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Synthesis of $Pb(Zr,Ti)O_3$ Nanopowders by Milling Coprecipitation Method

MYONG-HO KIM,[1,*] A. GOLOVCHANSKI,[1] SOON IL LEE,[3] TAE-GONE PARK[2] & TAE KWON SONG[1]

[1]*Department of Ceramics Engineering,* [2]*School of Mechatronics Engineering, Changwon National University, Sarim-Dong, Changwon, Gyeongnam 641-773, Korea*

[3]*Center for Dielectric Studies, Materials Research Institute, The Pennsylvania State University, University Park, PA 16802, USA*

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Abstract. Nano-size powders of lead zirconate titanate (PZT) were fabricated by a new milling coprecipitation method (MCP) improved from the conventional wet ball milling and precipitation. This method consists of slurry preparation from nanoparticles of TiO_2 with aqueous solution of $ZrO(NO_3)_2$ and $Pb(NO_3)_2$ with zirconia ball mill media, followed by precipitation with NH_4OH as precipitant. Milling media (1mm and 3mm balls) improves the precipitation homogeneity during processing. Single-phase perovskite structure of PZT was formed at a calcination temperature of 500°C and powders of 50 nm particle size were obtained. Powders were characterized using TG-DTA, SEM and XRD methods. Sintering ability of powders and piezoelectric properties of the ceramics were also investigated.

Keywords: PZT, piezoelectric, nano-size, coprecipitation, mechano-chemistry

Introduction

Lead zirconate titanate ($Pb(Zr_xTi_{1-x})O_3$ or PZT) ceramics are of great technological interest due to their excellent piezoelectric and ferroelectric properties [1]. In general, the PZT is processed by the traditional solid state reaction. However, there are undesirable features such as nonstoichiometry, compositional fluctuation and poor microstructure because of the high temperature processes. Therefore, it is necessary to process PZT at as low a sintering temperature as possible. Low firing temperature processing in ceramic fabrication demands fine precursor powders of high homogeneity of components mixing. Nanosized PZT precursor powder fabrication is of a special interest to sinter fine-grained piezoceramics without ferroelectric property degradation. Chemical methods such as coprecipitation and alkoxide sol-gel processes are employed nowadays to synthesize it [1–4]. Semi-chemical methods (mechano-chemical [5], partial oxalate [6–8]) can be used as well. In our recent work, the milling precipitation method of PZT powder fabrication was presented [9]. It was based on simultaneous oxide milling and one component precipitation.

The objective of this work is to study the milling coprecipitation method for nano-sized PZT powder synthesis. Main advantages of MCP method over coprecipitation and sol-gel process are lower cost and better stoichiometry control of final product.

Experimental Procedure

The raw materials used in this experiment were high purity titanium dioxide (P25, Korea University, particle size of 25 nm), zirconyl nitrate hydrate (Acros Organics), lead (II) nitrate (Daejung extra pure reagents) and ammonium hydroxide (Aldrich chemical Co.). The concentration of $ZrO(NO_3)_2$ water solution was determined by the gravimetric analysis. The same method was used to determine the assay of $Pb(NO_3)_2$. The

*To whom all correspondence should be addressed. E-mail: mhkim@changwon.ac.kr

piezoceramic composition in this study was chosen as $Pb(Zr_{0.53}Ti_{0.47})O_3$ (PZT), which is in the morphotropic phase boundary(MPB).

Powders of PZT were fabricated by a milling coprecipitation(MCP) technique. Appropriate amounts of TiO_2, $Pb(NO_3)_2$ and aqueous solution of $ZrO(NO_3)_2$ corresponding to the composition of $Pb(Zr_{0.53}Ti_{0.47})O_3$ were added into a plastic jar with zirconia balls. Ammonium hydroxide (20% excess of stoichiometric amount) was poured into the jar after 30 min. of milling. Precipitation of hydroxides took place while continuing milling for 2 hours. After washing and drying, the resulting powders were calcined at temperatures between 400°C and 850°C and the phase formation was studied by XRD. Calcined powders were re-milled for 20 hours, mixed with PVA binder and pressed to the disks of 10 mm diameter. Green disks covered with PZT powder were sintered in an air atmosphere at temperatures between 800 and 1100°C. The density of sintered disks was measured by the Archimedes method. Average particle size of powders was calculated by the line-interception method.

