single-phase perovskite product has been wildly reported.[3] In order to solve this problem, care must be taken into account during the processing with attention pored on the firing conditions. In this study, PT powders have been prepared by calcining PbO and TiO_2 precursors at various temperatures for 2 hours with constant heating/cooling rates of 5 ^{0}C/min. To study the phase development with increasing calcination temperature, all powders were examined by using X-ray diffraction technique (XRD). As shown in Fig.1,a high purity $PbTiO_3$ powder is obtainable only when the precusor is calcined at temperatures above 700 ^{0}C. SEM micrographs of all calcined powders are shown in Fig.2 (a-c). In general, the calcined PT powders consist of primary particle of 0.2 to 2 μm in size. They occures as large agglomerates of 0.5 to 3 μm in size in the samples calcined at 700 and 800 °C. However, at higher firing temperature,discreted particles with larger grains of 0.2 to 3 μm in size are clearly observed.

Acknowledgement

The authors wish to thank the Thailand Research Fund (TRF) for the financial supporting.

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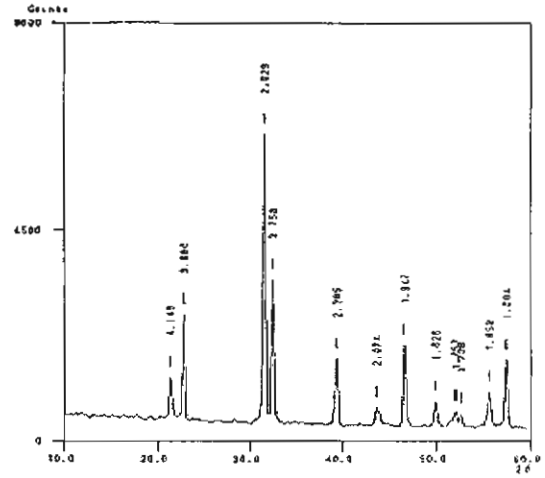

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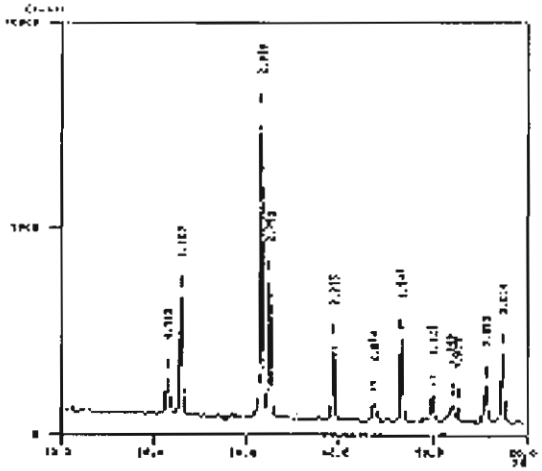

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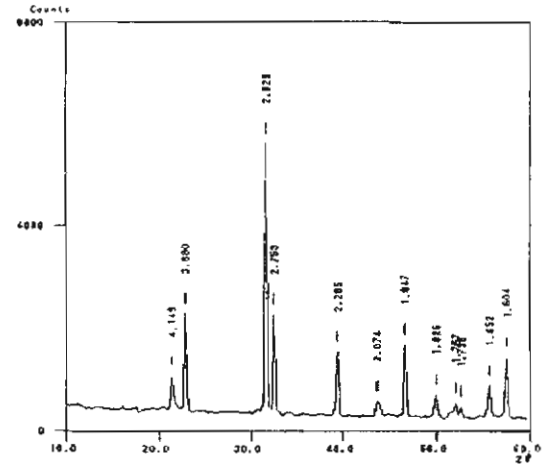

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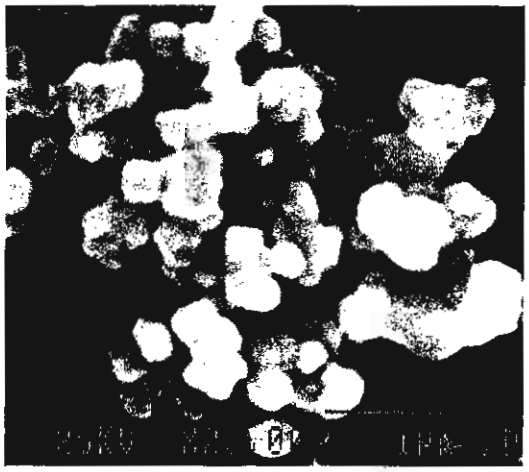
Figure 1. XRD patterns of $PbTiO_3$ powders calcined for 2 hours at : (a) 700 °C, (b) 800 °C, and (c) 1000 °C



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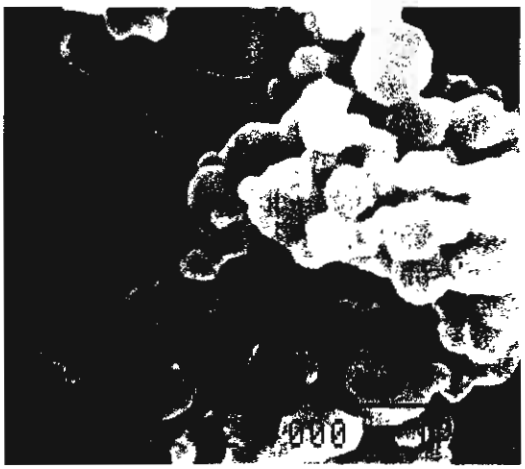

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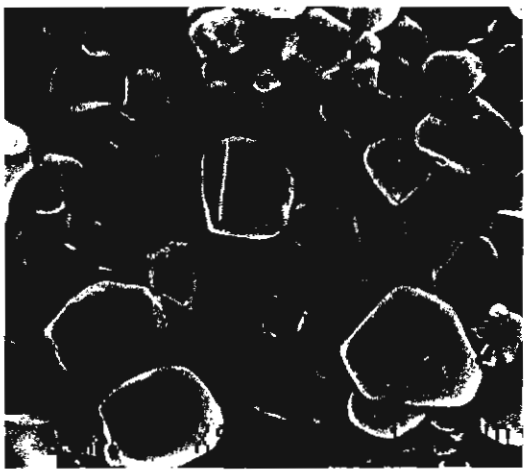

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Figure 2. SEM micrographs of $PbTiO_3$ powders calcined for 2 hours at : (a) 700 °C, (b) 800 °C, and (c) 1000 °C

Poster Presentation

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'. Thamjaree
Ananta
Tunkasiri

SEM and XRD Studies on PZT Powders Prepared by Using $PbZrO_3$ and $PbTiO_3$ Precursors

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g Mai 50200, Thailand

Perovskite type piezoelectric lead zirconate titanate, $Pb(Zr,Ti)O_3$ (PZT), exhibits excellent piezoelectric and electrostrictive properties, thus making it promising for several technologically demanding applications in electronics, ultrasonic transducers and electrostrictive actuators.[1] There are several types of very different fabrication routes that can be utilized to fabricate PZT.[2] While the effects of the processing variables have been qualitatively determined, the details of morphology evolution have not. There exists some controversy over the optimum processing sequence, which arises from unreported variations in powder preparation method, chemical composition and calcination conditions. Thus, in this study, we have looked at phase and morphology evolutions during firing of PZT powder under a variety of conditions and correlated the effects of calcining temperature on grain size and morphology evolution of the products. The composition of $Pb(Zr_{0.5}Ti_{0.5})O_3$ was prepared by a modified mixed oxides synthetic route using $PbZrO_3$ and $PbTiO_3$ procursors. Both precursors were fabricated by employing a conventional solid state reaction as previously described elsewhere.[3-4] The mixture of $PbZrO_3$ and $PbTiO_3$ powders was milled, dried and calcined in closed alumina crucible at the temperature range of 700 °C to 900 °C, for 4 hours. The phase identification of the calcined powders was conducted by X-ray diffraction (XRD) technique as shown in Fig. 1(a-c). Perovskite-like phase of PZT with some small amount of unknown phase (~11wt%) was observed in the sample calcined at the temperatures above 700 °C, whilst the unknown phase was found to decrease at higher firing temperatures. SEM micrographs of all calcined PZT powders are shown in Fig. 2(a-c). In general, the particles are agglomerate and basically irregular in shape. It is interesting to note that the average grain size was found gradually increased with the firing temperature. In the sample calcined at 700 °C, particles of different diameters ranging from 0.3-0.7 μm are revealed (Fig. 2(a)). Whilst, at 800 °C and 900°C, particles with the average grain size of about 0.7 μm (Fig.2(b)) and 0.9 μm (Fig.2(c)) are observed, respectively.

