

Phase Formation and Crystal Structure of 0.9PZT-0.1PZN Powders Prepared by Columbite Precursor

Naratip Vittayakorn^{1*} and Theerachai Bongkarn²

¹Chemistry Department, King Mongkut's Institute of Technology Ladkrabang,
Bangkok 10520 Thailand

²Department of Physics, Faculty of Science, Naresuan University,
Phitsanulok 65000 Thailand

*Corresponding author. E-mail: naratipcmu@yahoo.com

ABSTRACT

The perovskite structure of $0.9\text{Pb}(\text{Zr}_{1/2}\text{Ti}_{1/2})\text{O}_3-0.1\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ has been synthesized via columbite precursor method. Columbite structure ZnNb_2O_6 and wolframite structure ZrTiO_4 has been prepared for precursors. The phase, morphology and microstructures were characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM). It was found that the suitable calcination temperature to synthesize 0.9PZT-0.1PZN powders was successfully obtained at 800 °C for 4 h.

Keywords: Lead Zinc Niobate (PZN), Lead Zirconate Titanate (PZT), powder synthesis, calcinations, phase development

INTRODUCTION

Ferroelectric oxide materials are of immense interest for future electronic, optoelectronic, and multi-functional devices, where a tunable dielectric constant, switchable polarization, strong electro-optic properties, pyroelectric and piezoelectric properties may be exploited (Moulson and Herbert, 1990). In the last decade, normal ferroelectric lead zirconate titanate [$\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$, PZT] has become one of the most important commercially produced piezoelectric materials. Excellent piezoelectric properties have been observed in compositions close to the morphotropic phase boundary (MPB). This MPB is located around $\text{PbTiO}_3:\text{PbZrO}_3$ ~1:1 and separates the Ti-rich tetragonal phase from the Zr-rich rhombohedral phase (Uchino, 2000).

Lead zinc niobate, PZN, was firstly synthesized in the 1960s (Smolenskii and Agranovskaya, 1958). Its permittivity versus temperature curve displayed a

broad peak around 140°C (T_m) with a strong frequency dependence. Extremely high relative permittivities have been measured in the vicinity of the peak with a $\epsilon_r \sim 60,000$ reported for single crystals (Kuwata, Uchino and Nomura, 1981). Nanometer-level chemical heterogeneity in the form of short range order of Zn^{2+} and Nb^{5+} at B-sites was proposed to account for the observed diffuse phase transition. The crystal structure of PZN is rhombohedral ($3m$) at room temperature and transforms to cubic ($Pm3m$) at high temperatures. Although single crystals of PZN can routinely be grown by the flux method, it is known that perovskite PZN ceramics cannot be synthesized by the conventional mixed-oxide method without doping (Xu, 1991; A.Halliyal *et al.*, 1986). This is because PZN has a low tolerance factor and small electronegativity difference between the cations and the pyrochlore phase appears to be more thermodynamically stable than the perovskite phase (Halliyal, 1986).

Perovskite, $CaTiO_3$, is the type-structure for a large family of compounds with the formula ' ABX_3 '. When 'X' is oxygen, the value of the oxidation states of 'A' and 'B' must be added to six. A number of combinations are found which conform to this formula. Thus, 'A' may be divalent (Ca, Sr, Ba, Cd, and Pb) and 'B' may be quadrivalent (Ti, Th, Zr, Hf, Sn, and Ge), or 'A' and 'B' may be both trivalent (eg. $LaAlO_3$). A third alternative is for 'A' to be univalent and 'B' pentavalent (eg. $NaWO_3$). In perovskite itself, calcium is surrounded by twelve oxygens, and titanium is octahedrally coordinated by oxygen; these octahedra share apices (Xu, 1991).

Since both PZT and PZN have perovskite structure and are known to have excellent dielectric and piezoelectric properties, it is suggested to alloy PZN with PZT to stabilize and optimize the PZN ceramics. The purpose of this work was to perform a systematic study of the reaction of the precursors and to explore a Columbite-(Wolframite) Precursor route for production of $0.9PZT-0.1PZN$ powders. The phase formation characteristic of the powder, calcined at various temperature conditions, was also studied and discussed.

