

Preparation of Lead Zirconate by Homogeneous Precipitation and Calcination

Ersin Emre Oren, Ercan Taspinar, and A. Cüneyt Tas*

Department of Metallurgical and Materials Engineering, Middle East Technical University, Ankara 06531, Turkey

Antiferroelectric PbZrO₃ has been synthesized by homogeneous precipitation from aqueous solutions in the presence of urea (NH₂CONH₂) and calcination for 6 h at 700°C. SEM studies displayed the presence of submicrometer powder, with a significant degree of agglomeration.

I. Introduction

LEAD ZIRCONATE (PbZrO₃) is an antiferroelectric ceramic with a Curie temperature of 230°C. It is reported that the antiferroelectric (AFE) to ferroelectric transition (under the application of a strong electric field to the ceramic in the antiferroelectric state) leads to significant energy storage for a dc field. This feature of PbZrO₃ makes it a candidate material for energy storage applications.¹ Piezoelectric and dielectric properties of lead zirconate thin films, derived from a sol-gel technique, were studied and compared with the most significant piezoelectric compositions.^{2,3} PbZrO₃ was also searched for its microwave dielectric properties but it shows a dielectric relaxation near microwave frequencies.⁴ A strong correlation between the lattice defect concentration and dielectric loss at microwave frequencies has also been reported.^{5,6} The volatility of Pb species at the temperatures needed to prepare lead zirconate ceramics is believed to be the reason for the relaxation in PbZrO₃ phase.⁴ Therefore, a decrease in the processing temperature of lead zirconate phase may result in an improvement in the final electrical properties of the ceramic part.

Preparation of lead zirconate by conventional processes, that is, mixing and firing of the binary oxides (PbO and ZrO₂), requires the use of high temperatures at which PbO volatility also becomes significant. It is reported that the full development of pure PbZrO₃ phase occurs after sintering at temperatures above 1200°C for at least 2 h in controlled PbO atmospheres.^{4,5,7,8}

Lead zirconate was previously synthesized by a sol-gel method,⁸ which necessitated the use of complex processing practices and strict control of many process parameters, such as pH of the solutions, temperature, and concentrations of the cations. For the sol-gel method, the calcination temperature to yield pure PbZrO₃ was reported to be as low as 700°C for 6 h of soaking time.⁸ The phase formation temperature for pure PbZrO₃, by the citrate route, was also reported to be in the vicinity of 700°C.⁹

In the present study, the experimental details and results of the synthesis of the lead zirconate phase from water-soluble salts of Pb and Zr (chlorides) by homogeneous precipitation via urea decomposition are presented. The decomposition of urea in aqueous solutions is accompanied by the slow and controlled supply of ammonia and carbon dioxide into the solution.¹⁰ The

smooth pH increase obtained by the decomposition of urea, in unison with the steady supply of OH⁻ and CO₃²⁻ ions, typically leads to the precipitation of metal hydroxycarbonates of controlled particle morphology.¹¹⁻¹³ Homogeneous precipitation from aqueous solutions, in the presence of urea, has been used to produce dispersed spherical particles of basic lanthanide carbonates,¹⁴ cerium oxide,¹⁵ Y₃Al₅O₁₂,¹⁶ and LaAlO₃.¹⁷ In this study, homogeneous precipitation techniques, similar to those described in the literature,¹¹⁻¹⁷ were employed and shown to be successful for the preparation of phase-pure PbZrO₃ after calcination at 700°C.

II. Experimental Procedure

The lead source was 99.5% pure PbCl₂ (Merck, Darmstadt, Germany), whereas the zirconium source was 99% pure ZrCl₄ (Merck, Darmstadt, Germany). Appropriate amounts of ZrCl₄ and PbCl₂ were dissolved in distilled water to prepare 0.2M ZrCl₄ and 0.02M PbCl₂ stock solutions. Reagent-grade urea (CH₄N₂O, 99.5% Riedel-De Haen AG, Germany) was used as the precipitation agent.

(1) Homogeneous Precipitation

A total of 157 mL of cation stock solutions (i.e., lead and zirconium chlorides) was thoroughly mixed in a glass beaker. Distilled water (343 mL) containing 24.4 g of urea was then mixed with the above solution. The resultant clear solution was slowly heated (in about 2 h) to 90°C on a hot plate. Precipitation started in ~2 h with a slight turbidity in the clear solution. Precipitates were aged for 2 h at 90°C on the hot plate without stirring. Precipitation experiments were also repeated at larger volumes, e.g., 493 mL of cation solutions + 1081 mL of distilled water with 76.7 g of urea. After aging, the precipitates were separated from the mother liquor either by centrifugal filtration (at 4500 rpm) or by a filter-press. The recovered precipitates were washed twice with distilled water. The washed precipitates were oven-dried overnight at 90°C.