Acknowledgement

The authors wish to thank the Thailand Research Fund (TRF) for the financial support. Thanks are due to the staff of the Medical Science Research Equipment Center, Chiang Mai University for the SEM facilities.

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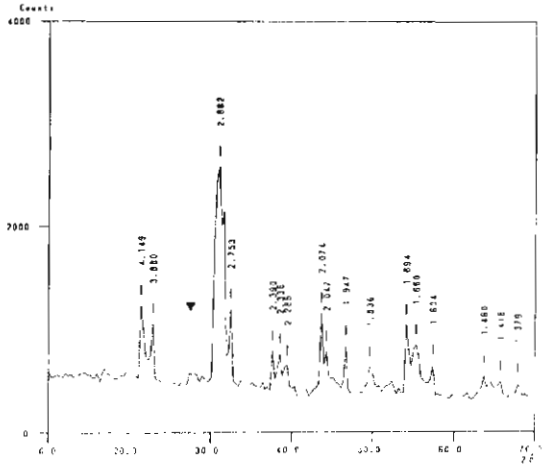

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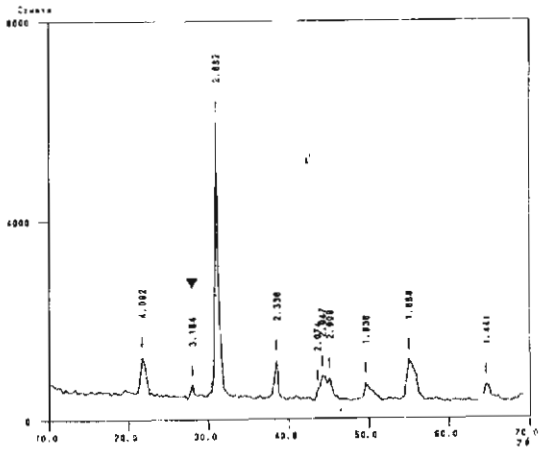

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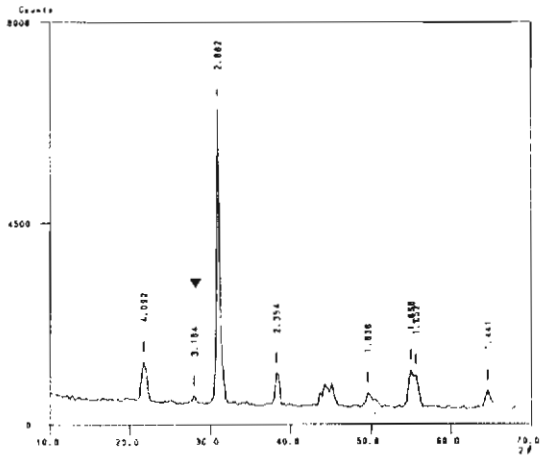

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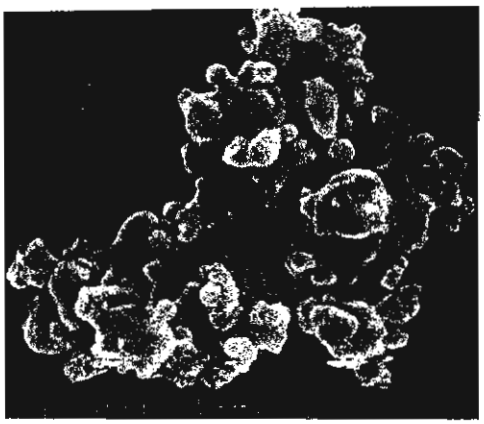
Figure 1. XRD traces of phase identification of the calcined powders (▼ refers to unknown phase)



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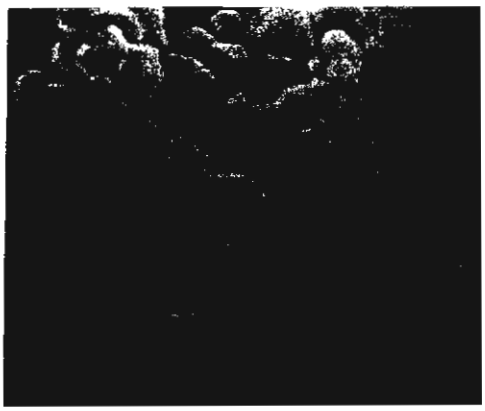

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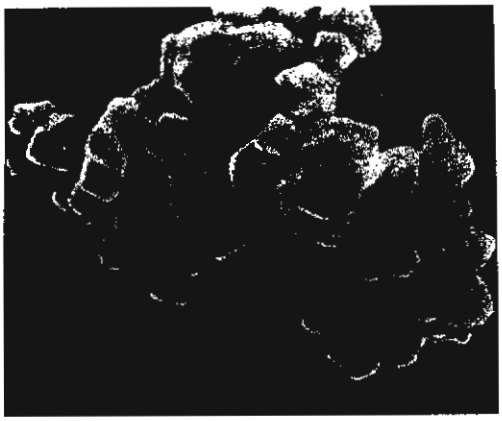

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Figure 2. SEM micrographs of calcined PZT powders.

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Lead Zirconate Titanate Powders Derived from A Modified Solid-State Reaction Technique

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For the past forty years, lead zirconium titanate ($Pb(Zr_xTi_{1-x})O_3$ or PZT) has been the most important piezoelectric perovskites among all the piezoelectric materials due to its excellent dielectric, piezoelectric, electro-optic, and many other properties. It has been used in wide range of applications, such as actuators, sensors, transducers and nonvolatile memories.[1] The conventional method of synthesizing PZT powders involves mixing the constituent oxides (PbO, TiO_2, ZrO_2) in stoichiometric ratios, followed by calcination at an appropriate temperature. It, however, often leads to particle coarsening and non-stoichiometry in composition of the resulting PZT powders.[2] In this work, PZT powders were prepared from intermediate phases of $ZrTiO_4$ (ZT) and PbO, which was treated by a solid-state reaction process. The phase formation and morphology of the calcined powders have been examined by using a combination technique between X-ray diffraction (XRD) and scanning electron microscopy (SEM). Fig.1 illustrates the X-ray diffraction patterns of powders calcined at different firing temperatures. It is seen that, after firing above 760°C, the majority peaks of the reflection patterns could be matched with the JCPDS file no.50-0346 for the perovskite phase $Pb(Zr_{0.44}Ti_{0.56})O_3$. The morphologies of powders formed by calcining the samples at various temperatures are show in Figure 1. In general, all powders exhibit hard agglomerated particles. These agglomerates were in fact made up of a substructure of smaller, ~ 0.3 μm, particles. The average particle size of the calcined powders is about 1-6 μm.

Acknowledgement

This work was supported by the Thailand Research Fund (TRF).