EXPERIMENTAL PROCEDURE

The powders of $0.9Pb(Zr_{0.5}Ti_{0.5})O_3 - 0.1Pb(Zn_{1/3}Nb_{2/3})O_3$ were synthesized using the columbite precursor method. Reagent-grade oxide powders of PbO , ZrO_2 , TiO_2 , ZnO , and Nb_2O_5 were used as raw materials. In this method, the columbite precursors $ZnNb_2O_6$ was prepared from the reaction between ZnO (99.9%) and Nb_2O_5 (99.9%) at 975°C for 4 h. The columbite-(wolframite) synthetic route employed is

shown schematically in Figure 1. The wolframite phase $ZrTiO_4$ was formed by reacting ZrO_2 (99.9%) with TiO_2 (99.9%) at $1400^\circ C$ for 4 h. The powders of $ZnNb_2O_6$ and $ZrTiO_4$ were then mixed in the required stoichiometric amounts with PbO (99.9%) with an excess of 2 mol% of PbO added. Stoichiometric amounts of the precursors were mixed and milled in isopropyl alcohol for 6 h using a ball-milling. The mixture was dried at $60^\circ C$ for 12 h. After grinding and sieving with 100 mesh, four calcination temperatures were selected to investigate the reaction to form zirconium titanate: 700, 750, 800, $850^\circ C$ all for 4 h.

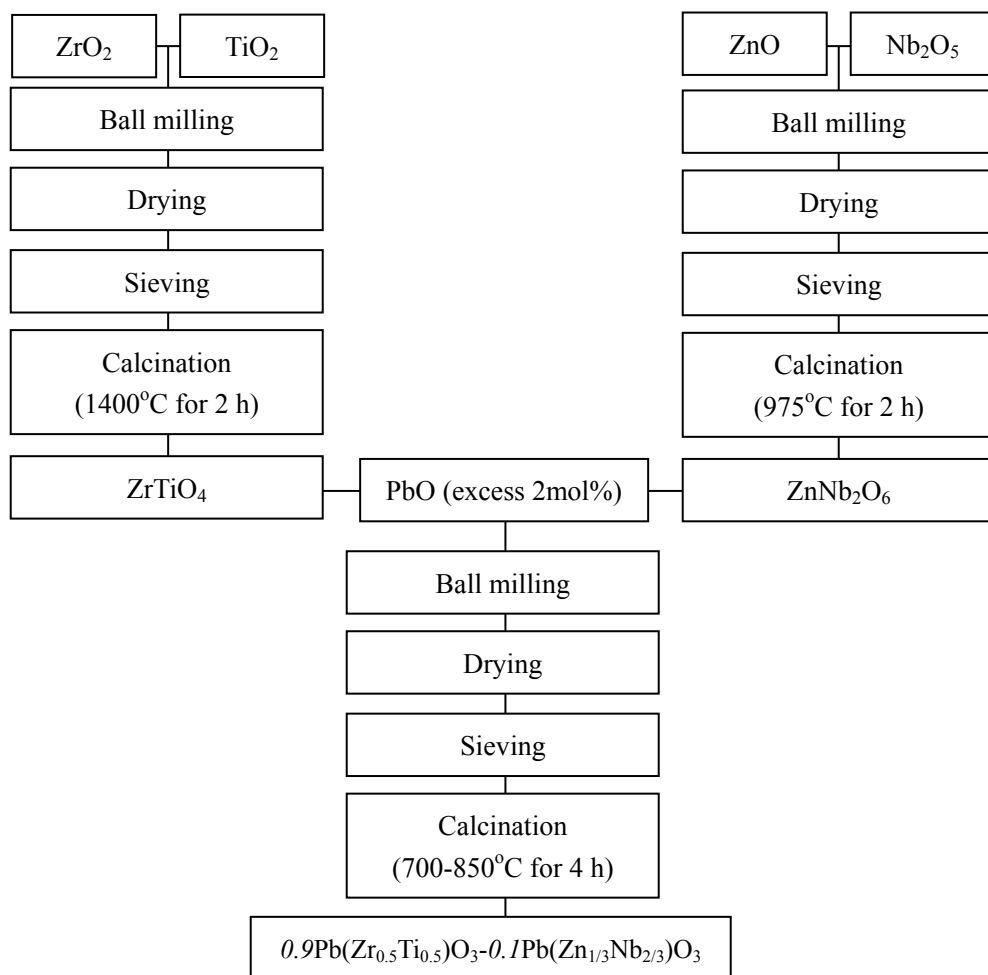


Figure 1 Preparation route for the $0.9Pb(Zr_{0.5}Ti_{0.5})O_3-0.1Pb(Zn_{1/3}Nb_{2/3})O_3$ powder.

