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# Synthesis of PZT fine particles using $Ti^{3+}$ precursor at a low hydrothermal temperature of 110 °C

Seok Han Kim, Sridhar Komarneni *

Materials Research Institute, The Pennsylvania State University, University Park, PA 16802, USA

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## Abstract

Lead zirconate titanate (PZT) fine particles (80 nm to 0.8 μm) were prepared by hydrothermal method using a $Ti^{3+}$ precursor, $TiCl_3$. In contrast with conventional hydrothermal methods using $Ti^{4+}$-reagents, pure PZT particles without lead titanate (PTO) impurities were synthesized using the $Ti^{3+}$-reagent at a low temperature of 110 °C which is lower than the previously reported temperatures of 160 and 130 °C, using $Ti^{4+}$-reagents of $TiO_2$ and $TiCl_4$, respectively. Additionally, the crystallization time using the $Ti^{3+}$-reagent is shorter than those using $Ti^{4+}$-reagents at the same temperature of 140 °C. The high reaction rate of the $Ti^{3+}$-reagent containing gels prepared here is probably due to the presence of much more defects in their PTO intermediates. The present hydrothermal method using $Ti^{3+}$ precursor could lead to energy savings because of low temperature synthesis and the present method is potentially useful for non-pressurized equipment in manufacturing plants for synthesizing PZT particles.
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*Keywords:* Lead zirconate titanate; Hydrothermal synthesis; $TiCl_3$ reagent

## 1. Introduction

Lead zirconate titanate ($Pb(Zr_xTi_{1-x})O_3$; PZT) is a widely used ferroelectric, piezoelectric, and pyroelectric material with applications in piezoelectric actuators, micro-electro-mechanical system (MEMS) and pyroelectric infrared detectors [1,2]. Several conventional mixed oxide methods, such as sputtering, chemical vapor deposition (CVD), and sol–gel methods, have been extensively used to synthesize PZT particles and films [3–5]. In comparison with these high-cost methods which use a high processing temperature of >600 °C, hydrothermal methods for preparing PZT have advantages related to energy savings and environmental recycling because the syntheses are accomplished at a relatively low temperature of <250 °C and chemicals in the closed reactors can be recovered and recycled [6–11]. Additionally, growing PZT on various substrates at relatively lower temperatures leads to little or no damage of the substrates during the process [10].

Ti reagents such as $TiO_2$, $(C_4H_9O)_4Ti$, and $TiCl_4$ containing $Ti^{4+}$ ions have been widely used for hydrothermal PZT synthesis [6–11]. The reaction temperature to obtain pure PZT particles was 160 and 175 °C by using $TiO_2$ with mineralizer KOH and using $(C_4H_9O)_4Ti$, respectively [6,10]. Additionally, at a much lower temperature of 130 °C pure PZT particles were also synthesized with $TiCl_4$ and NaOH [9]. It means that Ti precursors and mineralizers have a significant effect on the reaction temperatures of hydrothermal PZT syntheses. However, the above lowest temperature of 130 °C for the PZT synthesis is still too high to use non-pressurized equipments in manufacturing plants and its process time of >20 h is too long [9] although Komarneni et al. showed that a microwave-assisted hydrothermal method leads to rapid formation of PZT at 115 °C in 10 M KOH [11]. In contrast with $Ti^{4+}$ reagents, $Ti^{3+}$ reagents including $TiCl_3$ have been rarely tried on hydrothermal PZT synthesis because it is not easy to understand and design an additional step, i.e., the oxidation of $Ti^{3+}$ in reagents to $Ti^{4+}$ in PZT.

In this work, we have tried to develop a conventional-hydrothermal method, which had the lowest reaction temperature, i.e., 110 °C, to obtain pure PZT particles by using $TiCl_3$ instead of $Ti^{4+}$ containing reagents. Additionally, the effects of mineralizers, NaOH, KOH, and mixed NaOH and KOH on the syntheses of PZT with the $Ti^{3+}$ containing gel systems have been studied.

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* Corresponding author.
*E-mail address:* komarneni@psu.edu (S. Komarneni).

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## 2. Experimental

### 2.1. Materials

The reagents used in PZT [$Pb(Zr_{0.52}Ti_{0.48})O_3$] syntheses were $TiCl_3$ (20% $TiCl_3$ in 3% HCl solution, Alfa Aesar), $Pb(NO_3)_2$ (99.0%, Alfa Aesar), $ZrOCl_2{\cdot}8H_2O$ (98%, Alfa Aesar), KOH (85%, Alfa Aesar), NaOH (97.0%, Alfa Aesar), and deionized water.

### 2.2. Synthesis of PZT particles

The typical gel compositions for PZT syntheses prepared here were $0.63Pb(NO_3)_2{\cdot}0.32ZrOCl_2{\cdot}0.29TiCl_3{\cdot}10\mathit{M}OH{\cdot}67H_2O$ where *M* is Na, K, or mixed Na and K (Table 1). Each synthetic gel was prepared by the following procedure. $TiCl_3$ solution was firstly mixed with deionized water. The other reagents were added to the Ti containing solution in the order of $ZrOCl_2{\cdot}8H_2O$, $Pb(NO_3)_2$ and *M*OH while stirring. Each of the mixtures was charged into a Teflon-lined 125-mL autoclave and then heated using a conventional oven in the temperature range of 100–160 °C for 0–24 h without stirring under autogenous pressure (Table 1). After the vessel was cooled to room temperature, the white powders obtained by hydrothermal reactions were collected and washed repeatedly with deionized water by centrifugation at 2000 rpm for ~10 min. The powders were then dried at 60 °C in an oven.