(2) Powder Sample Characterization

Powder XRD spectra were obtained for the dried precipitates, as well as for powders heat-treated at 350°-700°C, in open alumina crucibles or dishes in a dry air atmosphere. A powder diffractometer (Model D-Max/B, Rigaku Co., Tokyo, Japan) was used with monochromatic FeK α radiation at a step size of 0.04° and a preset time of 1 s for runs performed to accomplish phase characterization and to check the phase purity of the synthesized ceramic powders.

Particle size and morphological characteristics of the powders were monitored through scanning electron microscopy (SEM) photomicrographs (Model JSM6400, JEOL, Tokyo, Japan). Prior to examination, the powder samples were sputter-coated with a layer of gold-palladium ~30 nm thick. Energy-dispersive X-ray spectroscopy (EDXS) (Kevex, Foster City, CA) was performed on the pelletized samples to acquire semi-quantitative elemental-distribution information. A pure sample of 1.1 at.% neodymium-doped yttrium aluminum garnet (Nd:YAG) polycrystalline disk (quantitatively analyzed by the inductively coupled plasma (ICP) method prior to this study)

G. L. Messing—contributing editor

Manuscript No. 191153. Received March 10, 1997; approved May 27, 1997.
*Member, American Ceramic Society.

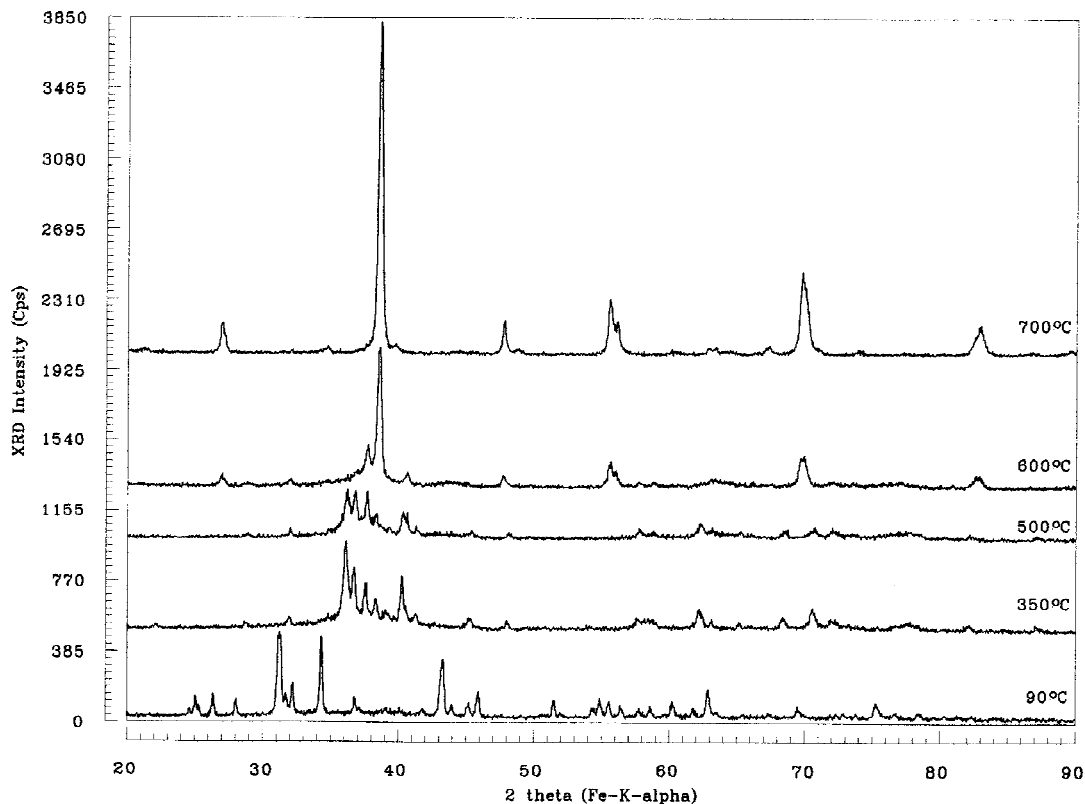


Fig. 1. XRD spectra of the PbZrO_3 precursor powders heated at various temperatures in a stagnant air atmosphere.

was used as a standard material in the EDXS runs. The analysis was performed on the polished ($0.1 \mu\text{m}$ diamond paste) surfaces of our samples. The EDXS information was believed to be accurate to about ± 3 wt%.

