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Preparation of PLZST antiferroelectric ceramics by hydroxide coprecipitation method

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Abstract

An improved coprecipitation method using buffer solution was developed for synthesizing $Pb_{0.97}La_{0.02}(Zr_{0.75}Ti_{0.08}Sn_{0.17})O_3$ antiferroelectric ceramics. It was found that the perovskite phase was formed when the precursor powders were calcined at 550 °C for 2 h and the average diameter of these particles was less than 100 nm. Moreover, the results showed that when the pH value of the precipitating solution was in the range of 8.9–9.0, in comparison with the ceramics prepared by conventional solid state reaction, the samples synthesized by coprecipitation method had a larger electric field-induced phase transition and higher breakdown strength, which lay a basis for preparing high power energy storage capacitors and pulsed power applications.

Keywords: B. Nanocomposites; C. Chemical preparation; D. Antiferroelectric ceramic; E. Capacitors

1. Introduction

In the past, PLZST based antiferroelectric (AFE) ceramics were widely used in high-density capacitor, high strain actuators and energy transducers owing to their outstanding field induced phase transitions and adjustable dielectric properties [1–4]. So far, the PLZST ceramics have been mainly prepared by the conventional solid state reaction method. Although this kind of method shows some advantages, such as low cost and easy control, it also has obvious disadvantages. Firstly, it cannot mix raw oxide components uniformly on molecular and atomic levels, so it needs high synthesis temperature to make the reaction happen. Moreover, due to high sintering temperature, the grain is relatively large, which is not good for improving the breakdown strength (BDS) of the ceramics. Further, the volatilization of excess PbO at such a high sintering temperature will lead to the formation of pyrochlore phase [5]. In order to solve these problems, wet chemical processing routes have been developed to synthesize highly pure, homogeneous, reactive precursors. Compared to the other wet chemical-processing routes, the coprecipitation method is relatively simple. Guiffard and Troccaz [6] fabricated $Pb(Zr_{0.52}Ti_{0.48})O_3$ by coprecipitation using NH_4OH and oxalic acid as precipitants at 700 °C. Akbas Lee[7] reported a new way to prepare citrate salts of PLZT 9/6.5/35 by drying (alcohol and/or freeze drying) and gelation of citrate solutions of PLZT. Xue et al. [8] synthesized homogeneous PLZST precursor by using a modified chemical coprecipitation route. Li [9] succeeded in fabricating PZT primary particle with a size distribution of 10–30 nm using aqua ammonia as the sedimentary agent, polyethylene glycol (PEG) as the surfactant and n-butyl alcohol as cosolvent. However, all of the mentioned ways have a defect that the range of pH value cannot be accurately controlled to precipitate the constituents designed simultaneously.

In this paper, an improved coprecipitation method using NH_4OH–NH_4NO_3 buffer solution, which could control the range of pH value within 8.9–9.0 accurately, was developed for the fabrication of $Pb_{0.97}La_{0.02}(Zr_{0.75}Ti_{0.08}Sn_{0.17})O_3$ powder. The electric properties of this AFE ceramics fabricated by the solid phase method and the improved coprecipitation method were compared.

2. Experimental procedure

The synthesis was based upon the co-precipitation of metal hydroxides $Zr(OH)_4$, $TiO(OH)_2$, $Sn(OH)_4$, $Pb(OH)_2$,

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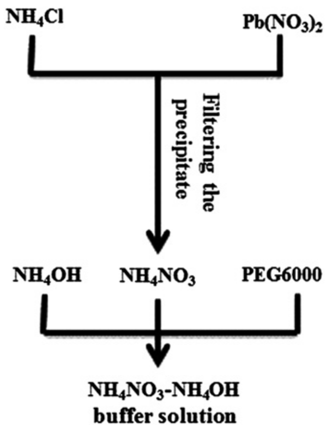

Fig. 1. Schematic flow chart for the preparation of NH_4OH-NH_4NO_3 buffer solution.

and $La(OH)_3$ in the range of pH 8.9–9.0 [8]. The starting materials used were $Pb(Ac)_2{\bullet}3H_2O$ (99%), $La(NO_3)_3$ (98.6%), $Zr(NO_3)_4{\bullet}5H_2O$ (94.8%), $TiCl_4$ (98.0%), and $SnCl_4{\bullet}5H_2O$ (99.0%). The buffer solution was NH_4OH–NH_4NO_3, and it acted as a precipitant. Polyethylene glycol (PEG6000) was used as a surfactant, and n-butyl alcohol was a detergent.

The schematic flow chart for the preparation of NH_4OH-NH_4NO_3 buffer solution is given in Fig. 1.

