NU Science Journal 2010; 6(2): 156- 164

Phase Formation and Microstructure of $(Ba_{0.6}\ Pb_{0.4})TiO_3$ Powders Prepared via the Combustion Technique

Ukrit Chaimongkon, Artid Laowanidwatana, Suphornpun Chootin and Theerachai Bongkarn*

Department of Physics, Faculty of Science, Naresuan University,
Phitsanulok, 65000, Thailand
Corresponding author. E-mail address: researchcmu@yahoo.com

ABSTRACT

In this work, the effect of calcination temperatures on phase formation and microstructure of $(Ba_{0.6}\ Pb_{0.4})TiO_3$, (BPT) powders was investigated. BPT powders were prepared via combustion technique by using urea as a fuel. The raw materials were heated at various calcination temperatures ranging from 700 to 1,150 ^{o}C for 2 h at a heating/cooling rate of 5 ^{o}C/min. Powder samples were characterized using thermogravimetric analysis (TGA), differential thermal analysis (DTA), X-ray diffractometer (XRD) and scanning electron microscopy (SEM). The results showed that a second phase such as PbO_2, $BaCO_3$, and TiO_2 was detected in the powders calcined below 1,100 ºC. A single perovskite phase of the BPT powders was found with calcination temperatures above 1,100 ºC. The lattice parameter *c* and *c/a* ratio increased while, the lattice parameter *a* decreased with increasing calcinations temperatures. The TGA-DTA results corresponded to the XRD investigation. The particle size tended to increase with increasing calcining temperature.

Keywords: Ferroelectric Perovskite, Barium Lead Titanate, Combustion Technique, Phase Formation

INTRODUCTION

Barium titanate ($BaTiO_3$; BT) ceramic is one of the most interesting and studied perovskite. The strong interest in this compound is because of its high dielectric constant, low dielectric loss and good piezoelectric properties. BT, with a tetragonal phase at room temperature, shows a Curie temperature (T_c) of about 120 ^{o}C. The Curie point of BT can be shifted to a lower temperature by substituting strontium for barium or zirconium for titanium and to a higher temperature by substituting lead for barium (Xing *et al.,* 2003). The barium lead titanate [$(Ba_{1-x}Pb_x)TiO_3$] was indexed in a tetragonal structure at room temperature and cubic structure above their Curie temperature (Yang and Haile, 2006). The Curie temperature (T_C) of $(Ba_{1-x}Pb_x)TiO_3$ materials rises monotonically with the Pb content, from 120 ^{o}C at x=0 to 490 ^{o}C at x=1 (Yanchevskii *et al.,* 2003). The lattice parameter of $(Ba_{1-x}Pb_x)TiO_3$ continuously changes with solubility, but the changes are nonlinear. The tetragonal distortion increased as the Pb-content increased (Xing *et al.,* 2003). Barium lead titanate ceramics also exhibit an anomalously large positive temperature coefficient of resistance (PTCR) near the Curie temperature (Yanchevskii *et al.,*2003).Furthermore, the high Curie temperature of $(Ba_{1-x}Pb_x)TiO_3$

with x= 0.2 and 0.5 (175 and 330 ^{o}C), make these materials appropriated to use as a high temperature PTCR (Xing *et al.*, 2003).

The conventional synthetic for $(Ba_{1-x}Pb_x)TiO_3$ ceramics mainly involve the solid-state reaction method (Yanchevskii *et al.*, 2003) and the polymerized citrate method (Arya *et al.*, 2003). Recently, the combustion method has become an interesting technique because of its simplicity, relatively low cost and the fact that it usually results in products with the desired structure and composition (Patil *et al.*, 1997). However, $(Ba_{0.6}Pb_{0.4})TiO_3$ powders prepared by the combustion method have not been studied. Thus, in this work, $(Ba_{0.6}Pb_{0.4})TiO_3$ (BPT) powders were prepared via the combustion method and the effect of firing temperatures on its phase formation and microstructure were investigated.