III. Results and Discussion

The formation of the solid phase in the glass aging beakers was governed by the controlled and slow generation of hydroxide and carbonate ions through the decomposition of urea. The decomposition behavior of urea appears to be dependent on the urea concentration, as well as other variables such as temperature and the concentrations of cations in the solution.

The precipitates recovered from the mother liquors and oven-dried at 90°C in air were found to be crystalline. The XRD spectrum labeled " 90°C " in Fig. 1 belongs to the oven-dried precursor powders. The phases detected in this spectrum were hydrocerussite [$\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$] of ICDD Powder Diffraction File (PDF) Card No. 13-131 and cerussite [PbCO_3] of ICDD PDF Card No. 5-417. Upon heating the precursor powders to 350°C (6 h), the phase mixture of lead carbonates and lead hydroxycarbonates decomposed into litharge (ICDD PDF Card No. 5-561) and massicot (ICDD PDF Card No. 5-570). ZrO_2 (ICDD PDF Card No. 24-1164) began to show up, for the first time in the XRD spectra, as a crystalline phase at 350°C . The phase assemblage remained almost unchanged (Fig. 1) when heated at 500°C (6 h) in a stagnant air atmosphere.

The free PbO phases (litharge and massicot) disappeared when the temperature of air calcination increased to 600°C (Fig. 1). There was still a mixture of two phases, i.e., PbZrO_3 (ICDD PDF Card No. 20-608 or 35-739) and ZrO_2 (ICDD PDF Card No. 24-1164 or 37-1413) in the XRD patterns of these powders. However, the only phase present in powders heated to 700°C (6 h) was PbZrO_3 (ICDD PDF Card No. 35-739), and this represented the temperature of complete conversion of the precursor powders produced by homogeneous precipitation into tetragonal lead zirconate. A typical SEM micrograph of

precursor powders heated at 700°C is given in Fig. 2, and it shows the submicrometer and spherical nature of the PbZrO_3 powder produced. It is apparent from this micrograph that the particles are not as uniformly sized and disperse as expected from the previously proven ability of the urea/homogeneous precipitation method tested in other material systems.¹⁰⁻¹⁶ However, our powders displayed a significant level of necking and bonding (Fig. 2) as if they were in the initial stages of sintering even at this low temperature of calcination of 700°C .

The semiquantitative EDXS analysis performed on the samples heated at 700°C typically produced the empirical composition of 58.8 wt% Pb, 26.9 wt% Zr, and 14.3 wt% O. These values were regarded to be in accordance with the theoretical composition of PbZrO_3 , as far as the accuracy of the technique used here is considered.

The lattice parameters and unit cell volume of synthesized

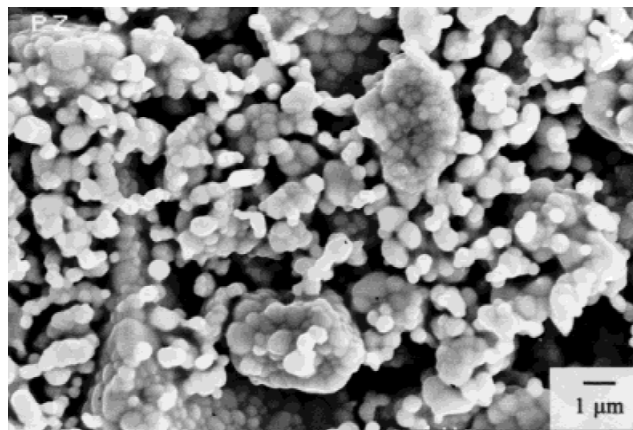


Fig. 2. SEM photomicrograph of the PbZrO_3 precursor powders heated at 700°C for 6 h.

PbZrO₃ powders (calcined at 700°C) were determined (by a least-squares refinement¹⁸ on the gathered XRD data) as $a = 11.769 \text{ \AA}$, $c = 8.229 \text{ \AA}$, and $V = 1139.81 \text{ \AA}^3$. These values coincided well with the lattice parameter data of ICDD PDF Card No. 35-739.