### 2.3. Characterization

Powder X-ray diffraction (XRD) patterns were measured on a PANalytical X'Pert MPD diffractometer operated at 45 kV voltage and 40 mA current with a PIXcel detector and Cu Kα radiation. Scanning electron microscope (SEM) and transmission electron microscope (TEM) images were observed by a Hitachi S-3500N and a Philips 420, respectively. TEM specimens were prepared by depositing a drop of the ethanol solution of PZT sample on a 300 mesh copper grid coated with an amorphous carbon film and evaporating the solvent in air at room temperature. Surface area of one PZT sample synthesized at 110 °C was determined by BET $N_2$ adsorption–desorption analysis using an Autosorb-1 instrument by Quantachrome corporation.

Table 1
Representative synthesis conditions and results.

| Run | Gel composition[a] | Crystallization | | Result | |
|---|---|---|---|---|---|
| | *M* | *T* (°C) | *t* (h) | Products | Size[b] |
| 1 | K | 100 | 24 | PZT[c] | 0.8 μm |
| 2 | K | 110 | 24 | PZT | 0.8 μm |
| 3 | K | 120 | 24 | PZT | 0.8 μm |
| 4 | K | 140 | 24 | PZT | 0.8 μm |
| 5 | K | 160 | 24 | PZT | 0.8 μm |
| 6 | Na, K[d] | 100 | 24 | PZT[c] | 0.5 μm |
| 7 | Na, K[d] | 120 | 24 | PZT[c] | 0.5 μm |
| 8 | Na, K[d] | 140 | 24 | PZT[c] | 0.5 μm |
| 9 | Na, K[d] | 160 | 24 | PZT[c] | 0.5 μm |
| 10 | Na | 140 | 24 | PZT[c] | 80 nm |
| 11–17[e] | K | 140 | 0–24 | PTO, PZT[f] | |

[a] Gel compositions for runs prepared here are $0.63Pb(NO_3)_2{\cdot}0.32ZrOCl_2{\cdot}0.29TiCl_3{\cdot}10\mathit{M}OH{\cdot}67H_2O$ where *M* is K, Na, or mixed K and Na.

[b] Averaged size of PZT particles. Estimated and measured from SEM or TEM images of the products.

[c] PTO peaks had low intensities as could be seen in the XRD patterns for these resulting products.

[d] The gel composition for runs 6–9 is $0.63Pb(NO_3)_2{\cdot}0.32ZrOCl_2{\cdot}0.29TiCl_3{\cdot}5KOH{\cdot}5NaOH{\cdot}67H_2O$.

[e] Runs with different crystallization times.

[f] Main products for runs 12–13 (1–2 h of heating) were PTO and for runs 14–17 (3–24 h of heating) were PZT.

## 3. Results and discussion

### 3.1. Mineralizer effect

The synthetic conditions and results for runs 4, 8, and 10 synthesized at 140 °C using different mineralizers, KOH, mixed NaOH and KOH and NaOH, respectively, are described in Table 1 and the XRD patterns are shown in Fig. 1. The XRD peaks (degrees, 2*θ*) near 21.7°, 22.3°, 30.9°, 31.3°, and 38.7° are generated by X-ray diffractions on (0 0 1), (1 0 0), (1 0 1), (1 1 0), and (1 1 1) planes of PZT, respectively [6,7,9,10,12]. The peaks at *ca.* 29.3°, 32.4°, and 37.1° indicate (1 0 1), (1 1 0), and (0 0 2) planes of PTO (lead titanium oxide; $PbTi_{0.8}O_{2.6}$), respectively [9]. The XRD patterns show PZT particles were obtained in runs 4, 8, and 10 which contained KOH, mixed NaOH and KOH and NaOH, respectively (Fig. 1). The highest XRD peak at 31.3° for run 4 is different from those at 30.9° for runs 8 and 10. It means that the PZT particles of run 4, which had no NaOH as a mineralizer have a preferred orientation of (1 1 0) and those of runs 8 and 10, which had NaOH are mainly (1 0 1) orientated. This result implies that the minenalizer NaOH had an effect on the preferred orientations for PZT synthesis. Both 8 and 10 runs containing NaOH in their gels also showed a small peak or shoulder at 32.4° related to (1 1 0) reflection of PTO in their XRD patterns. However, no other PTO peaks were observed in the XRD patterns. In contrast to the above runs, run 4 obtained from a gel containing no Na but containing K showed little or no PTO peaks. Thus small amounts of PTO impurities were in the resulting powders of runs 8 and 10 using NaOH but no PTO impurity was found in run 4, which is free of Na. In summary, both KOH and NaOH mineralizers are effective for PZT synthesis. However, KOH is a better mineralizer for preparing pure PZT particles because NaOH mineralizer led to small amounts of PTO impurities.