Corresponding to the composition the PLZST based ceramic $Pb_{0.97}La_{0.02}(Zr_{0.75}Ti_{0.08}Sn_{0.17})O_3$, quantities of $La(NO_3)_3$ (excess 0.6 wt%), $Zr(NO_3)_4{\bullet}5H_2O$ (excess 4 wt%), $TiCl_4$, $SnCl_4{\bullet}5H_2O$ (excess 3 wt%) were dissolved in deionized water and glacial acetic acid was also mixed by adding 6 molar ratio of glacial acetic acid to $Pb(Ac)_2{\bullet}3H_2O$ before $Pb(Ac)_2{\bullet}3H_2O$ being added into the blending solution. After that, the blending solution was added into the buffer solution slowly, while, ammonia was dropped on-demand to keep the pH value within 8.9–9.0 and it was stirred vigorously for coprecipitation to take place. The precipitate was washed several times by n-butyl alcohol and deionized water until no chloride ion was detected by silver nitrate solution.

The washed precipitate was dried in an oven and calcined at several temperatures. Then, the powders calcined at 550–800 °C were studied by X-ray diffraction (XRD, D8, Bruker. German). A particle size analyzer (MS2000, Malvern, Britain) was used to measure the particle size of powder calcined at 650 °C in air for 2 h after being ball milled in ethanol medium.

The calcined powder was pressed into pellets of 10 mm diameter and ~0.2 mm thickness. The pellets were then sintered at 1150 °C for 2 h in air and were coated with silver electrodes for the measurement of their hysteresis loops.

3. Results and discussion

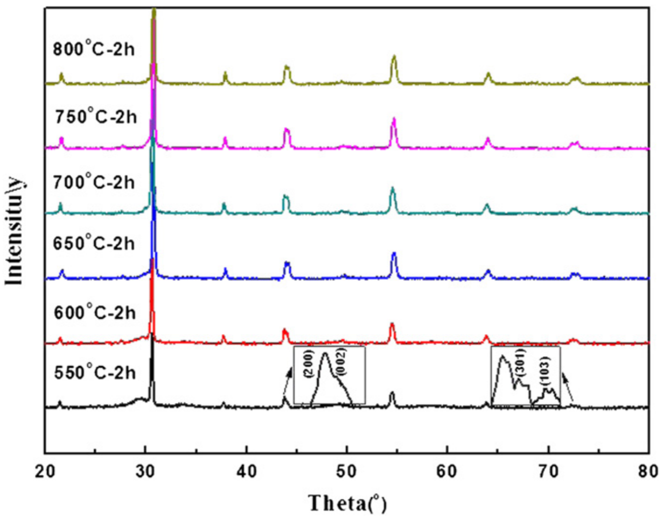

Fig. 2. X-ray patterns of PLZST powders calcined at different temperatures.

Fig. 2 shows the XRD patterns of the powder calcined at several temperatures. Two characteristic split peaks of AFE phase appear when the calcination temperature is 550 °C or higher, at the planes (200), (002) and (301), (103) at 43.8° and 72.5° respectively.

As we know, lead ions and chloride ions react and form precipitate. For cost saving, we may need to use inorganic salt of metallic ions which may contain chloride ions. So, sometimes the occurrence of precipitation was unavoidable. M.A. Akbas applied citric acid solution to avoid precipitation [7]. Another way is to strictly control the reaction temperature [10].. Hao et al. [11] used acetic acid to react with lead ions and acetic acid radical ions to prevent the combination of lead and chloride ions. In this paper, we used acetic acid as an anti-precipitant.

Fig. 3 shows the particle size as a function of the concentration of metallic cations in the blending solution. It shows that the particle size decreases with the increasing concentration of metal cations. Such a behavior is mainly attributed to the fact that high concentration solution has high supersaturation. The rate of grain and particle formation is high; thereafter, the particle size of precipitation is small. We also find that when the concentration of metallic cations is above 0.132 mol/L, it is difficult to get a transparent blending solution because the excess concentration of metallic cations results in the devitrification of resolution. 92% of the particles have the size smaller than 100 nm and the maximum size is ~110 nm as shown in the inset of Fig. 3.

Fig. 4 shows the particle size of powder with and without buffer solution. The particle size is obviously smaller when NH_4OH–NH_4NO_3 buffer solution is used. Corresponding to the peak diffraction, the percentage of diffraction number of powders prepared with buffer solution (13%) is higher than that without buffer solution (10%) and the particle size is smaller (60 nm and 71 nm respectively). This phenomenon mainly originates from the fluctuation of range of pH value that could seriously influence the reaction environment. From the coprecipitation and thermodynamic solubility curves of

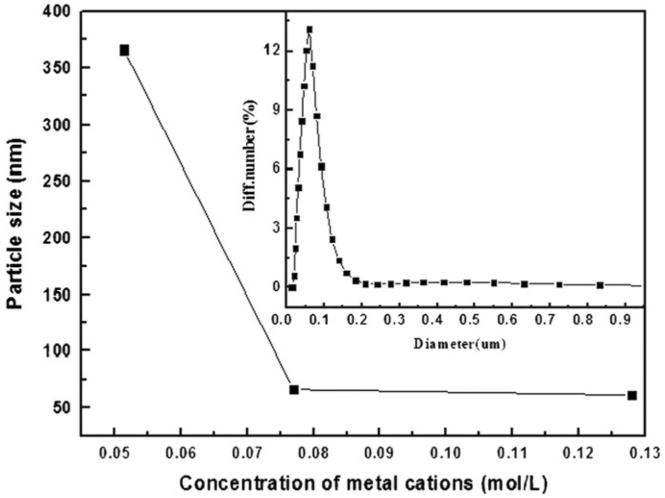

Fig. 3. Particle size of different metal cations concentration in blending solution. The inset shows the particle size of PLZST powders calcined at 650 °C for 2 h in air.

