JOURNAL OF MATERIALS SCIENCE **40** (2005) 2697–2699 LETTERS

Synthesis and characterization of PLZST prepared by coprecipitation

L. H. XUE, Q. LI*, Q. Y. GUO, R. LIU
Department of Chemistry, Tsinghua University, Beijing 100084, P.R. China
E-mail: qiangli@mail.tsinghua.edu.cn

Y. L. ZHANG
Department of Material Science and Engineering, Tsinghua University, Beijing 100084, P.R. China

Lanthanum-doped lead zirconate titanate stannate (PLZST) has been intensively investigated and has attracted much interest in literature because of its extremely high electric-field-induced longitudinal and volume strains. Therefore, this material has been investigated for various actuator applications [1–9]. The characteristic properties of materials are well known to be substantially influenced by the method of their preparation and the starting materials. Generally, the PLZST ceramics are mainly prepared by a traditional solid-state reaction [10]. Such a reaction often leads to compositional and structural inhomogeneities in the final products. Therefore, many wet chemical methods have been developed to produce PLZST ceramics [11–16]. Coprecipitation is a simple and convenient method. In coprecipitation methods reported in literature thus far, ammonia was used as precipitant reagent. The precipitates from coprecipitated hydroxide were colloidal and were not easy to filter, which made Cl^- difficult to eliminate and affected pure phase formation at low temperature. In this work, we use cupferron as precipitant reagent. Cupferron is an organic agent possessing reactive groups that enable it to form ring structures containing a metal atom, the product known as chelate compound is porous and easily filtered. Cupferron is well known in chemistry for its utilization in precipitation reactions in the metal analysis through gravimetric determination, and this way generating well-stabilized solids with a defined stoichiometry [17]. Therefore, we are encouraged to try the coprecipitation route for PLZST powders using cupferron as precipitant reagent. The composition of $Pb_{0.98}La_{0.02}(Zr_{0.66}Sn_{0.27}Ti_{0.07})O_3$ was chosen for the powder preparation. The starting materials used were reagent grade PbO, La_2O_3, $ZrOCl_2 \cdot 8H_2O$, $SnCl_4 \cdot 5H_2O$ and $TiCl_4$. PbO and La_2O_3 were initially dissolved in acetic acid. $ZrOCl_2 \cdot 8H_2O$, $SnCl_4 \cdot 5H_2O$ and $TiCl_4$ were dissolved in distilled water individually. Then the above solutions were mixed to get the PLZST clear solution, which was kept below pH 1 to avoid precipitation. A small amount of hydrogen peroxide added to the solution, according to the procedure described by Murata *et al.* [18]. Then the PLZST solution was added dropwise to a continuously stirred bath of cupferron solution (the cupferron to total metal ion ration was 8:1). During the coprecipitation, the pH of the bath was maintained 5.5–5.7 by adding aqueous ammonia as necessary. After the precipitation, the precipitate was filtered, washed several times with cold distilled water to eliminate Cl^-, and dried in an oven at 100 °C. The resultant precursor was subsequently calcined at different temperatures in air. The decomposition and crystallization of the precursor was analyzed by thermogravimetric and differential thermal analysis (TG/DTA) at a heating rate

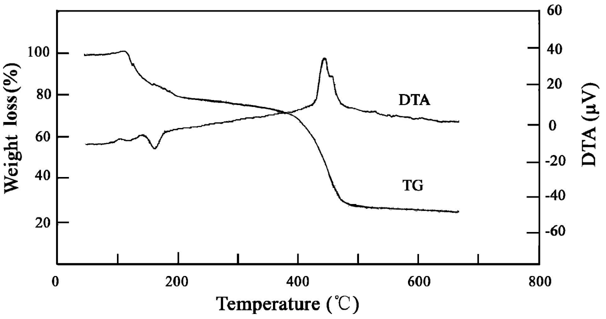

Figure 1 TG/DTA curves for the precursor.