Electroded samples were polarized in silicon oil by an applied electric field of 1.5 kV/mm at 110°C. Piezoelectic properties were measured after aging for 24 hrs with a resonance-anti-resonance method using HP4194 network analyzer. TG-DTA analysis was performed on Universal V2.5HTA Instruments. XRD measurements were conducted using Cu-Kα radiation (Philips X'PERT MPD). SEM micrographs were taken with JEOL JSM-2400.

Results and Discussion

Milling Coprecipitation Process

TG-DTA curves of PZT powder prepared by MCP process are shown in Fig. 1. From the weight loss curve in Figs. 1, 3 stages of powder transformation can be observed. Taking into account XRD data as well, the following transformation mechanism can be proposed.

$$Pb(OH)_2 * 0.53ZrO(OH)_2 * 0.47TiO_2 + H_2O(100\%) \rightarrow Pb(OH)_2 * 0.53ZrO(OH)_2 * 0.47TiO_2 \quad (250^\circ C, 95.1\%) \quad (1)$$

$$Pb(OH)_2 * 0.53ZrO(OH)_2 * 0.47TiO_2 \rightarrow Pb(OH)_2 * 0.53ZrO_2 * 0.47TiO_2 \text{ (amorphous)} \quad (400^\circ C, 92.6\%) \quad (2)$$

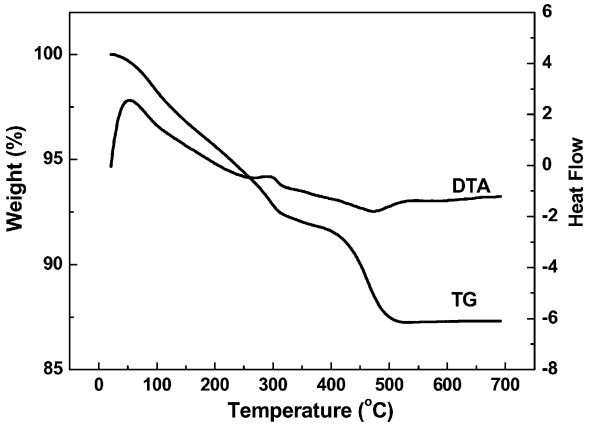

Fig. 1. TG-DTA curves of PZT powders produced by the Milling Coprecipitation (MCP) processing.

$$Pb(OH)_2 * 0.53ZrO_2 * 0.47TiO_2 \rightarrow Pb(Zr_{0.53}Ti_{0.47})O_3 \quad (500^\circ C, 87.7\%) \quad (3)$$

Lead zirconate titanate (PZT) nano-powders are usually prepared by a sol-gel process. The sol-gel-derived nanosize PZT powders were sintered to 96% of relative density at temperatures between 950° and 1000°C [2–4]. PZT particles fabricated by partial oxalate method [6–8] and milling precipitation method have similar sintering ability to sol-gel powders, although their particle size is 300–500 nm. This is because of the relatively high temperature of perovskite phase assembling (650–750°C).

On the other hand, the new milling coprecipitation process in this study has the following advantages to reduce the PZT phase forming temperature:

- diffusion stage of precipitation can be eliminated due to tumbling of media balls
- lead titanate precursor resulted in precipitation on the surface of titanium dioxide nano-particles, whereas lead zirconate one resulted in coprecipitation in the solution, which may reduce the difference in kinetics of $PbTiO_3$ and $PbZrO_3$ formation.

