

Preparation of Lead Zirconate Titanate ($\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$) by Homogeneous Precipitation and Calcination

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Preparation of phase-pure PZT ($\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$) powders was achieved, in the presence of urea ($\text{CH}_4\text{N}_2\text{O}$), by homogeneous precipitation. Aqueous solutions of PbCl_2 , $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, and TiCl_4 were used as the starting materials in the synthesis of phase-pure PZT powders. Phase evolution behavior of precursor powders was studied by powder X-ray diffraction (XRD) in air, over the temperature range of 90° to 750°C . The morphology of the formed powders was studied by scanning electron microscopy (SEM). Semiquantitative chemical analyses of the samples were performed by energy-dispersive X-ray spectroscopy (EDXS).

I. Introduction

LEAD ZIRCONATE TITANATE ($\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$) ceramics are of great technological interest because of their excellent piezoelectric and ferroelectric properties.^{1,2} PZT ceramics are extensively used as electromechanical transducer materials. The electromechanical response of these ceramics is maximum when x corresponds to the composition of the morphotropic phase boundary (MPB) which separates the tetragonal (T) and rhombohedral (R) phases toward Ti-rich and Zr-rich sides, respectively.

Conventionally, the PZT phase is prepared by solid-state reactive firing of the constituent oxides (i.e., PbO , ZrO_2 , and TiO_2). However, because of intermediate reactions which lead to the formation of PbTiO_3 (PT) and PbZrO_3 (PZ), the PZT formed by this method is chemically heterogeneous, including compositional fluctuations, which influence the electrical properties.^{3,4} The variations in composition may lead to a diffuse MPB between the tetragonal and rhombohedral PZT phases. Moreover, the completion of the reactions by long-range diffusion also requires temperatures in excess of 850°C . A lower calcination temperature, on the other hand, is always desirable since it yields fine powders of improved reactivity.

PZTs synthesized by chemical methods have resulted⁵⁻⁹ in powders with low compositional fluctuations, narrow MPB, and high reactivity. Among these chemical methods are a sol-gel technique^{6,8,9} and the methods of Kakegawa⁵ and Yamamoto.¹⁰ In the method proposed by Yamamoto,¹⁰ lead oxalate was precipitated on ZT particles processed by hydrothermal reaction, or on ZrO_2 and TiO_2 particles. However, the use of zirconia and titania particles also resulted in intermediate reaction products and a consequent deviation in the PZT stoichiometry. It was also reported by Singh *et al.*¹¹ that single-phase $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ powders were synthesized at about 600°C by a semiwet procedure.

In the present study, the experimental details of the synthesis of lead zirconate titanate phase from water-soluble chlorides of Pb, Zr, and Ti by homogeneous precipitation (via urea decomposition) are presented. The decomposition of urea in aqueous solutions was accompanied by the controlled supply of ammonia and CO_2 into the solution.¹² The smooth pH increase obtained by the decomposition of urea, in unison with the steady supply of OH^- and CO_3^{2-} ions, typically leads to the precipitation of metal hydroxycarbonates.¹³⁻¹⁵ Homogeneous precipitation from aqueous solutions has previously been used to produce submicrometer powders of basic lanthanide carbonates,¹⁶ CeO_2 ,¹⁷ YAG ($\text{Y}_3\text{Al}_5\text{O}_{12}$),¹⁸ LaAlO_3 ,¹⁹ YIG ($\text{Y}_3\text{Fe}_5\text{O}_{12}$),²⁰ BaTiO_3 ,²¹ and PbZrO_3 .²²

II. Experimental Techniques

PbCl_2 (99.5%, Merck, Darmstadt, Germany), $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (99%, Merck, Darmstadt, Germany), and TiCl_4 (98%, Merck, Darmstadt, Germany) were used as the starting chemicals; 0.2M ZrCl_4 and 0.02M PbCl_2 stock solutions were first prepared in deionized water. The as-received TiCl_4 (9.119M) was diluted to 2M in deionized water. Reagent-grade urea ($\text{CH}_4\text{N}_2\text{O}$, 99.5%, Riedel-De Haen AG, Germany) was used as the precipitation agent.

(1) Homogeneous Precipitation

A total of 160 mL of cation stock solutions (i.e., lead, zirconium, and titanium chlorides) was thoroughly mixed in a glass beaker; 27 g of urea dissolved in deionized water (350 mL) was then mixed with the above solution. The resultant solution was heated to 90°C for 1 h, in a water bath. Precipitation started by the end of the first 70 min with a slight turbidity in the clear solution. Precipitates were aged for 2 h at 90°C . pH values were continuously recorded as a function of time.