The X-ray diffraction measurements were carried out on powdered samples using a high-resolution SIEMENS D 500 diffractometer. Filtered $\text{CuK}\alpha$ $\lambda = 1.54056 \text{ \AA}$ (40 kV, 25 mA) was used. The diffraction diagram was measured from 20° to 60° in 2θ range with step size 0.02° (2θ) and 2 s counting time. The microstructure and grain growth of the calcined samples were examined using a scanning electron microscope (SEM).

RESULTS AND DISCUSSION

XRD patterns of the calcined $0.9\text{PZT}-0.1\text{PZN}$ powders at different calcination temperatures are shown in Figure 2. The XRD results show that the pyrochlore phase $\text{Pb}_{1.88}(\text{Zn}_{0.3}\text{Nb}_{1.25})\text{O}_{5.305}$ (JCPDS No.25-0446) was dominant at calcination temperatures below 750°C for all of the columbite-derived powders. The precursor phases PbO , ZrTiO_4 , ZnNb_2O_6 were also detected by XRD at below 800°C . It is assumed that the columbite phase ZnNb_2O_6 decomposed via reaction with PbO at low temperatures to form the pyrochlore phase $\text{Pb}_{1.88}(\text{Zn}_{0.3}\text{Nb}_{1.25})\text{O}_{5.305}$.

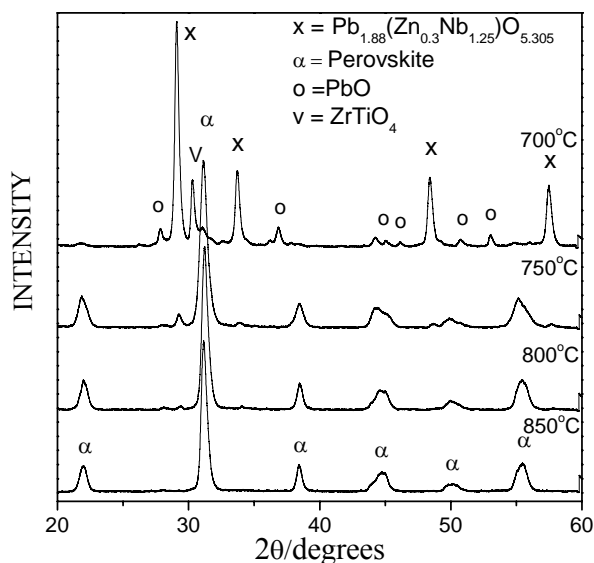


Figure 2 XRD patterns of $0.9\text{PZT}-0.1\text{PZN}$ powder calcined at various temperatures for 4 h with heating/cooling rate of $20^\circ\text{C}/\text{min}$.

At 800°C , the pyrochlore phase began to decrease and disappeared completely at 850°C for powder prepared by conventional method. This result

shows that at higher temperatures, the pyrochlore phase ($\text{Pb}_{1.88}(\text{Zn}_{0.3}\text{Nb}_{1.25})\text{O}_{5.305}$) transforms to perovskite phase ($0.9\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3-0.1\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$) with increasing calcination temperatures. The optimum calcination temperature for the formation of pure perovskite phase was found to be about 850°C for 4 h with heating/cooling rates as fast as 20°C/min.

The relative amounts of perovskite and pyrochlore phases were approximated by calculating the ratio of the major XRD peak intensities of the perovskite and pyrochlore phase via the following equation:

$$\text{Perovskite Intensity \%} = \left(\frac{I_{\text{perov}}}{I_{\text{perov}} + I_{\text{pyro}} + I_{\text{PbO}}} \right) \times 100$$

where I_{perov} , I_{pyro} , and I_{PbO} refer to the intensity of the (110) perovskite peak, (222) pyrochlore peak, and the intensity of the highest lead oxide peak, respectively. The perovskite phase formation at various calcination temperatures are shown in Figure 3.