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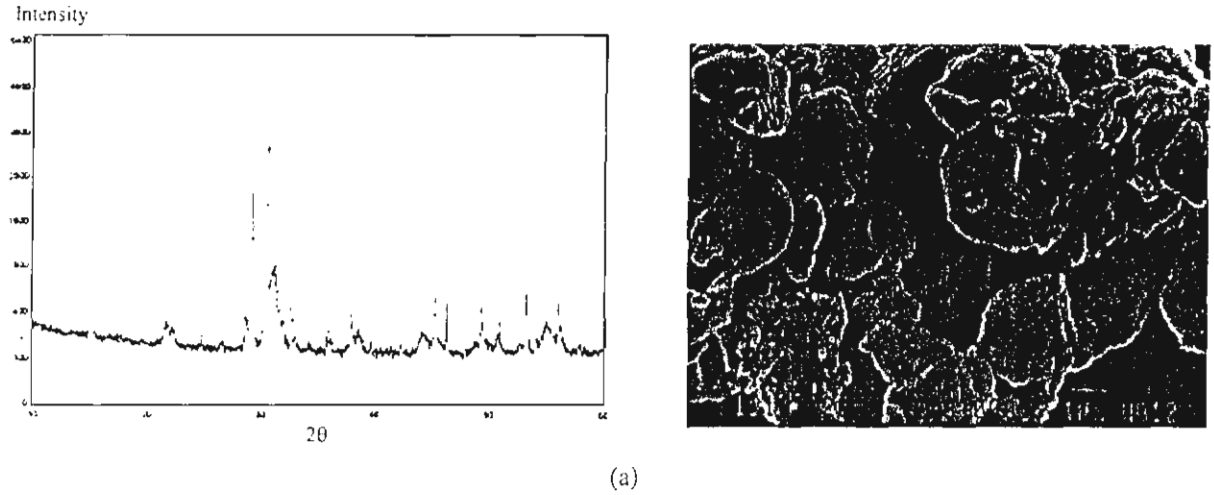

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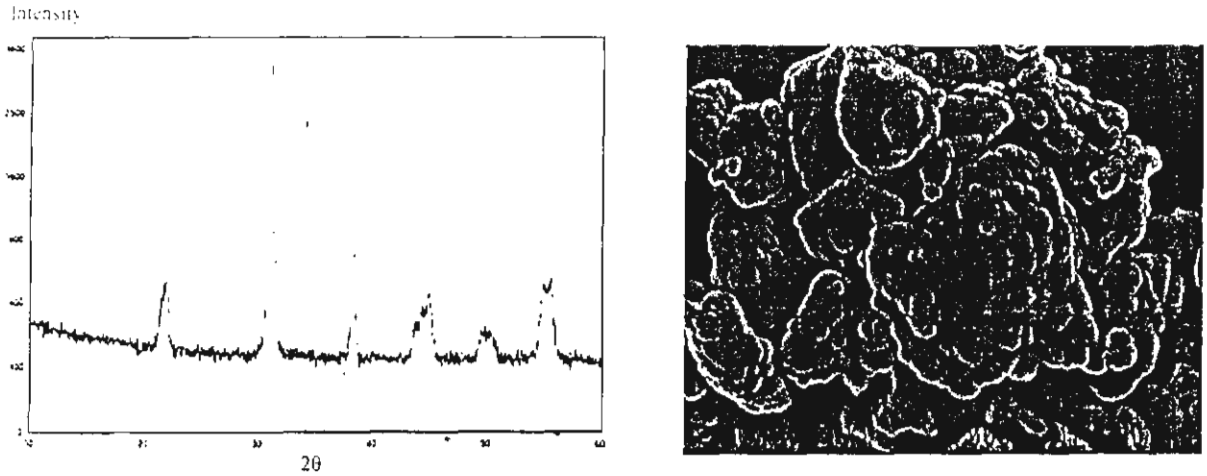

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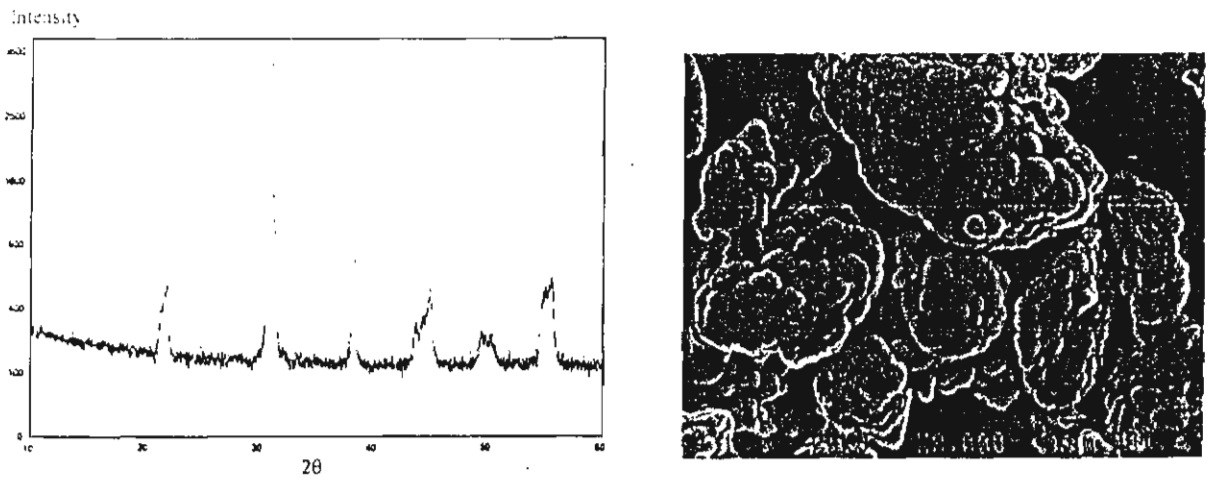

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Figure 1 X-ray diffraction patterns and microstructure of calcined powders at (*a*) 700 °C, (*b*) 760 °C and (*c*) 800°C for 2 h and heating/cooling rates of 2 °C/min.

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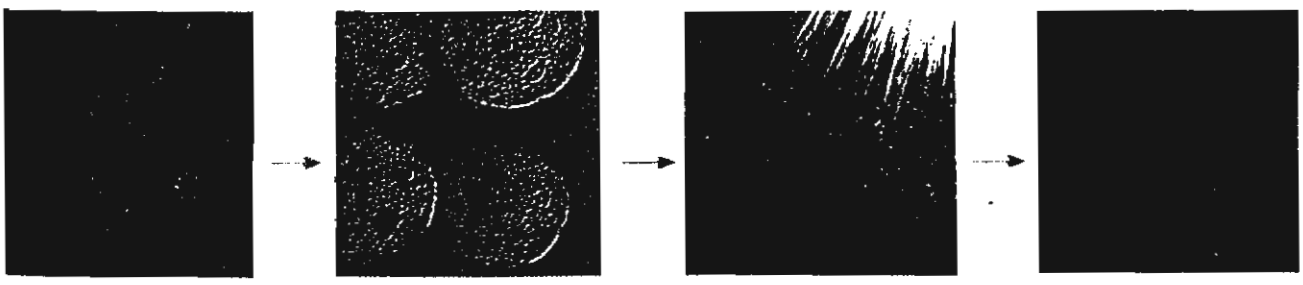


การตรวจสอบพฤติกรรมการเปลี่ยนเฟสของผงละเอียด $PbZrO_3$ หลังการแคลไซน์ที่อุณหภูมิต่างๆ ด้วยวิธี XRD

วันดี ธรรมจารี และ สุพล อนันตา

ห้องปฏิบัติการวิจัยอิเล็กโทรเซรามิกส์ ภาควิชาฟิสิกส์ คณะวิทยาศาสตร์ มหาวิทยาลัยเชียงใหม่ 50200