EXPERIMENTAL

BPT powders-$(Ba_{0.6}Pb_{0.4})TiO_3$-were prepared via the combustion technique as shown in Figure 1. The appropriate amounts of $BaCO_3$ (98.5 % purity), PbO (99 % purity) and TiO_2 (99 % purity) were mixed by ball milling for 24 h with ethanol using zirconia balls. After drying at 120 ^{o}C and sieving, the powders and urea were mixed in an agate mortar. Then, the mixed powders were calcined using various calcinations, i.e. temperatures ranging from 700 to 1,150 ^{o}C, for 2 h at heating/cooling rate of 5 ^{o}C/min. The reaction of uncalcinate BPT powders and urea fuel taking place during the heat treatment, were investigated by thermogravimetric analysis and differential thermal analysis (TGA-DTA). X-ray diffraction (XRD) was employed to identify the phase formed. The particle morphology was imaged, using scanning electron microscopy (SEM) and the average particle size was determined by using a mean linear intercept method (Lee and Rainforth, 1994)

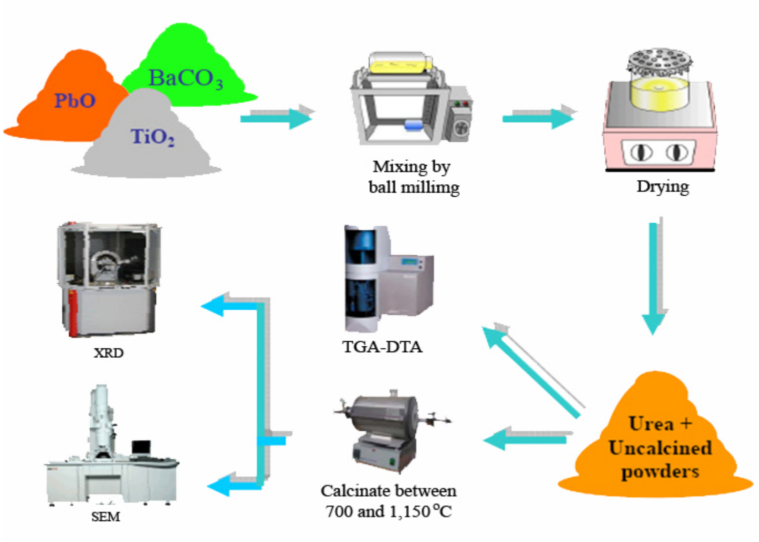


Figure 1 Preparation route for BPT powders

RESULTS AND DISCUSSION

Figure 2 shows the TGA-DTA curves of BPT powders prepared via the combustion technique. The BPT powders demonstrated a three-stage weight loss. The first weight loss occurred between 146.5 °C and 247.0 °C associated with endothermic peaks were which observed at 133.3 and 194.2 °C. These DTA peaks can be attributed to the melting of the urea (Xu *et al.*, 2005). The second weight loss was found from 289.7 °C to 709.8 °C and corresponded to the endothermic peak which existed at 349.6 °C and 474.2 °C, and is related to the vaporization of gas and water (Xu *et al.*, 2005). The last weight lost appeared above 877.4 °C which related to the endothermic peaks at 1,062 °C and this temperature may be the reaction temperature of the raw materials to form BPT.