The morphologies and sizes of the PZT particles obtained from runs 4, 8, and 10 were examined by SEM and TEM (Fig. 2). The SEM images show formation of aggregated cubic- or rectangular parallelepipe-shaped particles from runs 4 and 8. The TEM image for run 4 more clearly shows that these aggregated particles observed by SEM are almost cubic-shaped. The TEM image for run 10 shows well facetted and cubic-shaped PZT particles sized *ca.* 80 nm on an edge. Also, several sizes of PZT particles are observed from the SEM images. The averaged size of PZT particles for run 4 using

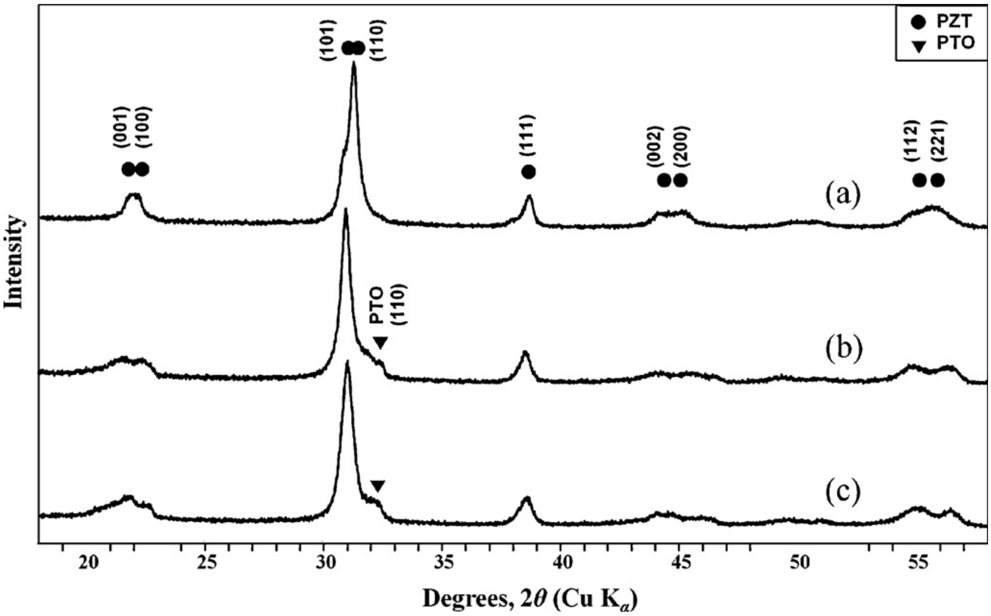

Fig. 1. Powder XRD patterns for products: (a)–(c) are from runs 4, 8, and 10, respectively, at 140 °C (see Table 1).

KOH only is 0.8 μm on an edge but that for run 8, which had both KOH and NaOH in its synthetic gel is 0.5 μm. On the other hand, run 10 using NaOH only has the smallest average size of PZT particles, 80 nm (Fig. 2d). It means that NaOH in gels led to a reduction of PZT particle sizes probably because of more nucleation owing to higher solubility of gel in NaOH.

### 3.2. Crystallization temperature effect

Two sets, runs 1–5 using KOH and 6–9 using both KOH and NaOH, were prepared at 100–160 °C for 24 h, respectively (Table 1). XRD patterns for runs 1–5 using KOH show that almost pure PZT was synthesized from these runs (Fig. 3).