บทนำ

ในอดีตนั้น ต่างก็เชื่อกันว่า เลดเซอร์โคเนต ($PbZrO_3$หรือเรียกโดยย่อว่า PZ) ซึ่งมีโครงสร้างผลึกเป็นแบบ perovskite มีสมบัติของความเป็นสารเฟร์โรอิเล็กตริก เนื่องจากความที่ PZ นี้มีค่าคงที่ไดอิเล็กตริกสูง (ε_r ~3500)[1] จนกระทั่งในปี ค.ศ. 1951 Sawaguchi et al.[2] ได้เริ่มทำการศึกษา PZ อย่างจริงจังและพบว่า PZ นั้นเป็นสารแอนติเฟร์โรอิเล็กตริก ที่มีโครงสร้างผลึกเป็นแบบ orthorhombic[3] โดยมีอุณหภูมิคูรีที่สาร PZ แสดงค่าคงที่ไดอิเล็กตริกสูงสุดที่ประมาณ 230 °ซ[1] จากนั้นมา PZ ก็เริ่มได้รับความสนใจในการศึกษาค้นคว้ามากขึ้นเรื่อยๆ ตามลำดับ จนกระทั่งถึงปัจจุบันนี้ก็ได้มีการดัดแปลงสารประกอบ $PbZrO_3$ มาประยุกต์ใช้ในอุปกรณ์ต่างๆ เช่น depth sounders, actuators, accelerometers, flow detector และ transducers เป็นต้น[4] แต่อย่างไรก็ตาม จากการค้นคว้างานวิจัยที่เกี่ยวข้อง พบว่า มีรายงานที่กล่าวถึงพฤติกรรมการเกิดเฟสของ $PbZrO_3$ อยู่น้อยมาก ด้วยเหตุผลดังกล่าว งานวิจัยนี้จึงได้ทดลองเตรียมผงละเอียดของสาร $PbZrO_3$ โดยจะมุ่งความสนใจไปที่การศึกษาถึงพฤติกรรมการเกิดและการเปลี่ยนแปลงของเฟสในการเตรียมผงละเอียดของ $PbZrO_3$ ที่ผ่านการเผาแคลไซน์ด้วยเงื่อนไขต่างๆ

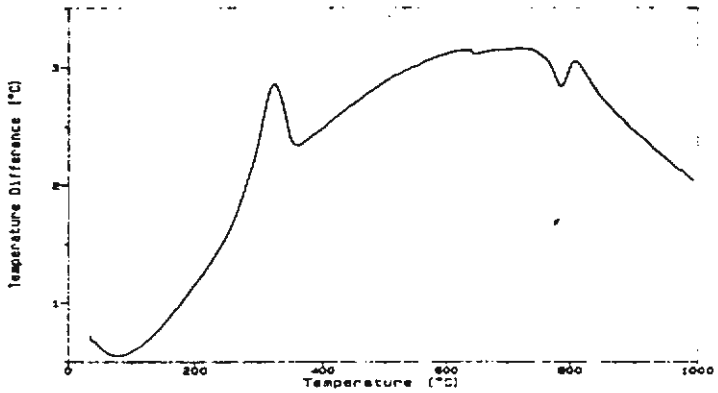
อุปกรณ์และวิธีการ

ในงานวิจัยนี้ได้ทดลองเตรียมเลดเซอร์โคเนต ($PbZrO_3$) โดยวิธี solid state ด้วยการผสมเลดออกไซด์ (PbO) กับเซอร์โคเนียมออกไซด์ (ZrO_2) ในอัตราส่วนที่เหมาะสมแล้วนำไปทำการ ball-milling เป็นเวลา 24 ชั่วโมง โดยใช้เอธานอลช่วยในการหล่อลื่นระหว่างการผสมสาร จากนั้นทำให้แห้ง บดให้ละเอียดแล้วนำผงของสารผสมที่ได้ไปตรวจสอบพฤติกรรมการเปลี่ยนแปลงทางความร้อนด้วยวิธีการ Differential Thermal Analysis (DTA) แล้วนำข้อมูลที่ได้นี้มาประกอบการเผาแคลไซน์สารผสมระหว่าง PbO กับ ZrO_2 ที่อุณหภูมิต่างๆ ตั้งแต่ที่ 700, 750, 800 และ 900 °ซ เป็นเวลานาน 2 ชั่วโมง โดยใช้อัตราการขึ้น/ลงของอุณหภูมิ (heating rate) คงที่ที่ 3 °ซ /นาที จากนั้นจึงนำสารที่ผ่านการเผาแคลไซน์ในแต่ละกรณีไปทำการตรวจสอบชนิด ปริมาณ และโครงสร้างผลึกของเฟสที่เกิดด้วยวิธีการ X-ray diffraction (XRD)

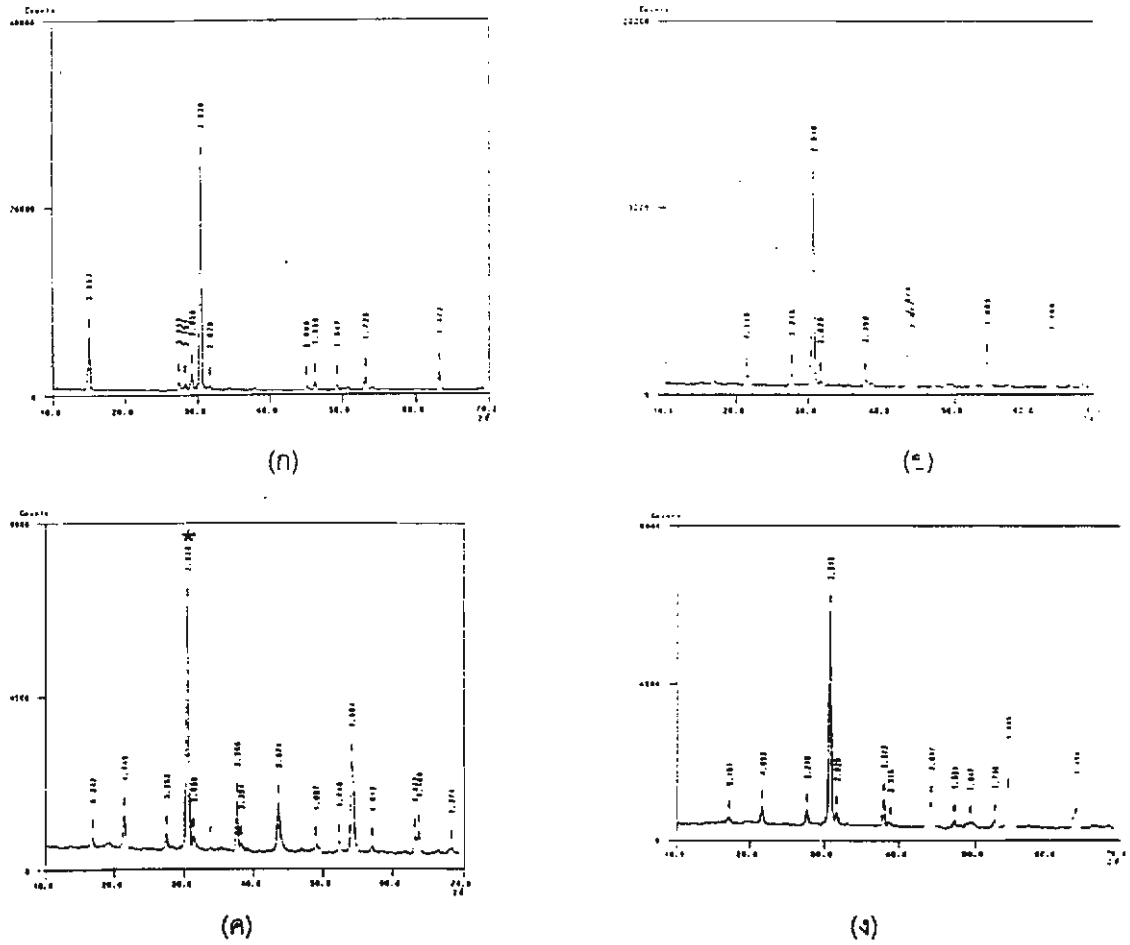
ผลการทดลองและวิจารณ์

จากการนำสารผสมของ PbO และ ZrO_2 มาตรวจสอบด้วย DTA เพื่อหาช่วงอุณหภูมิที่สารเกิดการเปลี่ยนแปลง พบว่ามีอยู่ 2 ช่วง คือ ที่อุณหภูมิประมาณ 300-400 °ซ ซึ่งคาดว่าน่าจะเป็นการเปลี่ยนแปลงที่เกิด

จากการเผาไหม้ของสารอินทรีย์ออกไปและอีกช่วงหนึ่งคือ ที่อุณหภูมิประมาณ 700-900 °ซ ซึ่งคาดว่าจะเป็นช่วงอุณหภูมิที่สารผสม เกิดการเปลี่ยนแปลงเฟส (ดังแสดงในรูปที่ 1)