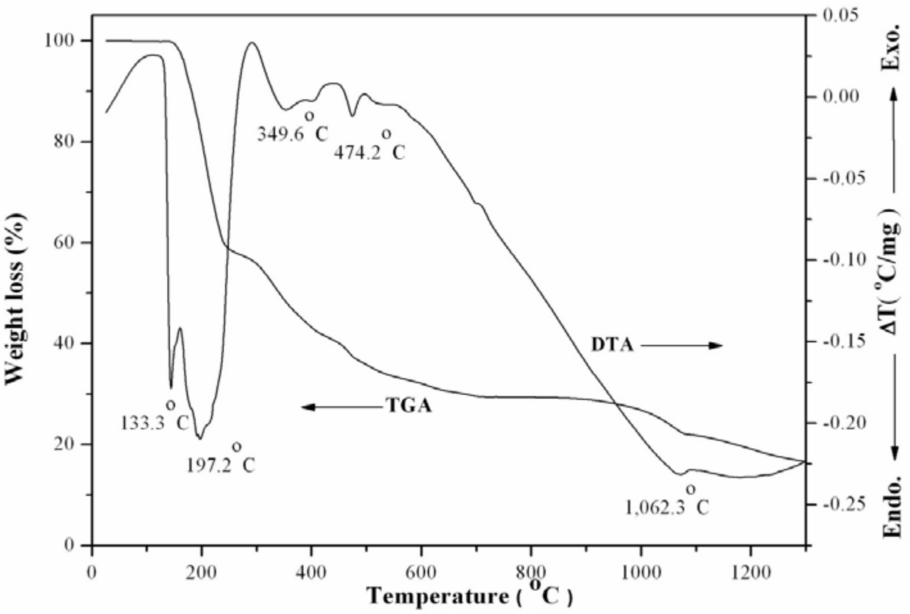


Figure 2 TGA-DTA curves for the mixture of $BaCO_3$, PbO, TiO_2 and urea powders.

The XRD traces of BPT powders, calcinated at different temperatures are shown in Figure 3. The structure of BPT, calcinated from 700 to 1,150 °C, is a tetragonal perovskite structure. The starting materials and impurity phases, such as PbO, PbO_2, $BaCO_3$, and TiO_2 were found in the BPT powders calcinate below 1,100 °C. Above 1,100 °C, they disappeared and the sample showed the pure perovskite phase. The XRD results corresponded to the TGA-DTA investigation.

The relative percentages in the perovskite and impurity phases were determined by measuring the major XRD peak intensities of the perovskite and the impurity phases. The percentage of the perovskite phase was estimated by the following equation:

$$\%perovskite\ \ phase = \left(\frac{I_{perov}}{I_{perov} + I_{PbO} + I_{PbO_2} + I_{BaCO_3} + I_{TiO_2}} \right) x100$$

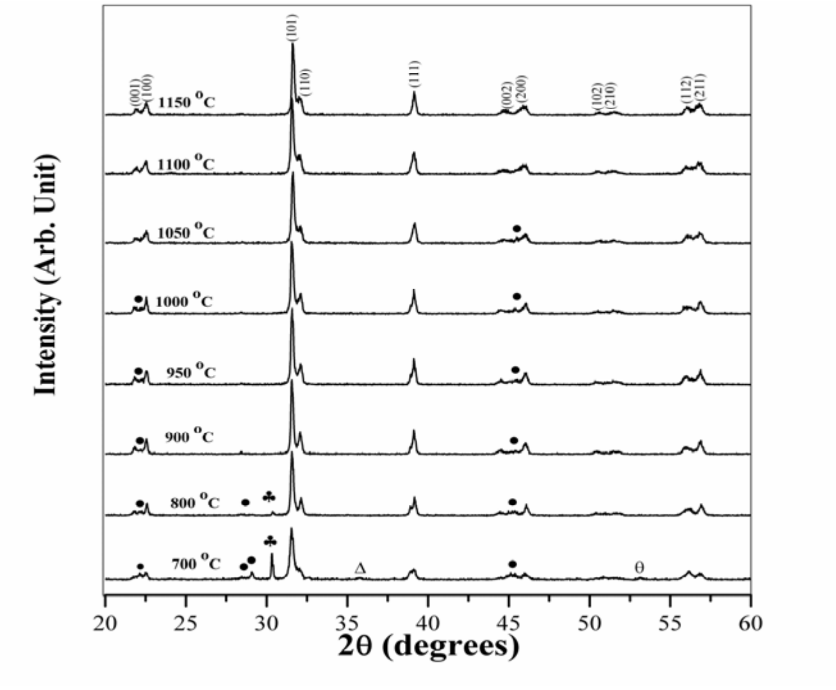


Figure 3 XRD patterns of BPT powder at various calcination temperatures; (Δ) PbO, (●) PbO_2, (♣) $BaCO_3$, (θ) TiO_2.