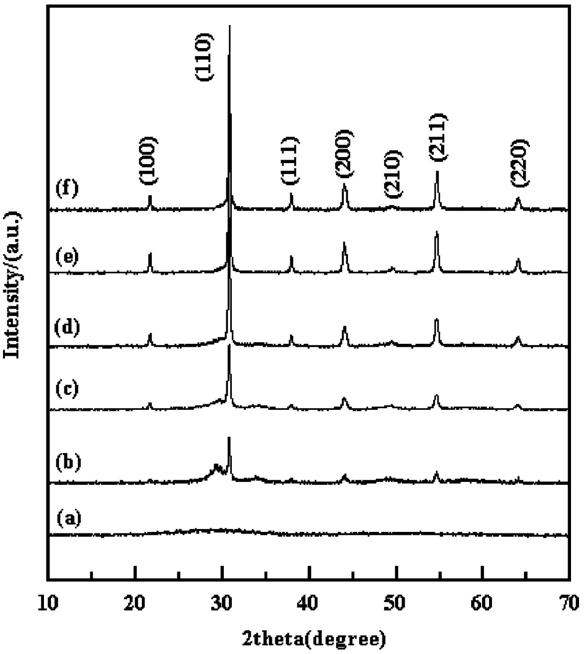

Figure 2 XRD of PLZST powders calcined at: (a) 350 °C, (b) 450 °C, (c) 550 °C, (d) 600 °C, (e) 650 °C, and (f) 700 °C for 2 hr.

---

*Author to whom all correspondence should be addressed.

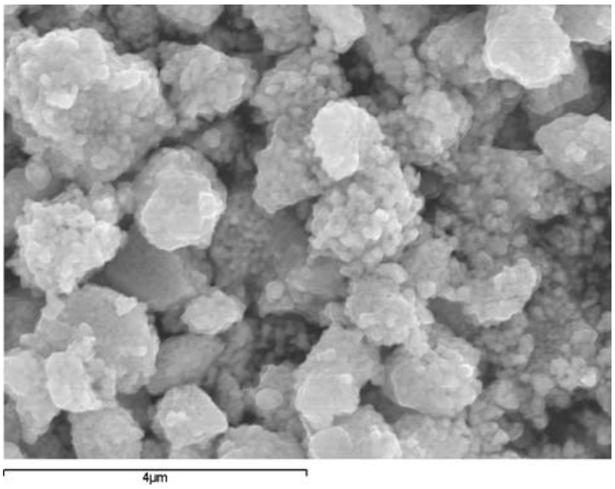

Figure 3 SEM micrograph of PLZST powders calcined at 650 °C for 2 hr.

of 5 °C/min. The phase structure was characterized by X-ray diffraction (XRD, D8 ADVANCE) with Cu K_α radiation. The morphology and size of the synthesized powders were studied by scanning electron microscopy (SEM, JSM-6301F).

To examine the sinterability of the nanosize powders produced, the powders obtained were subjected to axial pressing at 50 MPa to form disc specimens of 10 mm in diameter and of the order of a few millimeters thick. The disc specimens were sintered at 1100, 1150, and 1200 °C for 2 hr, respectively, in a lead-rich atmosphere. The sintered samples were then polished and covered with silver paste as the electrode. The polarization–electric field (P–E) hysteresis loop was measured using Sawyer–Tower circuit at room temperature.

Fig. 1 shows the TG/DTA results for the PLZST powders in the range from 30 °C to 700 °C. An endothermic peak is observed at about 160 °C accompanied by a noticeable weight loss, which can be ascribed to the dehydration of the precursor powders and the melting of remaining cupferron. Two kinds of exothermic peaks are observed, a strong one at around 450 °C and a shoulder one at around 458 °C. The main exotherm can be assigned to the major decomposition of the oxidation of the metal complexes, and the shoulder peak can be attributed to the oxidation of the residual carbonaceous mass, along with the slow crystallization of the amorphous structure. The thermal effect is accompanied by the evolution of gases (such as CO_2, NH_3, and water vapor) that is manifested in the second weight loss in the TG curve.