รูปที่ 1 แสดงผลการตรวจสอบการเปลี่ยนแปลงเฟสของสารผสม PbO กับ ZrO_2 ด้วยวิธี DTA



รูปที่ 2 แสดง X-ray diffraction pattern ของสารผสมที่ผ่านการเผาแคลไซน์ ณ อุณหภูมิ (ก) 700 °ซ (ข) 750 °ซ (ค) 800 °ซ และ (ง) 900 °ซ เป็นเวลา 2 ชั่วโมง (* = PbO)

เมื่อทำการตรวจสอบผงละเอียดที่ผ่านการเผาแคลไซน์ที่อุณหภูมิต่างๆ ด้วยวิธีการ XRD (ดังแสดงในรูปที่ 2) พบว่า พฤติกรรมการเกิดและการเปลี่ยนแปลงเฟสของสารในระบบ $PbZrO_3$ จะขึ้นกับอุณหภูมิที่ใช้ในการแคลไซน์อย่างมีนัยสำคัญ โดยพบว่า พีค X-ray ของสารที่ได้จากการเผาที่อุณหภูมิ 700 °ซ จะตรงกับ X-ray diffraction pattern ของสารผสม PbO และ ZrO_2 ที่ใช้เป็นสารตั้งต้น (รูปที่ 2(ก)) ในขณะที่ผล X-ray ของสารที่ผ่านการเผาที่อุณหภูมิ 750 °ซ สอดคล้องกับเฟสของ $PbZrO_3$ ที่ตรงกับข้อมูลใน JCPDS file No.35-739 (รูปที่ 2 (ข)) และเมื่อใช้อุณหภูมิแคลไซน์เพิ่มขึ้นเป็น 800 °ซ พบว่ามีพีค X-ray ของสารตั้งต้น PbO (*) ปะปนเข้ามาเล็กน้อยในพีค X-ray ของ $PbZrO_3$ (รูปที่ 2(ค)) ซึ่งอาจจะเป็นผลมาจากอุณหภูมิที่เพิ่มขึ้นนี้ไปทำให้เกิดการเปลี่ยนแปลงสัดส่วนขององค์ประกอบทางเคมี (stoichiometrical fluctuation) ใน $PbZrO_3$ เกิดเป็น PbO ส่วนเกินออกมาในปริมาณที่มากพอต่อการตรวจวัดด้วย X-ray แต่อย่างไรก็ตาม เมื่อพิจารณาผล X-ray ของสารที่ผ่านการเผาที่อุณหภูมิ 900 °ซ กลับพบว่ามีเพียงเฟสของ $PbZrO_3$ เท่านั้นที่คงอยู่ (รูปที่ 2(ง)) ซึ่งน่าจะเกิดจากการระเหยออกไปของสารปนเปื้อน PbO ที่เกินออกมาเหล่านี้ (จุดหลอมเหลวของ PbO อยู่ที่ประมาณ 828 °ซ)[5] เช่นเดียวกับกรณีที่พบกันในสารกลุ่มอื่นที่มีตะกั่วเป็นองค์ประกอบหลัก เช่น PMN หรือ PFN เป็นต้น[6]

สรุปผล

จากการวิจัยพบว่า สามารถทำการเตรียมผงละเอียดของ $PbZrO_3$ ที่มีความบริสุทธิ์สูงๆ ได้ด้วยวิธีการผสมออกไซด์โดยที่ พฤติกรรมการเกิดเฟสของ $PbZrO_3$ นี้จะขึ้นอยู่กับอุณหภูมิที่ใช้เผาแคลไซน์ ซึ่งในงานวิจัยนี้พบว่า เงื่อนไขที่เหมาะสมต่อการเตรียมผงละเอียดของ $PbZrO_3$ ให้มีปริมาณเฟส $PbZrO_3$ สูง คือ การเผาแคลไซน์ที่อุณหภูมิ 750 °ซ เป็นเวลา 2 ชั่วโมง ด้วยอัตราการขึ้น/ลงอุณหภูมิที่ 3 °ซ /นาที

กิตติกรรมประกาศ

ขอขอบคุณสำนักงานกองทุนสนับสนุนการวิจัย (TRF) ที่ได้ให้การสนับสนุนการวิจัยครั้งนี้

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file No.6-452 เป็นเฟสหลักโดยมีเฟสของ PbO (*) ที่ตรงกับข้อมูลใน JCPDS file No.5-570 ซึ่งเป็นสารตั้งต้นที่ใช้ปะปนอยู่เล็กน้อย ส่วนในกรณีของสารที่ผ่านการเผาแคลไซน์ที่อุณหภูมิ 900 °ซ เป็นเวลา 2 ชั่วโมงนั้นพบว่า จะได้พีค X-ray ที่เป็นเฟสของ $PbTiO_3$ ทั้งหมด และไม่ปรากฏพีคของสารตั้งต้นหรือ second phase ใดๆ เลย และเมื่อนำมาตรวจสอบลักษณะทาง morphology ด้วยวิธีการ SEM พบว่า ขนาดอนุภาคของผงละเอียด $PbTiO_3$ ที่เตรียมได้ในงานวิจัยนี้ จะมีขนาดเพิ่มขึ้น คือ จะมีค่าอยู่ในช่วง 0.2-0.3, 0.5-0.6 และ 0.8-1.1 μm เมื่อทำการเผาแคลไซน์ด้วยอุณหภูมิ 600, 800 และ 900 °ซ ตามลำดับ ดังรายละเอียดแสดงในรูปที่ 2 (a-c)

สรุปผล

จากการวิจัยพบว่า ในการเตรียมผงละเอียดของเลดติตาเนตด้วยวิธีการผสมออกไซด์ อุณหภูมิแคลไซน์ที่ใช้จะมีผลต่อพฤติกรรมการเกิดและการเปลี่ยนแปลงเฟสอย่างมีนัยสำคัญ และสามารถทำการเตรียมผงละเอียดของ $PbTiO_3$ ที่มีความบริสุทธิ์สูงได้ถึง 100% (ภายใต้ขีดความสามารถในการตรวจสอบของวิธีการ XRD) โดยการใช้อุณหภูมิแคลไซน์ที่ 900 °ซ เป็นเวลา 2 ชั่วโมง โดยใช้อัตราการขึ้น/ลงของอุณหภูมิที่ 3 °ซ / นาที นอกจากนี้ยังพบว่า เมื่ออุณหภูมิแคลไซน์มีค่าเพิ่มขึ้น จะส่งผลให้ขนาดของผงละเอียด $PbTiO_3$ นั้นมีค่าเพิ่มขึ้น

กิตติกรรมประกาศ

ขอขอบคุณสำนักงานกองทุนสนับสนุนการวิจัย (TRF) ที่ได้ให้การสนับสนุนการวิจัยครั้งนี้

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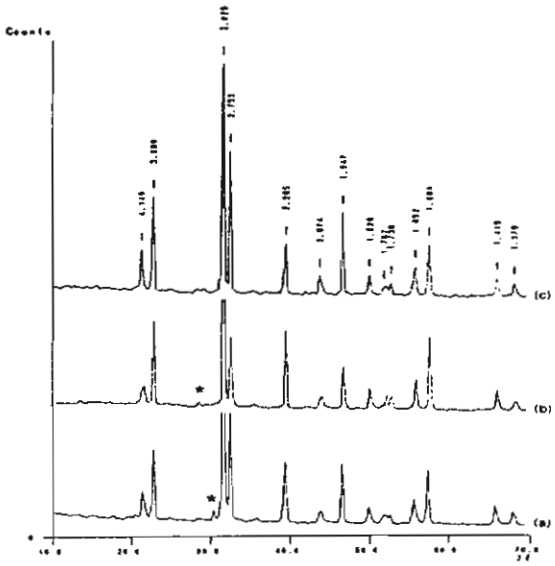
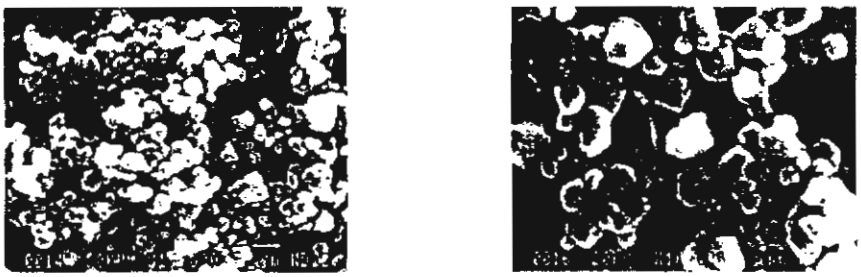