IV. Conclusions

The lead zirconate (PbZrO₃) phase has been synthesized from aqueous solutions, following calcination at 700°C in an air atmosphere. This study showed that it is possible to obtain chemically homogeneous submicrometer particles of PbZrO₃ by homogeneous precipitation throughout aqueous solutions of the chlorides of the respective cations via the decomposition of urea. A considerable decrease in the processing temperature is obtained when compared to the processes which involve powder mixing and reactive firing in the solid state. This decrease in synthesis temperature is also believed to help in eliminating the need for the use of atmosphere control to compensate for the problems of lead volatilization in commercial processing and firing steps.

References

- ¹K. Singh, "Antiferroelectric Lead Zirconate, A Material For Energy Storage," *Ferroelectrics*, **94**, 433 (1989).
- ²J.-F. Li, D. D. Viehland, T. Tani, C. D. E. Lakeman, and D. A. Payne, "Piezoelectric Properties of Sol-Gel-Derived Ferroelectric and Antiferroelectric Thin Layers," *J. Appl. Phys.*, **75** [1] 442-48 (1994).
- ³T. Tani, J.-F. Li, D. Viehland, and D. A. Payne, "Antiferroelectric-Ferroelectric Switching and Induced Strains for Sol-Gel-Derived Lead Zirconate Thin Layers," *J. Appl. Phys.*, **75** [1] 3017-23 (1994).
- ⁴M. T. Lanagan, J. H. Kim, S. Jang, and R. E. Newnham, "Microwave Dielectric Properties of Lead Zirconate," *J. Am. Ceram. Soc.*, **71**, 311 (1988).
- ⁵K. Wakino, M. Murata, and H. Tamura, "Far-Infrared Reflection Spectra of Ba(Zn_{1/3}Ta_{2/3})O₃-BaZrO₃ Dielectric Resonator Material," *J. Am. Ceram. Soc.*, **69**, 34-37 (1986).
- ⁶B. D. Silverman, "Microwave Absorption in Cubic Strontium Titanate," *Phys. Rev.*, **125** [6] 1921 (1962).
- ⁷W. N. Lawless, "Glasslike Thermal Properties of Lead Zirconate," *Phys. Rev. B*, **30**, 6555-59 (1984).
- ⁸D. M. Ibrahim and H. W. Henniske, "Preparation of Lead Zirconate by a Sol Gel Method," *Trans. J. Br. Ceram. Soc.*, **80**, 18-22 (1981).
- ⁹Y. S. Rao and C. S. Sunandana, "Low Temperature Synthesis of Lead Zirconate," *J. Mater. Sci. Lett.*, **11**, 595-97 (1992).
- ¹⁰H. Willard and N. K. Tang, "A Study of the Precipitation of Aluminum Basic Sulphate by Urea," *J. Am. Chem. Soc.*, **59**, 1190-92 (1937).
- ¹¹B. C. Cornilsen and J. S. Reed, "Homogeneous Precipitation of Basic Aluminum Salts as Precursors for Alumina," *Am. Ceram. Soc. Bull.*, **58**, 1199-200 (1979).
- ¹²J. E. Blendell, H. K. Bowen, and R. L. Coble, "High-Purity Alumina by Controlled Precipitation from Aluminum Sulphate Solutions," *Am. Ceram. Soc. Bull.*, **63**, 797-802 (1984).
- ¹³J. Sawyer, P. Caro, and L. Eyring, "Hydroxy-Carbonates of the Lanthanide Elements," *Rev. Chim. Miner.*, **10**, 93-104 (1973).
- ¹⁴D. J. Sordelet and M. Akinc, "Preparation of Spherical, Monosized, Y₂O₃ Precursor Particles," *J. Colloid Interface Sci.*, **122**, 47-59 (1988).
- ¹⁵P. Chen and I-W. Chen, "Reactive Cerium(IV) Oxide Powders by the Homogeneous Precipitation Method," *J. Am. Ceram. Soc.*, **76**, 1577-83 (1993).
- ¹⁶D. J. Sordelet, M. Akinc, M. L. Panchula, Y. Han, and M. H. Han, "Synthesis of Yttrium Aluminum Garnet Precursor Particles by Homogeneous Precipitation," *J. Eur. Ceram. Soc.*, **14**, 123-27 (1994).
- ¹⁷E. Taspinar and A. C. Tas, "Low Temperature Chemical Synthesis of Lanthanum Monoaluminate," *J. Am. Ceram. Soc.*, **80** [1] 133-41 (1997).
- ¹⁸D. E. Appleman and H. T. Evans, "Least-Squares and Indexing Software for XRD Data," Document No. PB-216188, U.S. Geological Survey, Computer Contribution No. 20, U.S. National Technical Information Service, Washington, DC, 1973. □