Precipitation experiments were also repeated for varying urea/cation ratios (i.e., 75, 60, 45, 30, 15, and 10) and for different aging times (120, 60, 30, and 10 min). Following aging, the precursors were quenched to room temperature. Precipitates were separated from the solutions by filtering. Recovered precursors were washed (4 \times) with deionized water. Washed precipitates were oven-dried at 90°C . Dried precursors were ground in an agate mortar and then calcined in an air atmosphere, in alumina boats, over the temperature range of 100° to 750°C for 6 h.

(2) Powder Characterization

Powder XRD spectra were obtained from the dried precipitates, as well as from powders heated at 100° to 750°C , in open alumina crucibles in an air atmosphere. An X-ray powder diffractometer (Rigaku, D-Max/B, Tokyo, Japan) was used in this study with $\text{CuK}\alpha$ radiation (0.02° steps, 1 s count time) to perform phase characterization, and to check the phase purity of the synthesized powders.

Particle size and morphological characteristics of the powders were monitored through scanning electron microscopy (SEM) photomicrographs (Model JSM6400, JEOL, Tokyo, Japan). An ultrasonic disrupter (Model XL 2015, Misonix, Inc.,

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New York) was used to form suspensions of PZT powders; 1 g of powder was ultrasonicated in 15 mL of isopropyl alcohol for 10 min, prior to evaporation to dryness on tiny glass slides. Energy dispersive X-ray spectroscopy (Kevex, Foster City, CA) analysis (accurate to about ± 3 wt%) was performed on PZT pellets.

III. Results and Discussion

The high-temperature behavior of PZT precursors produced by homogeneous precipitation experiments was monitored by the XRD charts of the isothermally heated powder samples. Figure 1 shows the phase distribution and crystallization characteristics of these powders as a function of temperature. It was observed that the powders calcined, in air, at 100° and 200°C were already crystalline, and composed of phases of cerussite (PbCO_3 : ICDD PDF 5-417), hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$: ICDD 13-131), and laurionite (PbClOH : ICDD 31-680).

Following calcination at 300°C for 6 h, the PZT precursors were composed of phases of litharge (PbO : ICDD 5-561), zirconia (ZrO_2 : ICDD 37-31), and titanium oxide (Ti_7O_{13} : ICDD 18-1403). This observation showed that over the temperature range of 200° to 300°C, lead hydroxycarbonate phases (i.e., cerussite and hydrocerussite) were mostly converted into their oxides (i.e., litharge). It was also interesting to note that at about 300°C the free phases of zirconium and titanium oxides crystallized from the precursor powders. Upon calcination at 400°C, the phases of litharge and zirconia completely disappeared, and the initial formation of PbZrO_3 (ICDD 35-739 and 20-608) was observed, and a small amount of PZT

($\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$: ICDD 33-784) evolved. This temperature was considered to be the starting temperature for the formation of the PZT phase.

Calcination of precursor powders at temperatures higher than 400°C (in air atmosphere), as shown in Fig. 1 (urea/cation ratio = 45), all yielded single-phase PZT by XRD. Pyrochlore phase was not observed. Therefore, it can be stated that 500°C was the temperature of formation of PZT in powders prepared by homogeneous precipitation. The EDXS analysis performed on the 700°C-calcined samples gave the mean atomic percentages of 20.04:10.29:9.67 (for Pb:Zr:Ti, respectively), which are expected for single-phase perovskite stoichiometry.

Figure 2 shows the solution pH versus time curves recorded in the precipitation solutions, for various urea/cation ratios, in real time. It appeared that the initial drop in pH might be due to both the presence of acidic cations in the solution and, although not directly suggested by the data of Fig. 2, the formation of the intermediate complex HCNO ,¹⁶ followed by an increase in the dissociation constant of water.¹⁹ The pH started to rise after about the first 30 min of aging at 90°C. It was reported by Cornilsen and Reed¹³ in alumina precipitation (in the presence of urea) that urea itself decomposes above 80°C. The rise in pH coincided with the observation of slight turbidity in the solution at the start of precipitation. A further slow increase in pH was observed until hydrolysis of cations was complete. As the urea concentration of the solutions increased, the final pH values (Fig. 2) also increased. The unique shoulders in the pH data corresponded to the precipitation start points.

By using the data obtained in Fig. 2, it was concluded that the critical "urea/cation ratio" in the solutions must be set to 15 or above, for the homogeneous precipitation of single-phase PZT powders. At the ratio of 10, the PZT phase did not form, and the resulting phases were only a mixture of cerussite and hydrocerussite upon calcination at 700°C. The typical morphology of the synthesized powders is depicted in Fig. 3. PZT powders of this study were weakly agglomerated, but were of submicrometer particle size.