This equation is a well-known equation which is widely employed in the preparation of complex perovskite structure materials (Vittayakorn *et al.*, 2004; Vittayakorn *et al.*, 2003). Here $I_{perov}, I_{PbO}, I_{PbO_2}, I_{BaCO_3}, I_{TiO_2}$ refer to the intensity of the (101) perovskite peak are the intensities of the highest PbO, PbO_2, $BaCO_3$, and TiO_2. The percent of the perovskite phase increased with an increase in the calcining temperature as seen in Figure 4. A hundred percent of the perovskite phase was obtained from the samples calcined at temperatures higher than 1,100 °C for 2 h. The $(Ba_{1-x}Pb_x)TiO_3$ powders can be obtained from the solid state reaction method by three calcinations at 950 °C for 24 h. While, the combustion technique used only one calcination at 1,100 °C for 2 h. This indicated that the combustion technique is uncomplicated and saves time and energy. The lattice parameter *c* increased and lattice parameter *a* decreased with an increase in the calcining as shown in Table 1. The *c/a* increased and unit cell volume decreased with increased calcination temperatures as seen in Figure 5. The changing of calcinations temperatures affected the lattice strain, which is determined as the change in the *d* spacing and the lattice parameters of the sample (Eitssayeam *et al.*, 2008). The result was also similar with the previous works (Xing *et al.,* 2003; Arya *et al.,* 2003).

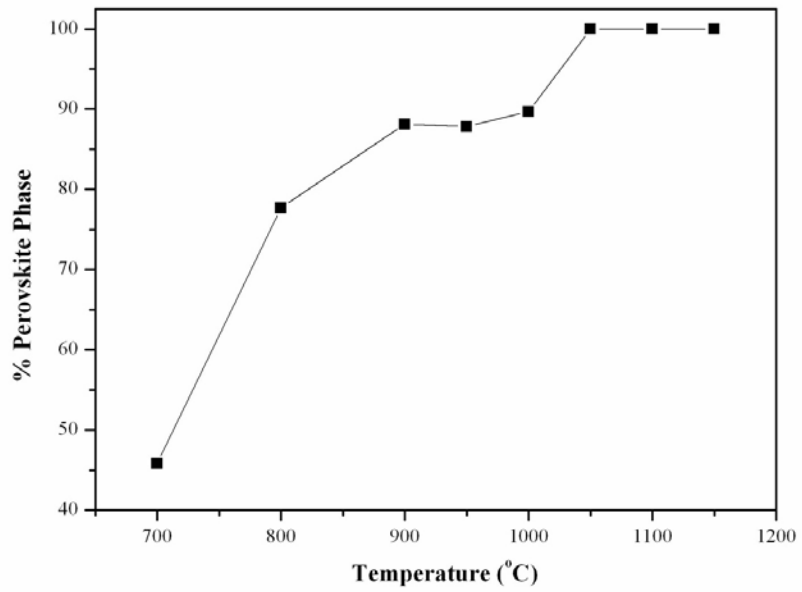


Figure 4 The percent of the perovskite phase with various calcination temperatures.

The SEM photographs of BPT calcined powders with different temperatures are illustrated in Figure 6. These powders exhibited an almost spherical morphology and have porous agglomerate. The average particle size obtained from a linear intercept method tended to increase with the increasing of calcination temperatures (Table 1).

CONCLUSIONS

Perovskite BPT powders can be successfully obtained by the combustion technique. The pure perovskite tetragonal phase was discovered at 1,100 ºC after 2 h. The calcination temperatures have a strong influence on: the crystal structure, percent perovskite phase, lattice parameter, tetragonality, particle size and unit cell volume of the BPT powders. The lattice parameter *c* increased while, lattice parameter *a* decreased with an increase in the calcining temperature. The *c/a* increased and unit cell volume decreased with increased calcination temperatures. The average particle sizes increased from 266 to 867 nm with increased calcinated temperatures.