The X-ray diffraction patterns of powders calcined at different temperatures are shown in Fig. 2. At the temperature of 350 °C the sample is amorphous. The crystalline perovskite phase appears after being calcined at 450 °C for 2 hr and the pure perovskite phase

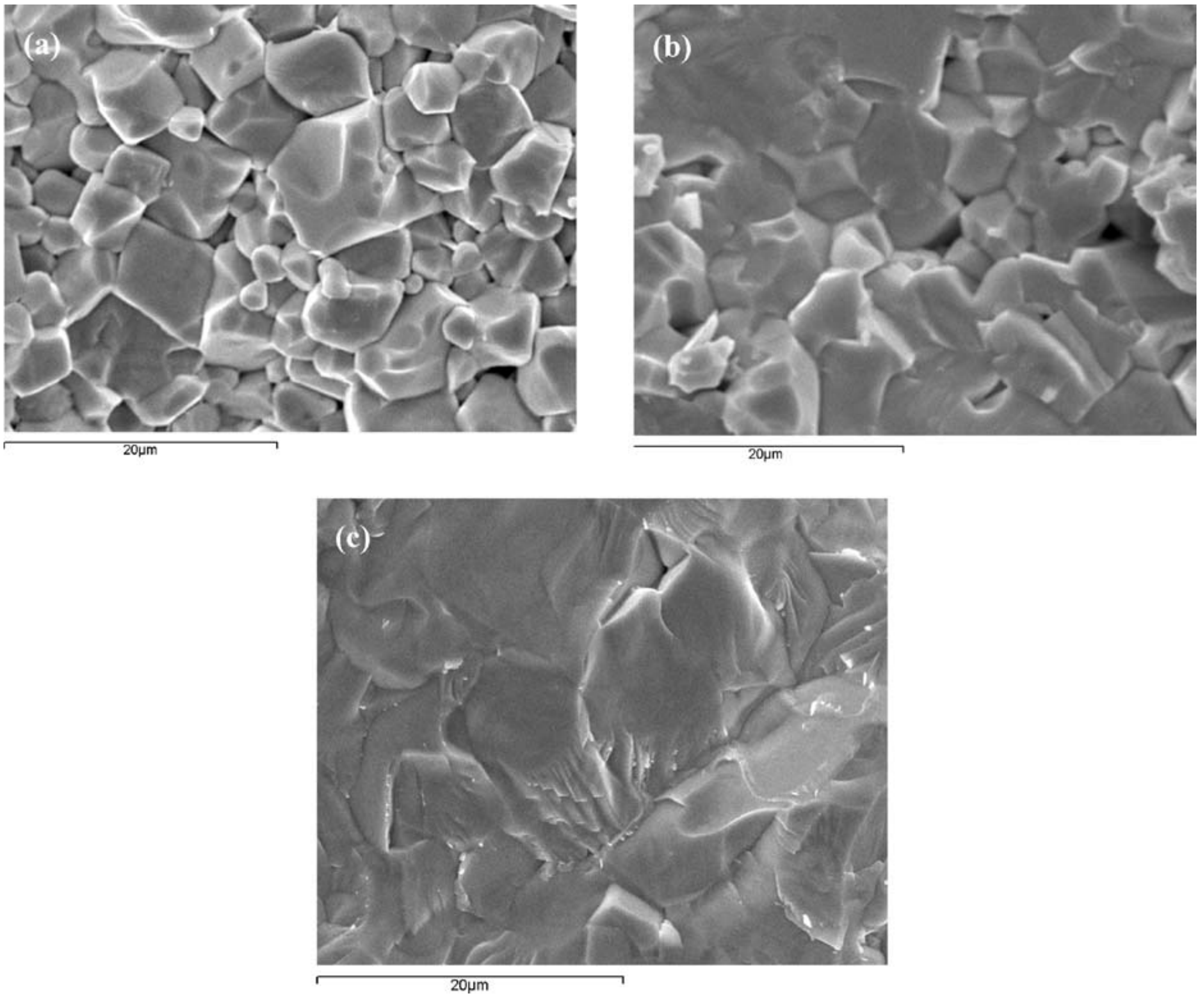

Figure 4 SEM photographs of fractured surface of ceramics sintered at: (a) 1100 °C/2 hr, (b) 115 °C/2 hr, and (c) 1200 °C/2 hr.