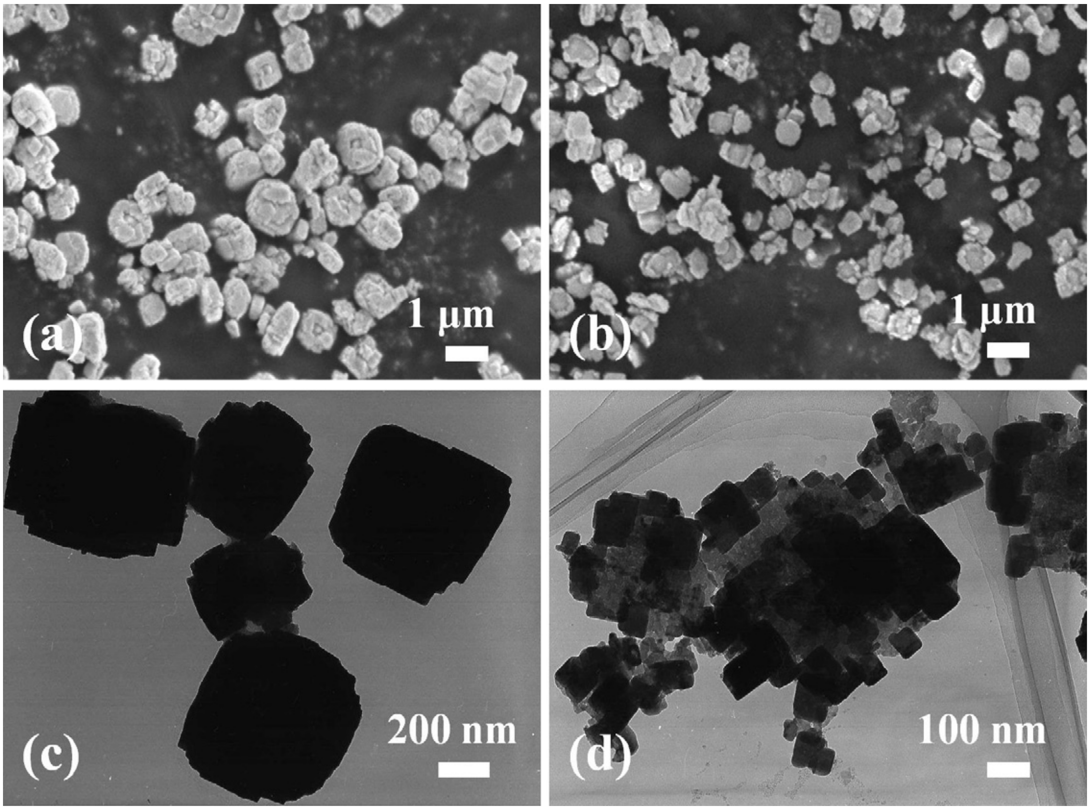

Fig. 2. SEM (a) and (b) obtained from runs 4 and 8, respectively and TEM (c) and (d) images for runs 4 and 10, respectively, at 140 °C (see Table 1).

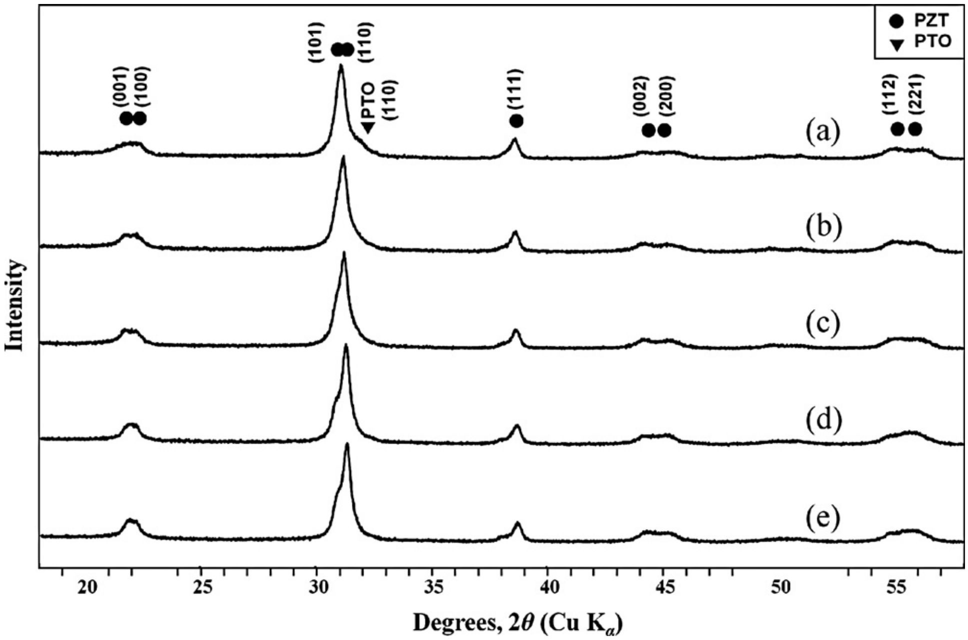

Fig. 3. Powder XRD patterns for products using KOH mineralizer: (a)–(e) are from runs 1 to 5, obtained at 100, 110, 120, 140, and 160 °C, respectively (see Table 1).

Although the XRD patterns of runs 2, 3, 4, and 5 prepared at 110, 120, 140, and 160 °C, respectively show little or no shoulder near 32°, run 1 obtained at 100 °C has a small peak or shoulder at 32.0° that can be related to (1 1 0) of PTO. In contrast, each of four XRD patterns for runs 6–9 using both KOH and NaOH as mineralizers have a PTO (1 1 0) peak near 32.5° (Fig. 4). These results suggest that pure PZT particles can be synthesized at and above 110 °C from synthetic gels containing $Ti^{3+}$ reagent, $TiCl_3$, and a single mineralizer, KOH. The temperature of 110 °C for run 2, a hydrothermal condition for pure PZT with no PTO, is much lower than those for other conventional methods. Additionally, this temperature is lower than the lowest synthetic temperatures reported by others for hydrothermal syntheses of pure PZT using $Ti^{4+}$ sources such as $TiO_2$ (160 °C) and $TiCl_4$ (130 °C) [9,10].

The XRD peaks near 31° two theta are related to (1 0 1) and (1 1 0) planes of PZT, which are shifted to higher angles among runs 1-5 with the increase of crystallization temperature (Fig. 3) although the XRD patterns including peak positions and relative intensities for runs 6–9 are similar to each other even