รูปที่ 1 แสดง XRD patterns ของสารผสมระหว่าง PbO กับ TiO_2 ที่ผ่านการเผาแคลไซน์ ณ อุณหภูมิ (a) 600 °ซ (b) 800 °ซ และ (c) 900 °ซ เป็นเวลา 2 ชั่วโมง (* แทนพีค X-ray ของ PbO)



(a) (b)

(c)

รูปที่ 2 แสดงภาพถ่าย SEM ของผงละเอียด $PbTiO_3$ ที่ผ่านการเผาแคลไซน์ ณ อุณหภูมิ (a) 600 °ซ (b) 800 °ซ และ (c) 900 °ซ เป็นเวลา 2 ชั่วโมง

บทคัดย่อ
EXTENDED ABSTRACTS

การประชุมวิชาการ
วิทยาศาสตร์และเทคโนโลยีแห่งประเทศไทย ครั้งที่ 26
18 - 20 ตุลาคม 2543
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26th Congress on Science and Technology of Thailand
18 - 20 October 2000
Queen Sirikit National Convention Center, Bangkok, Thailand

สมาคมวิทยาศาสตร์แห่งประเทศไทยในพระบรมราชูปถัมภ์
THE SCIENCE SOCIETY OF THAILAND UNDER THE PATRONAGE OF HIS MAJESTY THE KING

คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
FACULTY OF SCIENCE, CHULALONGKORN UNIVERSITY

วทท STT THE BEST DOMESTIC CONVENTION AWARD 1993

การตรวจสอบลักษณะเฉพาะของผงพีแซดทีด้วยวิธีการเลี้ยวเบนของรังสีเอกซ์
X-RAY DIFFRACTION APPROACH TO THE CHARACTERISATION OF PZT POWDERS

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บทคัดย่อ: หนึ่งในบรรดาสารประกอบเพียโซอิเล็กตริกประเภทที่มีตะกั่วเป็นองค์ประกอบหลัก ที่มีสูตรโครงสร้างทั่วไปเป็น $Pb(Zr,Ti)O_3$ นั้นจัดได้ว่าเป็นสารที่ได้รับความสนใจทางด้านการค้า เนื่องจากเป็นวัสดุที่มีสมบัติเพียโซอิเล็กตริกที่ดี(1-2) โดยสามารถนำมาประยุกต์ใช้งานต่างๆ ได้ เช่น ทรานสดิวเซอร์, เซ็นเซอร์ และแอคชูเอเตอร์ เป็นต้น(3) สมบัติต่างๆ ของสารดังกล่าวนี้จะขึ้นอยู่กับสารตั้งต้น และกระบวนการผลิต ซึ่งเป็นขั้นตอนที่สำคัญอย่างยิ่งต่อการผลิตเซรามิก PZT ในการศึกษานี้ได้ทำการเตรียมผงของ PZT โดยวิธี solid state reaction แล้วทำการตรวจสอบพฤติกรรมการเกิดเฟสและหาเงื่อนไขของการแคลไซน์ที่เหมาะสมต่อการเตรียม PZT ด้วยวิธีการเลี้ยวเบนของรังสีเอกซ์ จากการทดลองพบว่า อุณหภูมิและเวลาที่ใช้ในการแคลไซน์เป็นปัจจัยที่สำคัญอย่างมากต่อการกำหนดพฤติกรรมการเกิดเฟสของ PZT

III

Abstract: One of the piezoelectric family of lead-based complex perovskite compounds, with the general formula $Pb(Zr,Ti)O_3$, have commercial interest, because of their excellent piezoelectric properties (1-2). These characteristics facilitate their application in many areas, including transducers, sensors and actuators (3). Control of the properties, which, in turn, is strongly dependent on their initial powder and the processing conditions, is a very crucial step in the fabrication of PZT ceramics. In the present study, powder of PZT was prepared by employing a solid-state reaction method. The formation of phases and optimal conditions for the calcination were determined by using X-ray diffraction (XRD) technique. It is seen that the calcination temperature and time are the two crucial factors dictating the formation of PZT phase.

Experimental Procedure : The perovskite-like phase of $Pb(Zr,Ti)O_3$ or PZT powder was prepared by using a conventional mixed-oxide synthetic route. Starting reagent powders of PbO, ZrO_2 and TiO_2 (÷99.0% purity) were mixed and milled in ethanol for 24 h. After drying at 120 °C for 2 h, the powders were calcined in closed alumina crucible at different firing temperature in the range 600-950 °C for 2 h. Having established the optimum calcination temperature, alternative calcination times of 1, 3 and 4 h were applied at several temperatures. The formation of phases in all calcined powders were examined as a function of calcination temperature and dwell time by X-ray diffractometer.

Results, Discussion and Conclusion: From X-ray diffraction patterns of all calcined powders, it was found that X-ray peaks indicating the unreacted starting precursors of PbO, ZrO_2 and TiO_2 were observed in the samples calcined at 600 °C/2 h, 700 °C/2 h and 700 °C/4 h. However, at higher calcination temperatures, i.e. from 750 °C to 950 °C, the major phase of perovskite-like PZT was obtained. To the first approximation, this PZT phase could be matched with the JCPDS file no. 33-784, for the tetragonal phase with cell parameter a = 4.036 Å and c = 4.146 Å. The amount of perovskite phase present in each calcined powder may, in principle, be calculate from the intensities of the major X-ray reflections for the perovskite and second phases using equation advocated by Swart and Shrout (4). It is seen that optimisation of calcination conditions can lead to a 91 % yield of PZT in a tetragonal phase.

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Keywords: piezoelectric, lead zirconate titanate, XRD

การตรวจวิเคราะห์เฟสของผงเลดติตาเนตที่ผ่านการแคลไซน์แล้วด้วยวิธีการเลี้ยวเบนของรังสีเอกซ์

PHASE ANALYSIS OF CALCINED LEAD TITANATE POWDERS BY X-RAY DIFFRACTION

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บทคัดย่อ: ในปัจจุบันนี้ การแสวงหาผงที่มีลักษณะเฉพาะเหมาะสมต่อการเตรียมวัสดุอิเล็กทรอนิกส์ นิยมกระทำโดยมุ่งความสนใจมาที่วิธีการผลิตผงเป็นสำคัญ(1) ดังเป็นที่ทราบกันดีว่า เลดติตาเนต ($PbTiO_3$) นั้นเป็นหนึ่งในบรรดาสารกลุ่ม perovskites ที่มีตะกั่วเป็นองค์ประกอบหลัก และเป็นที่สนใจต่อการพัฒนาเพื่อทำเป็นชิ้นส่วนของพวกวัสดุอิเล็กทรอนิกส์ในทางการค้า(2) งานวิจัยนี้จึงได้มุ่งความสนใจมาที่การสังเคราะห์และการตรวจสอบผงเลดติตาเนตที่เตรียมขึ้นด้วยวิธีผสมออกไซด์ โดยได้ทำการศึกษาครอบคลุมไปถึงชนิดและปริมาณของเฟสต่างๆ ที่ปรากฏในผงเลดติตาเนตหลังการแคลไซน์ด้วยเงื่อนไขต่างๆ ด้วยวิธีการเลี้ยวเบนของรังสีเอกซ์ ซึ่งผลจากการตรวจวิเคราะห์ผงที่ผ่านการแคลไซน์ทั้งหมดนี้ได้แสดงให้เห็นถึงอิทธิพลของเงื่อนไขการเผาแคลไซน์ที่มีต่อการเกิดเฟส โดยในงานวิจัยนี้สามารถเตรียมผงเลดติตาเนตที่ความบริสุทธิ์สูงสุดได้ด้วยการเผาแคลไซน์ที่อุณหภูมิ 750 °ซ เป็นเวลานาน 2 ชั่วโมง

Abstract: Recently, the quest for optimal powder characteristics in the preparation of electronic materials has directed attention particularly towards powder production techniques(1). As is well known, lead titanate ($PbTiO_3$) is one of the family of lead-based perovskites which is of interest as a component in commercial electronic materials(2). In this work, consideration is given to the synthesis and characterisation of $PbTiO_3$ prepared by a mixed oxide route. The study encompasses identification of phases and their concentrations in the powders calcined at different conditions via X-ray diffraction technique. The characterisation of all calcined powders showed the influence of the different calcination conditions on the phase formed. A single phase of $PbTiO_3$ was successfully obtained for a calcination temperature of 750 °C with a dwell-time of 2 h.