IV. Conclusions

The lead zirconate titanate ($\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$) phase has been synthesized from aqueous solutions, following calcination at 500°C in an air atmosphere. This study showed that it is possible to obtain chemically uniform submicrometer powders of $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ by homogeneous precipitation in aqueous solutions containing urea, starting with the chlorides of the respective cations. A considerable decrease in the processing

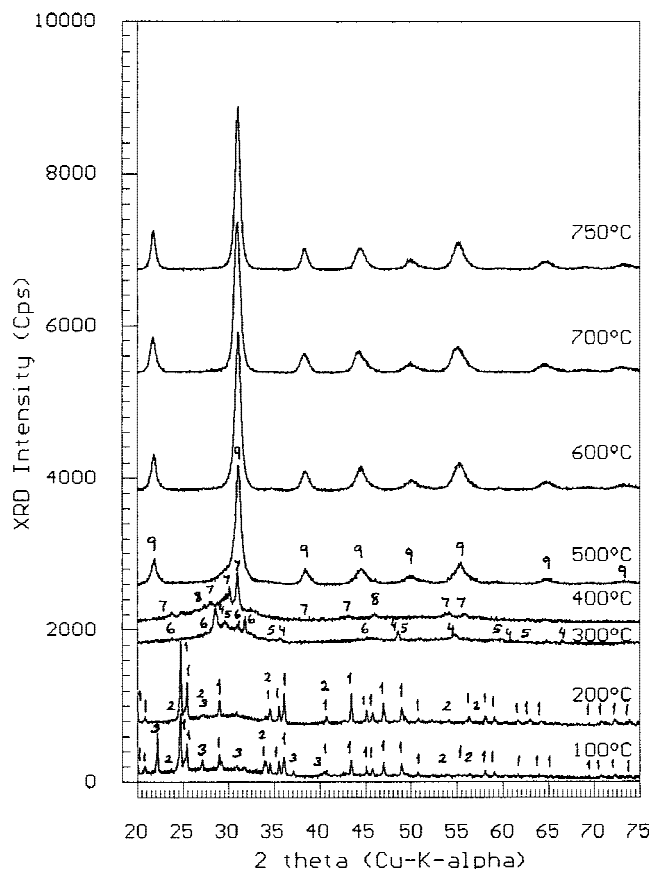


Fig. 1. XRD spectra of PZT precursor powders (urea/cation ratio = 45) heated at various temperatures for 6 h in an air atmosphere. ICDD PDF: (1) cerussite (5-417), (2) hydrocerussite (13-131), (3) laurionite (31-680), (4) litharge (5-561), (5) zirconia (37-31), (6) Ti_7O_{13} (18-1403), (7) PbZrO_3 (35-739), (8) PbZrO_3 (20-608), (9) perovskite PZT (33-784).

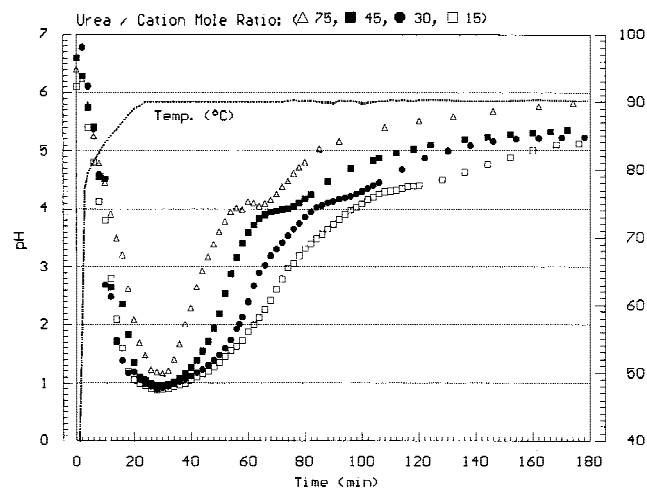


Fig. 2. pH versus time plots of PZT precursor powders aged at different urea/cation ratios.

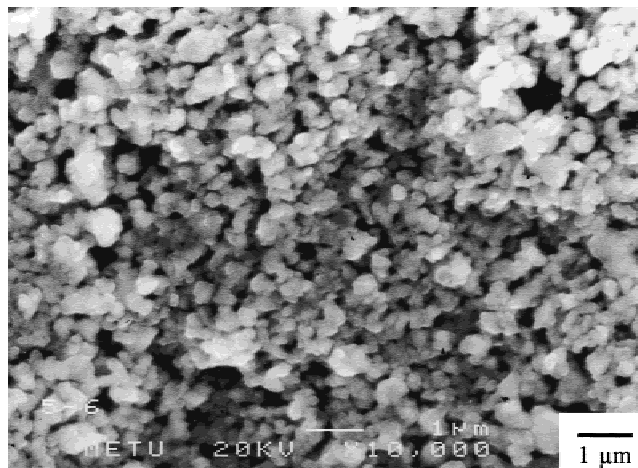


Fig. 3. SEM micrograph of PZT powders calcined at 700°C for 6 h (urea/cation ratio = 30).

temperature has been obtained in comparison to processes, which involve powder mixing and solid-state reactive firing at higher temperatures.

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