TABLE I XRF analysis of PLZST powder calcined at 650,°C for 2 hr

	Pb	La	Zr	Ti	Sn
Formula	0.98	0.02	0.66	0.07	0.27
Measured	0.975	0.017	0.663	0.074	0.263

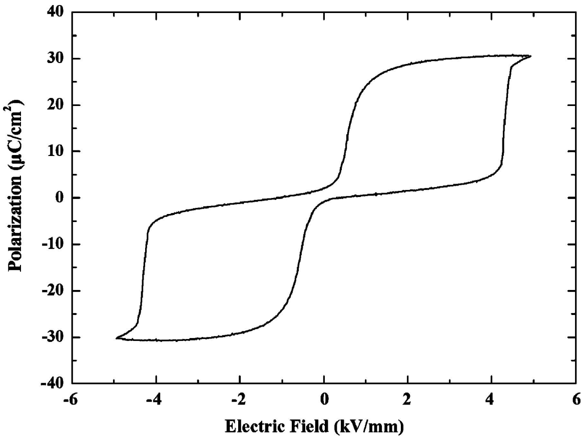

Figure 5 P-E hysteresis loop of the PLZST ceramic.

of PLZST powders could be obtained at 650 °C for 2 hr. This is significantly lower calcining temperature than that required for conventional mixed oxide process (e.g. 1350 °C for 2 hr) [10]. The compositions of the powders calcined at 650 °C for 2 hr were analyzed by XRF. The results in Table I show that the ratios are in agreement with the assumption that all components are completely precipitated by this method.

Fig. 3 shows morphologies of the synthesized powders prepared at 650 °C for 2 hr. The powders have particle size around 150 nm and a spherical shape, being all grouped in agglomerate. The particle size distribution is highly homogeneous.

Fig. 4 shows the microstructure of the sintered PLZST ceramic. It can be seen that the ceramic body is well densified and the fracture characteristics change from intergranular to transgranular fracture with the temperature increasing. This indicates that the powders prepared by this method have higher sinterability than that by mixed oxide process.

Fig. 5 shows the room temperature *P–E* hysteresis loops of the specimen sintered at 1200 °C for 2 hr. A typical antiferroelectric double hysteresis loop is observed with maximum polarization of 30.1 μC/cm^2. The forward-switching field is 4.2 kV/mm and the backward-switching field is 0.5 kV/mm. These values are comparable to those reported in literature [3]. This indicates that coprecipitation by organic reagent is a promising way to prepare PLZST ceramics.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (no. 50272030).

References

1. D. BERLINCOURT, H. H. KRUEGER and B. JAFFE, *Phys. Chem. Solids*. **25** (1964) 659.
2. W. Y. PAN, Q. ZHANG, A. BHALLA and L. E. CROSS, *J. Amer. Ceram. Soc.* **72** (1989) 571.
3. K. MARKOWSKI, S.-E. PARK, S. YOSHIKAWA and L. E. CROSS, *ibid.* **79** (1996) 3297.
4. J. H. LEE and Y. M. CHIANG, *J. Mater. Chem.* **9** (1999) 3107.
5. A. STERNBERG, E. BIRKS and L. SHEBANOY, *Ferroelectrics* **226** (1999) 217.
6. O. ESSIG, P. WANG and M. HARTWEG, *J. Eur. Ceram. Soc.* **19** (1999) 1223.
7. W. H. CHAN, Z. XU and Y. ZHANG, *J. Appl. Phys.* **94** (2003) 4563.
8. K. UCHINO and S. NOMURA, *Ferroelectrics* **50** (1983) 517.
9. Z. XU, D. VIEHLAND and P. YANG, *J. Appl. Phys.* **74** (1993) 3406.
10. Q. F. YAN, Q. LI and Y. L. ZHANG, *J. Inorg. Mater.* **16** (2001) 649.
11. M. CHEN, X. YAO and L. Y. ZHANG, *J. Eur. Ceram. Soc.* **21** (2001) 1159.
12. X. BAOMIN, G. P. NEELESH and L. E. CROSS, *Mater. Lett.* **34** (1998) 157.
13. J. H. LEE and Y. M. CHIANG, *J. Mater. Chem.* **9** (1999) 3107.
14. L. H. XUE, Q. LI and Y. L. ZHANG, *Rare Metal Mat. Eng.* **33** (2004) 157.
15. L. B. KONG, J. MA and T. S. ZHANG, *J. Mater. Sci.-Mater. Electron.* **13** (2002) 89.
16. Y. P. ZENG, A. ZIMMERMANN and L. J. ZHOU, *J. Eur. Ceram. Soc.* **24** (2004) 253.
17. J. W. FRANK, in "Organic Analytical Reagents" (Toronto, 1947) p. 355.
18. M. MURATA and K. WAKINO, *Mater. Res. Bull.* (1976) 323.

Received 17 June
and accepted 24 September 2004