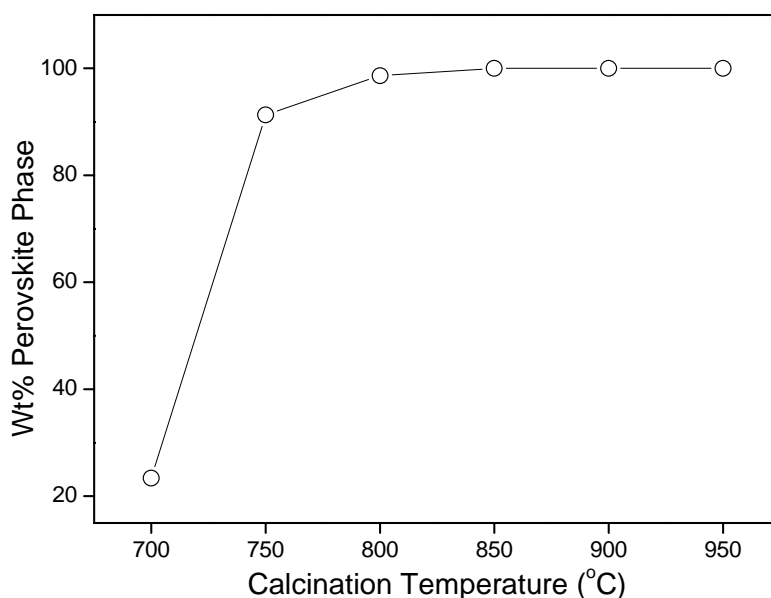


Figure 3 Percentage of perovskite phase as a function of calcination temperature.

Because the raw materials used consist of multiphase, the formation reaction of the perovskite phase belongs to the heterogeneous system. A model used to treat multiphase reaction kinetics was derived by Johnson and Mehl and the equation for this reaction is

$$\ln[1/(1-y)] = (kt)^n$$

where y is the constant of the perovskite phase formed; k is the reaction rate constant; t is the calcination time; and n is the reaction order. The relation of $\ln(\ln [1/(1-y)])$ versus $\ln(t)$ is plotted in Figure 4.

From this graph, it was found that the phase transformation of perovskite phase obeys the theory of phase transformations (Christian, 2002).

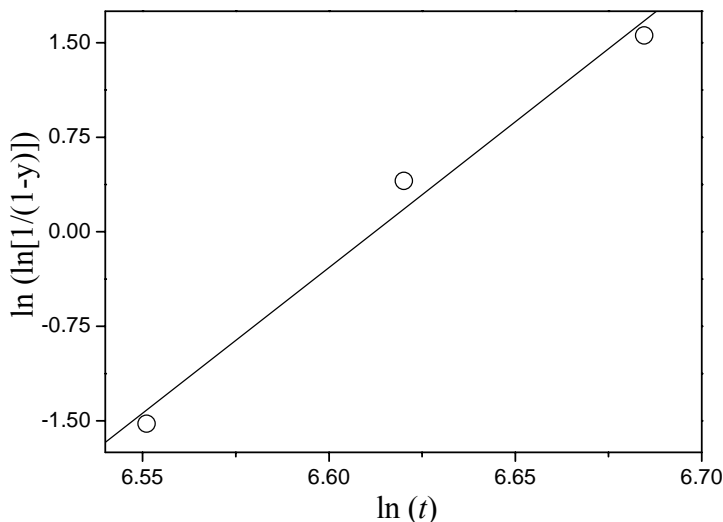


Figure 4 Reaction kinetics following the Johnson-Mehl-Avrami equation for $0.9\text{PZT}-0.1\text{PZN}$.

XRD patterns of the calcined $0.9\text{PZT}-0.1\text{PZN}$ powders at 950°C for 4 h are shown in Figure 5. The XRD results shows strong (200) peak splitting which is indicative of the tetragonal phase. It is known that the strongest reflections apparent in the majority of the XRD patterns indicate the formation of two lead zirconate titanate phases (Uchino, 1998). These can be matched with JCPDS file numbers 50-346 and 73-2022 for the rhombohedral $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ and tetragonal $\text{Pb}(\text{Zr}_{0.44}\text{Ti}_{0.56})\text{O}_3$ respectively. The most obvious different between the patterns of rhombohedral and tetragonal PZT phases concerns the presence of a splitting of (002)/(200) peak at two-theta about 42° - 46° for the latter phase. With the properly indexed peaks, lattice parameter was determined using UnitCell, a linear least squares refinement program. The tetragonal unit cell was found to have the following dimensions: $a = 4.0455 (\pm 0.0004)$ and $c = 4.1037 (\pm 0.005)$ Å.