Phase Formation and Effect of Ball Size of Milling Media

Figure 2 shows XRD diffraction patterns of PZT powders, prepared by milling coprecipitation (MCP) method after the calcination at different temperatures,

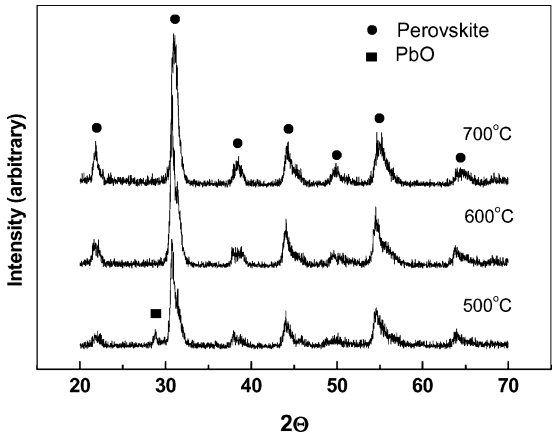

Fig. 2. XRD diffraction patterns of PZT powders, prepared by Milling Coprecipitation (MCP) method after calcinations at different temperatures (3 mm balls).

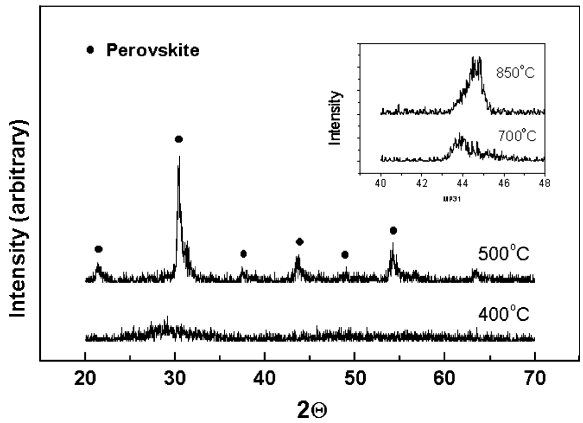

Fig. 3. XRD diffraction patterns of PZT powders, prepared by the Milling Coprecipitation (MCP) method after calcinations at different temperatures (1 mm balls).

in which 3 mm zirconia balls were used as a milling media. Perovskite phase formation went through intermediate phases and was completed at 600°C.

Figure 3 shows calcination behaviors of PZT powders, prepared by MCP when 1mm balls were used as milling media. Perovskite phase formation was completed at 500°C after crystallization of amorphous phase. From these results, it can be explained that the number of impacts during milling significantly reduces the temperature of PZT formation, because it improves the homogeneity of component mixing. The perovskite phase was of rhombohedral structure in both cases in spite of the equilibrium tetragonal structure of $Pb(Zr_{0.53}Ti_{0.47})O_3$. This is typical for most chemical methods of PZT powder fabrication [4–8].

SEM micrographs of PZT powders with different milling history are shown in Fig. 4. The average particle size of agglomerated powders was 150 nm (600°C, 3 mm balls) and 50 nm (500°C, 1mm balls) respectively. The sintering ability of 50 nm powders after re-milling for 24 hr was investigated to study the influence of the powder agglomeration. Figure 5 shows that the relative density depends on sintering temperature (curve b). At temperature of 950°C the density was the highest value and was in the range of typical values for chemistry route powders. The difference of sinterability in Fig. 5 can be explained by the agglomeration of powders during the calcination process. The results of non-calcined PZT powders are shown in Fig. 5 (curve a). In the case of non-calcined powders, the sintering ability of powders is significantly higher than previous results. A relative density of 94% was achieved at a sintering temperature of 800°C and 98% at 900°C. Because of the higher sintering ability, the reaction sintering may be the dominant sintering mechanism in the non-calcined powders. As the weight loss during heat treatment is only 12% (Fig. 1), shrinkage of the ceramics during sintering is relatively low, which avoids crack formation.

Piezoelectric Properties

Dielectric and piezoelectric properties of MCP- PZT ceramics are shown in Table 1. The mechanical quality factor and dielectric constant were typical for PZT ceramics. However, the piezoelectric coupling factor

Table 1. Dielectric and piezoelectric properties of MCP-PZT ceramics, sintered at various temperatures.