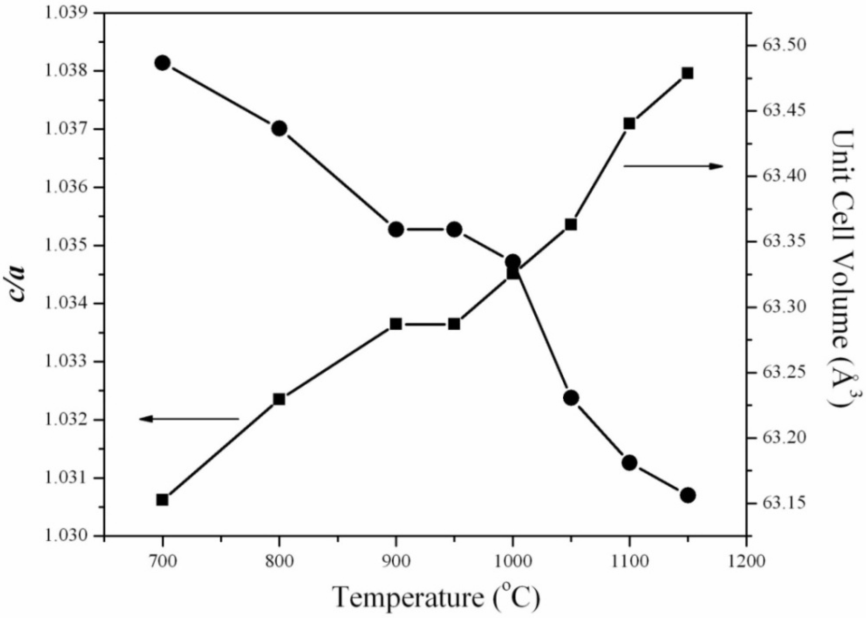
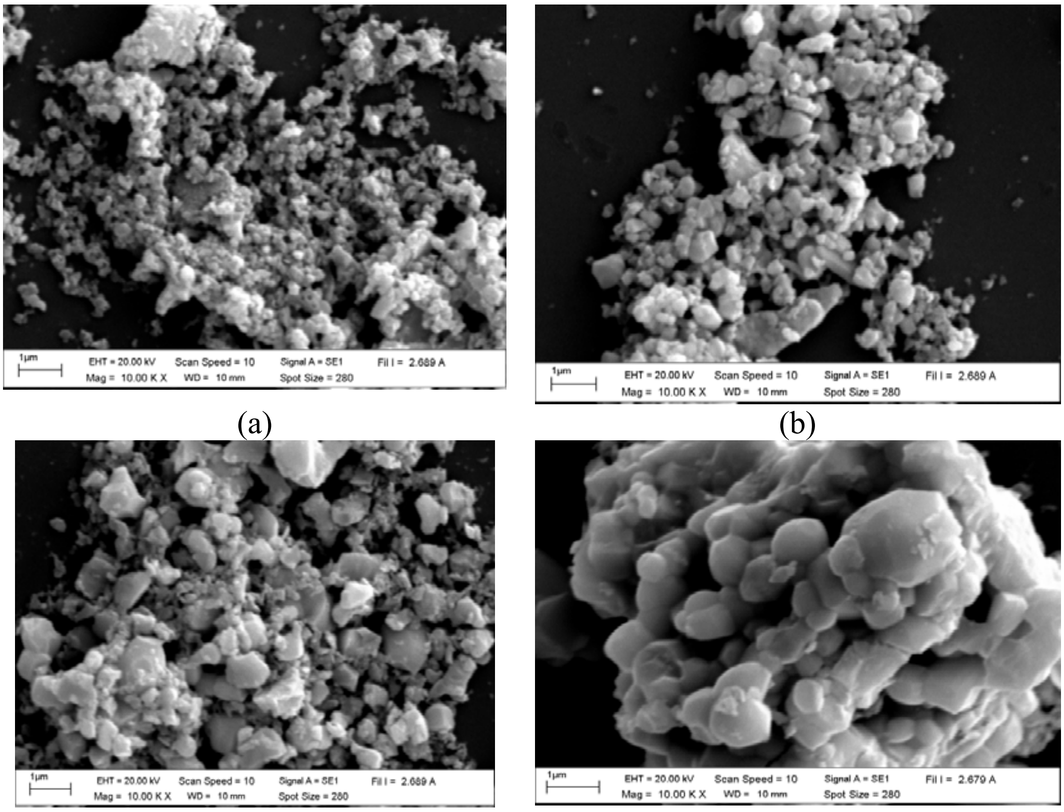


Figure 5 The *c/a* ratio and unit cell volume with various calcination temperatures.