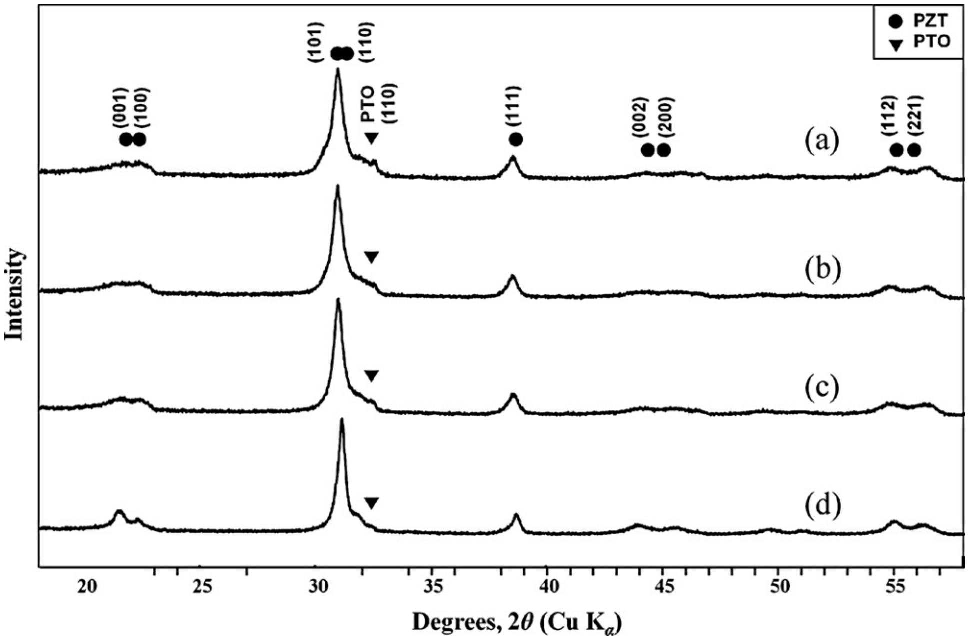

Fig. 4. Powder XRD patterns for products using mixed NaOH and KOH mineralizers: (a)–(d) are from runs 6 to 9, obtained at 100, 120, 140, and 160 °C, respectively (see Table 1).

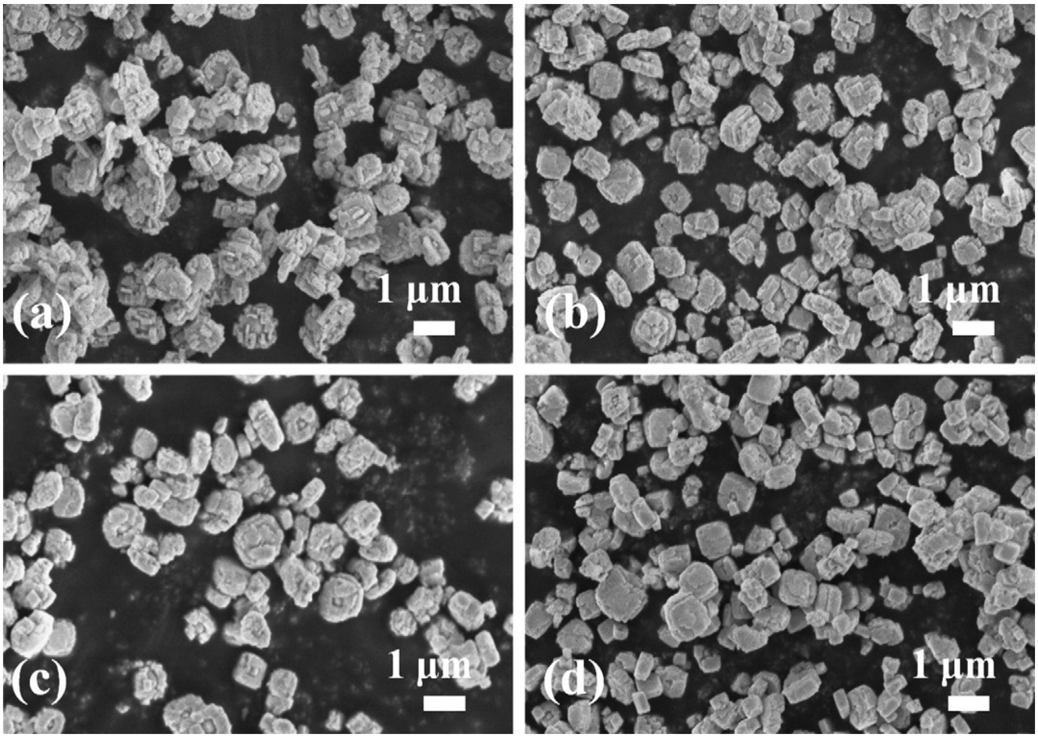

Fig. 5. SEM images for products using KOH mineralizer: (a)–(d) are from runs 1 and 3–5, obtained at 100, 120, 140, and 160 °C, respectively (see Table 1).

though the temperatures of their crystallization are different (Fig. 4). Runs 2, 3, 4, and 5 using KOH prepared at 110, 120, 140, and 160 °C, respectively, have two peaks at 30.8° and 31.3° resulting from (1 0 1) and (1 1 0) planes of PZT, respectively, but the intensity of (1 0 1) peaks for these runs decreases when the crystallization temperature increases.