Experimental Procedure: Perovskite-like $PbTiO_3$ was synthesised by the solid state reaction of appropriate amounts of reagent grade lead oxide (PbO) and titanium oxide (TiO_2). The powders were mixed, ball milled under ethanol for 24h, dried and calcined at 600, 700, 750, 800 and 900 °C, all for 2 h. Having established the optimum calcination temperature, alternative calcination times of 1, 3 and 4 h were applied at this temperature. All calcined powders were examined by X-ray diffraction (XRD) using CuK_α radiation to identify the phases formed and the optimum calcination temperature and time for the formation of perovskite-like $PbTiO_3$.

Results, Disscussion and Conclusion: From powder XRD patterns of all calcine powders, the strongest reflections apparent in the majority of the patterns indicate the formation of perovskite $PbTiO_3$, which could be matched with JCPDS file no. 6-452. This major phase possesses a tetragonal structure with lattice parameters a = 3.89 Å and c = 4.15 Å in space group P4/mmm (No. 129). As expected, there is evidence that, even for a wide range of calcination conditions single phase $PbTiO_3$ cannot easily be produced. This study shows that a minor amount of the unreacted PbO and TiO_2 phases co-exists along with the perovskite $PbTiO_3$ phase, after calcination in the range 600-900 °C. By using X-ray diffraction technique, it has been found that a single phase of $PbTiO_3$ was successfully obtained for a calcination temperature of 750 °C with a dwell-time of 2 h.

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Keywords: powder, phase formation, lead titanate, perovskite

อิทธิพลของอุณหภูมิแคลไซน์ต่อพฤติกรรมการเกิดเฟสและการกระจายตัวของอนุภาคผงละเอียดเลดเซอร์โคเนต

EFFECT OF CALCINATION TEMPERATURE ON THE PHASE FORMATION AND PARTICLE SIZE DISTRIBUTION OF LEAD ZIRCONATE POWDERS

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บทคัดย่อ: เลดเซอร์โคเนต ($PbZrO_3$) เป็นหนึ่งในบรรดาวัสดุกลุ่มแอนติเฟร์โรอิเล็กตริกที่มีการศึกษาค้นคว้าอย่างกว้างขวาง ทั้งเพื่องานวิชาการและการประยุกต์ใช้งานด้านเทคโนโลยี แต่อย่างไรก็ตาม เอกสารงานวิจัยที่เน้นหนักในเรื่องของกระบวนการเตรียมผงเลดเซอร์โคเนตนั้นยังมีอยู่น้อยมาก ดังนั้นในงานวิจัยนี้จึงได้ทำการเตรียมผงละเอียดของสารแอนติเฟร์โรอิเล็กตริกเลดเซอร์โคเนต ($PbZrO_3$) ด้วยวิธีการผสมออกไซด์แบบดั้งเดิม จากนั้นจึงทำการศึกษาพฤติกรรมการเกิดเฟสของ $PbZrO_3$ ที่ผ่านการเผาแคลไซน์ ณ อุณหภูมิต่างๆ ด้วยวิธีการเลี้ยวเบนของรังสีเอกซ์ และทำการศึกษาพฤติกรรมการกระจายตัวของขนาดอนุภาคผงละเอียดที่เตรียมได้ด้วยวิธีเลี้ยวเบนของแสงเลเซอร์ ซึ่งจากการวิจัยพบว่า สามารถเตรียมผงละเอียดที่เป็นเฟสของ $PbZrO_3$ 100% ได้โดยมีโครงสร้างผลึกอยู่ในรูปของออโธรอมบิค แต่อย่างไรก็ตาม ในหลายๆ กรณีแคลไซน์นั้นมักจะพบเฟสของสารตั้งต้น PbO และ ZrO_2 หลงเหลือปะปนอยู่กับเฟสหลักของ $PbZrO_3$

Abstract: Lead zirconate ($PbZrO_3$) is one of the family of antiferroelectric materials which has been widely investigated both for academic science and for technological applications(1). However, there are only a few articles directly devoted to the preparation of $PbZrO_3$ powder itself(2-3). In this work, fine powders $PbZrO_3$ were prepared by mixed oxide synthetic route. The formation of $PbZrO_3$ phases was investigated as a function of calcination temperature by X-ray diffraction. The particle size distribution of the calcined powders was determined by laser diffraction technique.. It has been found that optimisation of calcination temperatures can lead to a 100% yield of $PbZrO_3$ in an orthorhombic phase. However, it is seen that the unreacted PbO and ZrO_2 phases tend to form together with $PbZrO_3$.

Experimental Procedure: Powders of the $PbZrO_3$ were prepared using standard laboratory reagent grade starting powders : PbO and ZrO_2. The powders were mixed and ball milled under ethanol for 24 h and calcined in alumina crucible at 700 °C, 750 °C, 800 °C and 900 °C for 2 h, respectively. All calcined powders were subsequently examined by X-ray diffraction (CuK_α radiation), to identify the phases formed and optimum firing conditions. The particle size distributions of the powders were finally determined by laser diffraction techniques.

Results, Discussion and Conclusion: From powder XRD patterns of the calcined $PbZrO_3$ powders, it may be concluded that, over a wider range of calcination temperatures (700-900 °C/2h), single phase $PbZrO_3$ cannot be produced easily. This study shows that a minor amount of the unreacted PbO and ZrO_2 phases co-exist along with the lead zirconate $PbZrO_3$ phase. However, single phase of perovskite $PbZrO_3$ powders were successfully obtained for a calcination temperature of 750 °C for 2 h. By employing the laser diffraction technique, appreciable size fractions at approximately 1.5 μm diameter within the range of 0.2 to 5.0 μm can be determined.

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Keywords: lead zirconate, perovskite phase, calcination, XRD

บทคัดย่อ
EXTENDED ABSTRACTS

การประชุมวิชาการ
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สมาคมวิทยาศาสตร์แห่งประเทศไทยในพระบรมราชูปถัมภ์
THE SCIENCE SOCIETY OF THAILAND UNDER THE PATRONAGE OF HIS MAJESTY THE KING

คณะวิทยาศาสตร์ มหาวิทยาลัยสงขลานครินทร์
FACULTY OF SCIENCE, PRINCE OF SONGKLA UNIVERSITY

การตรวจสอบลักษณะเฉพาะของผงพีแซดทีที่เตรียมโดยใช้เลดเซอร์โคเนตและเลดติตาเนตเป็นสารตั้งต้น