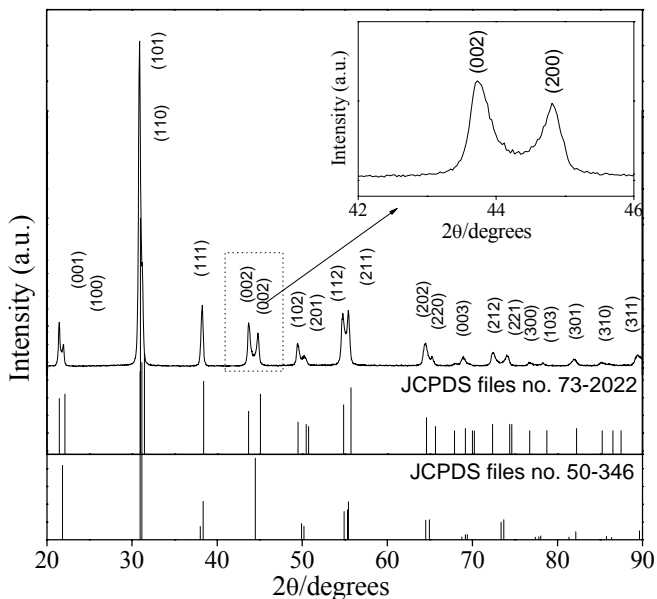


Figure 5 Computerised JCPDS data-matched and a measured XRD pattern of $0.9\text{PZT}-0.1\text{PZN}$.

SEM micrographs of the calcined $0.9\text{PZT}-0.1\text{PZN}$ powders are given in Figure 6. In general, the particles are agglomerated and basically irregular in shape, with a substantial variation in particle size and morphology. Particle size can be estimated from SEM micrographs to be in the range of 300-600 nm.

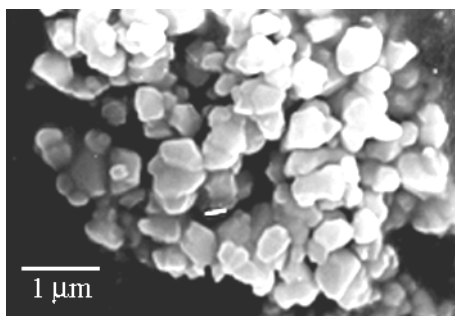


Figure 6 SEM micrographs of the $0.9\text{PZT}-0.1\text{PZN}$ powders calcined at 850°C for 4 h, with heating/cooling rate $20^\circ\text{C}/\text{min}$.

CONCLUSION

Polycrystalline powders of 0.9PZT-0.1PZN were synthesized using solid state synthesis using corresponding oxides as starting materials. Evidence has been obtained for a 100% yield of perovskite at a calcination temperature of 850°C for 2 h with heating/cooling rates of 20°C/min. XRD showed the compound to be the perovskite structure, having tetragonal lattice parameters of $a = 4.0455 (\pm 0.0004)$ and $c = 4.1037 (\pm 0.005) \text{ \AA}$.

ACKNOWLEDGEMENTS

The authors are grateful to The Thailand Research Fund (TRF), Faculty of Science, King Mongkut's Institute of Technology Ladkrabang and Faculty of Science, Naresuan University for their financial supports.

REFERENCES

- Halliyal, A., Shrout, T.R, Umesh, K. and Safari, A. (1986). Stability of perovskite phase in $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ and other $\text{A}(\text{B}'\text{B}'')\text{O}_3$ perovskite. Paper read at IEEE Int'l Confr. on Appl. of Ferro., at Lehigh University, Bethlehem, PA.
- Christian, J.W. (2002). *The Theory of Transformations in Metals and Alloys: Part I*. Oxford: Pergamon Press.
- Halliyal, A. (1986). Stability of perovskite phase in PZN and other $\text{A}(\text{B}'\text{B}'')\text{O}_3$ perovskite. Paper read at Proceedings of the IEEE International symposium on the application of Ferroelectrics., at Lehigh University, Bethlehem, PA.
- Kuwata, J., Kenji U. and Nomura, S. (1981). Phase transition in the PZN-PT system. *ferroelectrics*, 37, 579.
- Moulson, A.J. and Herbert, J.M. (1990). *Electroceramics: Materials, Properties, Applications*. New York: Chapman and Hall.
- Smolenskii, G.A. and Agranovskaya, A.L. (1958). Dielectric polarization of and loss of some complex compounds. *Sov. Phys.-Tech. Phys.*, 1380.
- Uchino, K. (1998). High electromechanical coupling piezoelectrics: relaxor and normal ferroelectric solid solutions. *Solid State Ionics*, 108(1-4), 43.
- . (2000). *Ferroelectric Devices*. New York: Marcel Dekker, Inc.
- Xu, Y. (1991). *Ferroelectric Materials and Their Application*: Elsevier Science Publishers B.V.