(a) (b)

(c) (d)

Figure 6 SEM morphology of BPT powders calcined at (a) 700 °C (b) 800 °C (c) 1,100 °C (d) 1,150 °C.

Table 1 Lattice parameter *a*, *c* and average particle size of BPT powders

Calcination temperatures (ºC)	Lattice parameter *a* (Å)	Lattice parameter *c* (Å)	Average particle size (nm)
700	3.9380	4.0703	266
800	3.9348	4.0720	446
900	3.9332	4.0755	715
950	3.9300	4.0790	732
1,000	3.9284	4.0808	800
1,050	3.9268	4.0842	846
1,100	3.9256	4.0860	864
1,150	3.9236	4.0877	945

ACKNOWLEDGEMENTS

This work was financially supported by the Thailand Research Fund (TRF) and Commission on Higher Education (CHE). Thanks also to Department of Physics, Faculty of Science, Naresuan University for supporting facilities. Acknowledgements are also to Mr. Don Hindle, for helpful comments and corrections of the manuscript.

REFERENCES

Arya, P. R., Jha, P., Subbanna, G. N. and Ganguli, A. K. (2003). Polymeric citrate precursor route to the synthesis of nano-sized barium lead titanate. *Materials Research Bulletin, 38,* 617-628.

Eitssayeam, S., Intatha, U., Pengpat, K., Rujijanagul, G., MacKanzie, K.J.D. and Tunkasiri, T. (2008). Ferroelectric, pyroelectric and dielectric properties of complex perovskite-structured $Pb_{0.84}Ba_{0.16}(Zr_{0.44}Ti_{0.40}Fe_{0.08}Nb_{0.08})O_3$ ceramics. *Current Applied Physics*, *8*, 266-269.

Lee, W. E. and Rainforth, W. M. (1994). *Ceramic microstructure property control by processing*. London: Chapman & Hall, 220.

Patil, K. C., Aruna, S. T. and Ekambaram, S. (1997). Combustion synthesis. *Current Opinion in Solid State &Materials Science, 2*(2), 156-1 65.

Vittayakorn, N., Rujijanagul, G., Tunkasiri, T., Tan, X. and Cann, D.P. (2003). Perovskite phase formation and ferroelectric properties of the lead nickel niobate-lead zinc niobate-lead zirconate titanate ternary system. *Journal of Materials Research, 18*(12), 2882-2889.

Vittayakorn, N., Rujijanagul, G., Tunkasiri, T., Tan, X. and Cann, D.P. (2004). Influence of processing conditions on the phase transition and ferroelectric properties of PZN-PZT ceramics. *Materials Science and Engineering B.*, *108*(3), 258-265.

Xing, X., Deng, J., Zhu, Z. and Liu, G. (2003). Solid solution $Ba_{1-x}Pb_xTiO_3$ and its expansion. *Journal of Alloys Compounds, 353,* 1-4.

Xu, J., Xue, D. and Yan, C. (2005). Chemical synthesis of $NaTaO_3$ powder at low-temperature. *Materials Letters, 59*, 2920-2922.

Yanchevskill, O. Z., V' yunov, I.O. and Belous, A.G. (2003). Fabrication and properties of semiconducting barium lead titanate ceramics containing low-melting glass additions. *Inorganic Materials, 39*(6), 645-651.

Yang, W. D. and Haile, S. M. (2006). Characterization and microstructure of highly preferred oriented lead barium titanate thin films on MgO (100) by sol-gel process. *Thin Solid Films, 510*, 55-61.