These results imply that mineralizers such as KOH and NaOH, probably have a significant effect on PZT crystallization

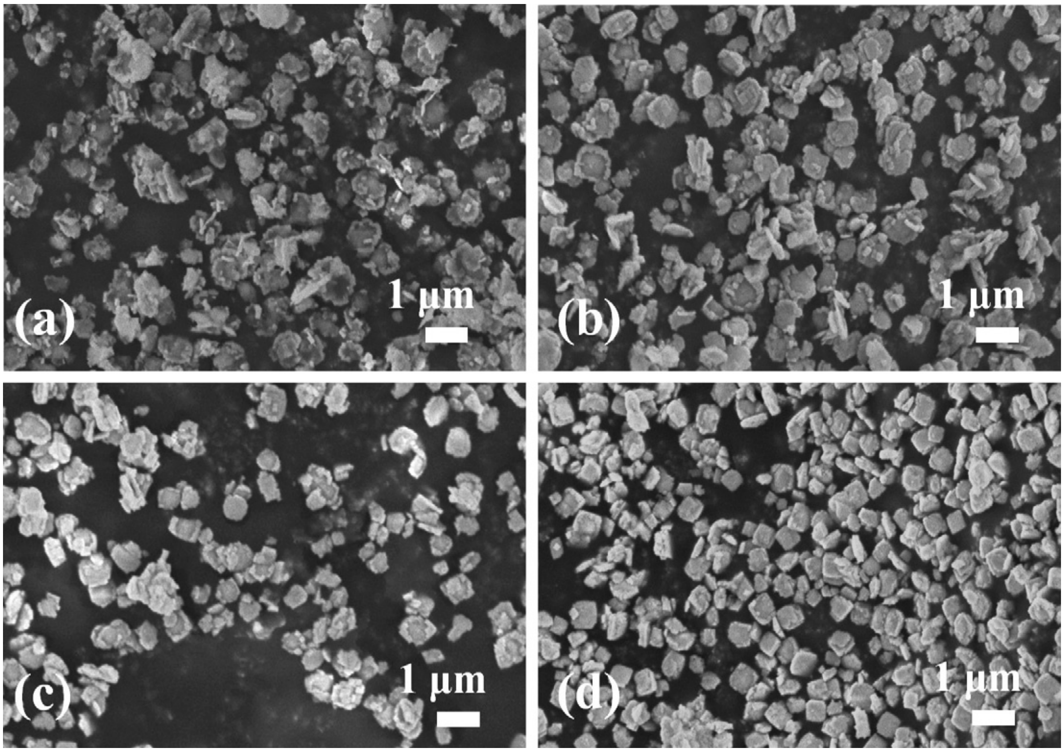

Fig. 6. SEM images for products using mixed NaOH and KOH mineralizers: (a)–(d) are from runs 6 to 9, obtained at 100, 120, 140, and 160 °C, respectively (see Table 1).

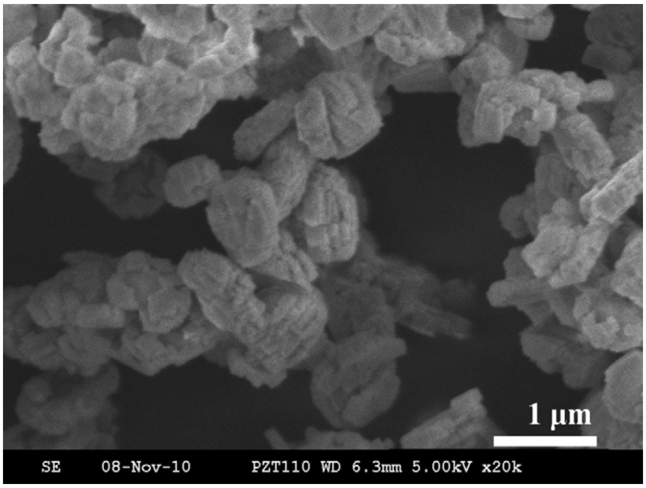

Fig. 7. SEM image of PZT obtained at 110 °C using KOH mineralizer (run 2, see Table 1).

(Figs. 3 and 4) in addition to the crystallization temperature as can be seen with the specific case of synthesis using KOH (Fig. 3). The different temperatures of PZT synthesis for runs 1–5 using KOH do not only show the extents of PTO impurities but also show the nature of preferred orientations for PZT particles (Fig. 3).

In short, all the runs from 6 to 10 using NaOH as a mineralizer have PTO impurities because NaOH in the gel apparently promotes the formation of PTO or disturbs the transition from PTO to PZT. In contrast, Na-free runs of 2–5 obtained in the range of 110–160 °C with KOH have few or no PTO impurities although run 1 prepared at the lowest temperature of 100 °C, has a small amount of PTO. The crystallization temperatures for Na-free but KOH containing runs show an effect on PTO impurities and some effects on the preferred orientations of PZT particles.

The average sizes of PZT particles obtained at different temperatures are similar for runs 1 and 3–5 (Fig. 5) and runs 6–9 (Fig. 6), respectively. The PZT particles of runs 1 and 3-5 using KOH and of runs 6–9 using mixed KOH and NaOH have average sizes of 0.8 and 0.5 µm on an edge, respectively. The pure PZT synthesized here at the lowest temperature of 110 °C also showed an average particle size of 0.8 µm (Fig. 7 and Table 1) and the surface area for this sample was determined to be 22 $m^2/g$. The synthetic temperatures showed no significant effect on the sizes of PZT particles for the temperature conditions used here.