Samples	$T_{sint.}$ (°C)	Density (g/cm^3)	K_p	Q_m	ε_{33}^T
Calcination	900	7.55	0.2	60	778
at 500°C	950	7.77	0.35	114	876
	1000	7.50	0.41	113	801
Without	800	7.52	0.25	57	688
calcination	900	7.85	0.58	66	880

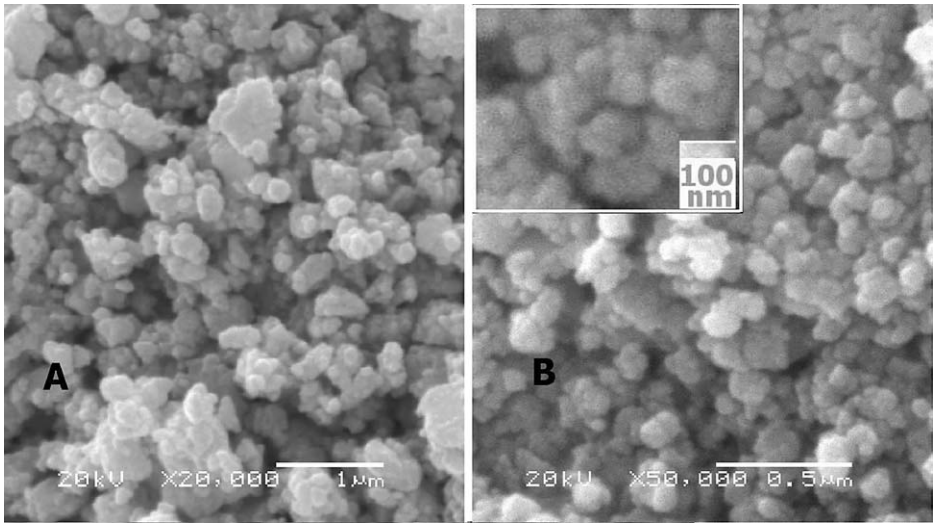

Fig. 4. SEM micrograph of PZT powders after calcinations at different temperatures (A: 3 mm balls, 600°C. B: 1 mm balls, 500°C).

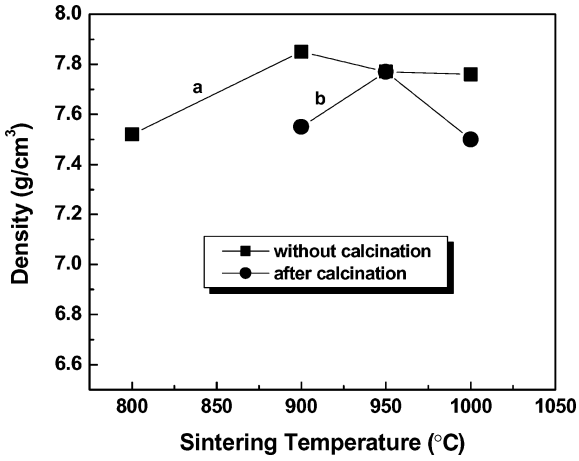

Fig. 5. Density of MCP-PZT ceramics, sintered at various temperatures (a: without calcination. b: calcined).

was lower than typical, except for ceramics of density 7.85 g/cm^3. This may be explained by the relatively low poling field of 1.5 kV/mm.

Conclusions

The results obtained in this study are summarized as follows:

1. Nanosized powders of PZT were synthesized by a new milling coprecipitation method (MCP), improved from the conventional wet ball milling and precipitation.
2. Single-phase perovskite structure of PZT was formed at a calcination temperature of 500°C and an average particle size of 50 nm was obtained.
3. In the case of non-calcined powders, the sintering ability of PZT powders is significantly higher and a relative density of 98% was achieved at a sintering temperature of 900°C. Because of the higher sintering ability, the reaction sintering may be the dominant sintering mechanism in the non-calcined powders.
4. The mechanical quality factor and dielectric constant were typical for PZT ceramics. However, the piezoelectric coupling factor was lower than typical, except for ceramics of density 7.85 g/cm^3.

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