CHARACTERISATION OF PZT POWDER PREPARED BY USING LEAD ZIRCONATE AND LEAD TITANATE PRECURSORS

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บทคัดย่อ: เลดเซอร์โคเนตติตาเนต (PZT) เป็นสารที่มีโครงสร้างแบบเพอรอฟสไคท์ ซึ่งเป็นที่รู้กันโดยทั่วไปว่า สามารถที่จะแสดงสมบัติทางพิโซอิเล็กตริกและสมบัติในการเปลี่ยนแปลงพลังงานได้ดี ดังนั้นจึงได้มีการนำอาสารพีแซดทีนี้มาประยุกต์ใช้ในงานเชิงอุตสาหกรรมอย่างกว้างขวาง โดยเฉพาะอย่างยิ่งในอุปกรณ์อิเล็กทรอนิกส์ประเภทต่างๆ อาทิเช่น ตัวแปลงไฟฟ้าพลังกัน, อุปกรณ์ที่มีสัมประสิทธิ์อุณหภูมิเป็นบวก, ตัวขับเร้าระดับไมโคร และตัวตรวจรู้ทางไฟฟ้าที่อุณหภูมิสูง (1-2) เป็นต้น ซึ่งการเตรียมสารพีแซดทีนั้นสามารถกระทำได้หลายวิธีที่มีความแตกต่างกันไป(3) โดยในงานวิจัยนี้ ได้ทดลองเตรียมผงพีแซดทีด้วยวิธีการผสมออกไซด์แบบดั้งเดิม ที่มีการใช้ผงเลดเซอร์โคเนต และผงเลดติตาเนตในอัตราส่วนโดยโมล 1:1 เป็นสารตั้งต้น บดผสมกัน แล้วนำไปเผาแคลไซน์ด้วยเงื่อนไขต่างๆ จากการนั้นจึงนำไปทำการตรวจสอบด้วยเทคนิคการเลี้ยวเบนของรังสีเอกซ์ ซึ่งจากการทดลองพบว่า อุณหภูมิและเวลาที่ใช้ในการเผาแคลไซน์เป็นปัจจัยสำคัญอย่างยิ่งต่อการกำหนดพฤติกรรมการเกิดเฟสของพีแซดที

Abstract: Perovskite type lead zirconate titanate (PZT) has been known to exhibit excellent piezoelectric and electrostrictive properties. Thus, it has been widely used in several industries especially in electronics parts, for example, piezoelectric transducer, positive temperature coefficient devices, microactuators and pyroelectric sensor (1-2), etc. There are several types of very different fabrication route that can be utilized to fabricate PZT (3). In this work, modified mixed oxide method was employed for the synthesis of PZT powders. The 1:1 molar ratio of lead zirconate ($PbZrO_3$) and lead titanate ($PbTiO_3$) were mixed, ball-milled and calcined under different conditions. The optimized of calcining conditions were determined by X-ray diffraction (XRD) technique. Experimental results indicate that the calcinations temperature and time are the important factors dictating the formation behaviour of PZT powders.

Methodology: The perovskite-like phase of PZT powder was prepared by using a modified mixed-oxide synthetic route. The starting powders, $PbZrO_3$ and $PbTiO_3$, were prepared by employing a solid-state reaction. The 1:1 molar ratio of $PbO:ZrO_2$ and $PbO:TiO_2$ were mixed and milled in ethanol for 24 h. After drying, the mixed powders were calcined at 750 °C for 2 h. Then, 1:1 by mole of $PbZrO_3$ and $PbTiO_3$ were mixed and milled together and calcined in closed alumina crucible with different firing temperatures in the range of 700-1000 °C for 4 h. The other factors, dwell time and heating/cooling rates were also investigated. The phase formation behaviour of all calcined powders were examined by X-ray diffractometer.

Results, Discussion and Conclusion: From the results it is seen that the major phase of all calcined powders could be matched with the JCPDS file no. 33-784, for the tetragonal PZT phase with cell parameters $a = 4.036$ Å and $c = 4.146$ Å. The pervoskite-like phase of PZT with some small amount of unknown phase were observed in the sample calcined at the temperature above 700 °C. The amount of this unknown phase was calculated from equation advocated by Swartz and Shrout (4). By increasing the firing temperature, the unknown phase decreased. It may be concluded that a 92% yield of perovskite PZT phase can be successfully obtained with this modified mixed oxide route.

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Keywords: lead zirconate titanate, mixed oxide, powder, X-ray diffraction

การตรวจวิเคราะห์เฟสของผงเซอร์โคเนียมติตาเนตที่แคลไซน์แล้วด้วยวิธีการเลี้ยวเบนของรังสีเอกซ์

PHASE ANALYSIS OF CALCINED ZIRCONIUM TITANATE POWDERS BY X-RAY DIFFRACTION

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บทคัดย่อ: เซอร์โคเนียมติตาเนต ($ZrTiO_4$) เป็นสารที่มีสมบัติเหมาะสมต่อการนำไปประยุกต์ใช้งานในหลากตัวเร่งปฏิกิริยาเกรด-ยุคใหม่ ประสิทธิภาพสูง และหลากสารไดอิเล็กตริกได้ดี (1-2) นอกจากนี้ยังมีการนำไปใช้เป็นสารตั้งต้นสำหรับการสังเคราะห์เลดเซอร์โคเนตติตาเนต ซึ่งเป็นหนึ่งในบรรดาวัสดุพิโซอิเล็กตริกที่นิยมนำไปใช้เป็นส่วนประกอบในอุปกรณ์อิเล็กทรอนิกส์ทางการค้าต่างๆ (3) ซึ่งในงานวิจัยนี้ได้มุ่งความสนใจมาที่เรื่องของการเตรียมและการตรวจหาลักษณะเฉพาะของผง $ZrTiO_4$ ที่เตรียมขึ้นมาด้วยวิธีมิกซ์ออกไซด์ โดยได้ทำการตรวจสอบลักษณะการเกิดเฟสของผง ZT ที่ผ่านการเผาแคลไซน์ด้วยเงื่อนไขต่างๆ โดยใช้เทคนิคการเลี้ยวเบนของรังสีเอกซ์ จากผลการทดลองพบว่ามีเฟสของสารตั้งต้น ZrO_2 และ TiO_2 หลงเหลือปะปนอยู่กับเฟสหลักของ ZT ที่ได้ โดยจะขึ้นกับเงื่อนไขที่ใช้ในการเผาแคลไซน์เป็นสำคัญ และสามารถเตรียมผง ZT ที่เป็นเฟสเชิงเดี่ยวได้ด้วยการแคลไซน์ที่อุณหภูมิ 1300 °ซ โดยมีระยะเวลาเผาแช่นาน 4 ชั่วโมง

Abstract: Zirconium titanate ($ZrTiO_4$) has been found to have an excellent properties for an effective acid-base bifunctional catalyst and dielectric applications (1-2). It is also used as a precursor for the synthesis of lead zirconate titanate (PZT), one of the piezoelectric materials which is of interest as a component in commercial electronic devices (3). In this work, attention has been paid on the preparation and characterisation of $ZrTiO_4$ powder prepared by a mixed oxide route. The formation of ZT phases was examined as a function of calcination conditions via X-ray diffraction technique. It has been found that the unreacted ZrO_2 and TiO_2 phases tend to from together with ZT phase, depending on calcination conditions. A single phase of $ZrTiO_4$ was obtained for a calcination temperature of 1300°C with a dwell time of 4 h.

Methodology: Zirconium titanate ($ZrTiO_4$) powders were synthesised from commercially available oxides using a mixed oxide synthetic route. The starting materials were zirconium oxide, ZrO_2 (+99.9% purity) and titanium oxide, TiO_2 (~99.9% purity). The powders were mixed, ball-milled under ethanol for 24 h. After drying at 100°C for 2 h, powders were calcined in closed alumina crucibles at 1300°C, 1350 °C and 1400°C, all for 2, 3 and 4 h. All calcined powders were examined by X-ray diffraction (XRD) using CuK_α radiation to identify the phase formed and the optimum calcination condition for the formation of $ZrTiO_4$.

Rusults, Discussion and Conclusion: By employing XRD techniques, it has been found that the strongest reflections in the majority of all XRD traces indicate formation of the $ZrTiO_4$ phase. This could be matched with JCPDS file no. 34-415. To a first approximation, this major phase has an orthorhombic form in space group *Pnab* (No. 60), with cell parameters a = 5.035 Å, b = 5.487 Å and c = 4.801 Å. However, it is seen that the unreacted ZrO_2 and TiO_2 precursors tend to co-exists along with the major phase of $ZrTiO_4$, depending on calcination conditions. In this study, it may be concluded that a single phase of $ZrTiO_4$ successfully obtained in all samples calcined at 1300°C for 4 hours.

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Keywords: zirconium titanate, powder, X-ray diffraction