### 3.2.1. *Formation of PZT from PTO on hydrothermal synthesis*

Fig. 8 shows the phase changes for PZT batches synthesized by the conventional hydrothermal method using different crystallization times. No PZT peak was found at the initial stages (0–2 h) of their crystallizations, however, (1 0 1) and (1 1 0) peaks of PTO near 29.3° and 32.5° exist (Fig. 8b and c). After 3 h of hydrothermal treatments at 140 °C the PTO peaks

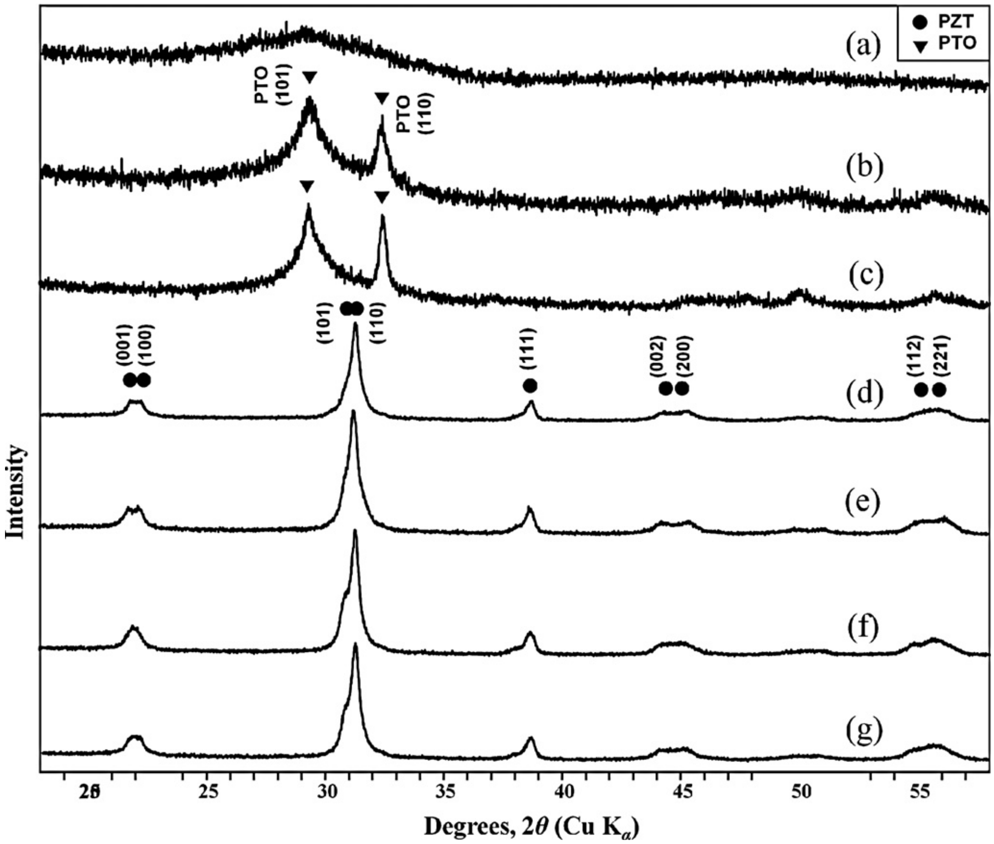

Fig. 8. Powder XRD patterns for products using KOH mineralizer: (a)–(g) are from runs 11–17 that are crystallized at 140 °C for 0, 1, 2, 3, 4, 8, and 24 h, respectively (see Table 1).

disappeared, however, new peaks appeared near 22.0°, 31.0°, and 38.5°, which are related to PZT (0 0 1)/(1 0 0), (1 0 1)/(1 1 0), and (1 1 1) planes, respectively.

The transition from PTO to PZT implies a reaction mechanism. Firstly, $TiCl_3$ and $Pb(NO_3)_2$ molecules make Ti–O–Ti and Pb–O–Pb units in the high alkaline system provided by KOH and/or NaOH and then PTO (Pb–O–Ti) networks seem to form in the initial stage. The PTO observed here probably has imperfect structure because the XRD patterns of the intermediates, runs 12 and 13, have very broadened PTO peaks near 29.3° and 32.5° (Fig. 8b and c). Therefore, the Zr–O–Zr moieties from $ZrOCl_2$ may then be reacting with the PTO intermediates, which had many defects and then form highly crystalline PZT structure. The change of XRD patterns for PZT (run 14, 3 h, Fig. 8d) and PTO (run 13, 2 h, Fig. 8c) also shows that the PZT produced from PTO has a well-ordered structure (Fig. 8d) even though the PTO intermediate is poorly crystalline with probably lots of defects (Fig. 8c). The XRD patterns of runs 14–17 (Fig. 8d–g), which had no PTO peaks also imply that the PZT is much more stable than PTO in this system. The transition from PTO to PZT is probably an irreversible reaction because PZT is stable in the highly alkaline gels while PTO and lead zirconate (PZO) units in these gels are metastable and easily reacted and changed to PZT.

### 3.3. Discussion on the PZT synthesis using $Ti^{3+}$ reagent

$Ti^{4+}$-containing reagents, $TiCl_4$, $TiO_2$, and others, have been widely selected for PZT synthesis because the $TiO_2$ unit that makes up PZT structure has the oxidation state of 4+. In contrast, $Ti^{3+}$-containing reagents including $TiCl_3$ have been rarely tried in the synthesis of PZT and no significant result has been shown in the literature. When $Ti^{3+}$ is used, it should be oxidized in highly alkaline solutions and a chemical equation may be expected as follows:

$$TiCl_3(Ti^{3+}) + 3KOH \rightarrow TiO_2(Ti^{4+}) + 3KCl + H_2O + 0.5H_2(H^0)$$

The formation and release of lots of gas was observed when KOH and/or NaOH was added into the $TiCl_3$ contained solutions. The viscosity of the solutions dramatically increased during the mixing and then resulting in gels prior to hydrothermal heating.

The temperature of 110 °C for $Ti^{3+}$-used hydrothermal synthesis here for pure PZT is lower than 160 °C and 130 °C, for $Ti^{4+}$-used syntheses using $TiO_2$ and $TiCl_4$, respectively [9,10]. The crystallization time for pure PZT at 140 °C is $\leq$3 h (Fig. 8). The time is much shorter than that (10 h) for $TiCl_4$-used synthesis at 140 °C and similar to that (4 h) for $TiO_2$-used synthesis at 160 °C [9,10]. These results imply that the intermediate, PTO, provided by $Ti^{3+}$-reagents probably has more structural defects than those made by $Ti^{4+}$-reagents and hence Zr–O units can easily enter between the PTO units using $Ti^{3+}$-containing systems under relatively low temperature and/or short heating times. Finally, PTO and Zr–O units react to form highly stable PZT structure.

## 4. Conclusions

Pure PZT particles with no PTO impurity have been synthesized by a hydrothermal reaction using a $Ti^{3+}$ reagent, $TiCl_3$ at a low temperature of 110 °C. Probably, the more unstable PTO intermediates prepared by $Ti^{3+}$-reagents can easily react with Zr–O units compared with those from $Ti^{4+}$-reagents. The hydrothermal temperature of 110 °C, for $Ti^{3+}$-used reaction here is lower than 160 and 130 °C, using $Ti^{4+}$ reagents of $TiO_2$ and $TiCl_4$, respectively, and the crystallization time of $\leq$3 h at 140 °C for pure PZT using $TiCl_3$ is much shorter than that using $TiCl_4$ at the same hydrothermal temperature. Additionally, the low temperature of 110 °C is near or under boiling point of the synthetic gel. It means that this hydrothermal method using $Ti^{3+}$-precursor can be adopted for synthesizing pure PZT particles to save energy with probably non-pressurized equipment.

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## References

[1] R. Ramesh, Thin Film Ferroelectric Materials and Devices, Kluwer, Boston, 1997.

[2] S.S. Roy, H. Gleeson, C.P. Shaw, R.W. Whatmore, Z. Huang, Q. Zhang, S. Dunn, Growth and characterization of lead zirconate titanate (30/70) on indium tin oxide coated glass for oxide ferroelectric-liquid crystal display application, Integr. Ferroelectr. 29 (2000) 189–213.

[3] K. Sreenivas, M. Sayer, Characterization of lead zirconate titanate thin films deposited from multi-element metal targets, J. Appl. Phys. 64 (1988) 1484–1493.

[4] J.-W. Moon, S. Tazawa, K. Shinozaki, N. Wakiya, N. Mizutani, Impact of thin $SrTiO_3$ seed layer to achieve low-temperature crystallization below 300 °C and ferroelectricity of lead zirconate titanate thin film, Appl. Phys. Lett. 89 (2006) 202907.

[5] G. Yi, Z. Wu, M. Sayer, Preparation of lead zirconate titanate thin films by sol gel processing: electrical, optical, and electro-optic properties, J. Appl. Phys. 64 (1988) 2717–2724.

[6] Y. Lin, Y. Liu, H.A. Sodano, Hydrothermal synthesis of vertically aligned lead zirconate titanate nanowire arrays, Appl. Phys. Lett. 95 (2009) 122901.

[7] G. Xu, W. Jiang, M. Qian, X. Chen, Z. Li, G. Han, Hydrothermal synthesis of lead zirconate titanate nearly free-standing nanoparticles in the size regime of about 4 nm, Cryst. Growth Des. 9 (2009) 13–16.

[8] D.J. You, W.W. Jung, S.K. Choi, Domain structure in a micron-sized $PbZr_{1-x}Ti_xO_3$ single crystal on a Ti substrate fabricated by hydrothermal synthesis, Appl. Phys. Lett. 84 (2004) 3346–3348.

[9] Z.-C. Qiu, J.-P. Zhou, G. Zhu, P. Liu, X.-B. Bian, Hydrothermal synthesis of $Pb(Zr_{0.52}Ti_{0.48})O_3$ powders at low temperature and low alkaline concentration, Bull. Mater. Sci. 32 (2009) 193–197.

[10] S. Harada, S. Dunn, Low temperature hydrothermal routes to various PZT stoichiometries, J. Electroceram. 20 (2008) 65–71.

[11] S. Komarneni, Q. Li, K.M. Stefansson, R. Roy, Microwave-hydrothermal processing for synthesis of electroceramic powders, J. Mater. Res. 8 (1993) 3176–3183.

[12] A. Yamano, H. Kozuka, Effects of the heat-treatment conditions on the crystallographic orientation of $Pb(Zr,Ti)O_3$ thin films prepared by polyvinylpyrrolidone-assisted sol–gel method, J. Am. Ceram. Soc. 90 (2007) 3882–3889.