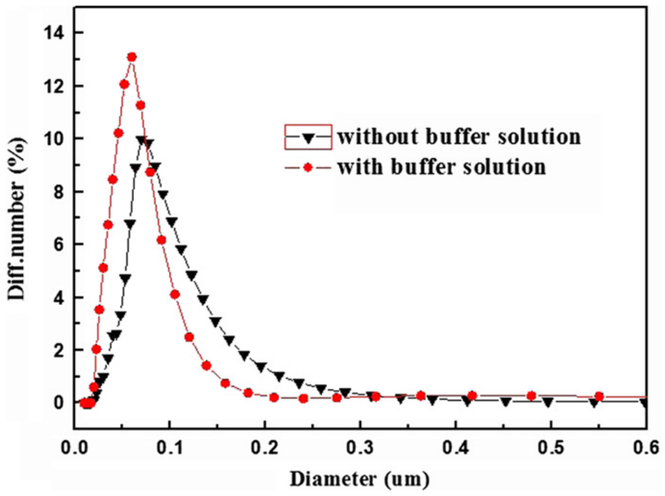

Fig. 4. Particle size of powder obtained without and with buffer solution.

Pb, La, Zr, Sn, and Ti [12], the optimal coprecipitation pH value is within this range of 8.9–9.0. If the pH value is not in the range, the powder will deviate from its established composition and will be unable to have co-precipitation. Generally, by mixing the blending solution with the precipitant without buffer solution it will be difficult to maintain the chemical reaction environment of pH value within 8.9–9.0. Weak alkali (ammonia) and conjugate base (ammonium nitrate) act as buffer to keep the pH value stable if we add a little strong acid or strong alkali into it. As the buffer capacity is limited, applying appropriate amount of ammonia in drops is necessary and effective during the coprecipitation reaction. As long as it is in the optimal reaction environment, the coprecipitant reacts very fast and continually toward the end. As a result the particle size is more uniform and smaller.

P–E hysteresis loops of the ceramics prepared with buffer solution ceramics and without buffer solution are shown in Fig. 5. The loops were measured up to the breakdown strength (BDS) at room temperature. There are no obvious changes on forward and backward phase transition field for both samples; but the saturated polarization of ceramics (P_s) with buffer solution sample is larger than that without the buffer solution (30 μC/cm^2 and 20 μC/cm^2).

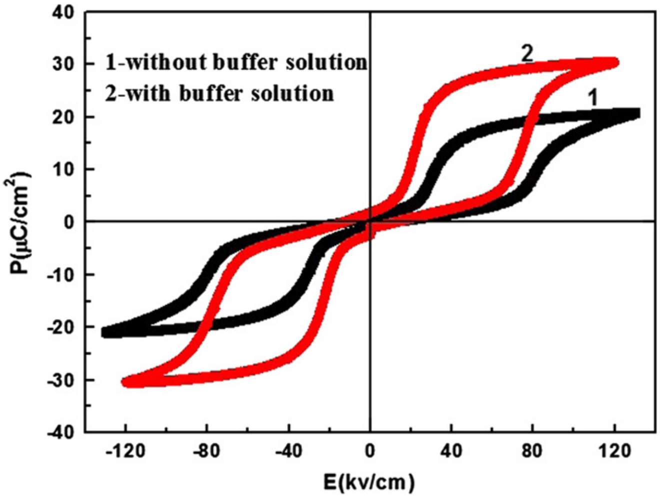

Fig. 5. *P–E* hysteresis loops for ceramics with and without buffer solution at room temperature.

The *P–E* hysteresis loops for the solid state reaction ceramics and the coprecipitation reaction ceramics at room temperature are compared in Fig. 6. As shown in the figure, there is an obvious improvement of BDS for the coprecipitation reaction ceramics in comparison to the solid state reaction ceramics (120 kV/cm and 85 kV/cm). Although the coprecipitation reaction ceramics have a low P_s, the remanent polarization (P_r) of the coprecipitation reaction ceramics is close to zero, while the solid state reaction ceramics show a large P_r (~15.1 μC/cm^2). In addition, the critical fields required to induce AFE to ferroelectric (FE) and FE to AFE phase for the solid state reaction ceramics (E_{AFE-FE}=43 kV/cm, E_{FE-AFE}=−6 kV/cm) are much lower than those of the coprecipitation reaction ceramics samples (E_{AFE-FE}=67 kV/cm, E_{FE-AFE}=−16 kV/cm). As we know, the energy storage density of dielectric materials is equal to the integral

$$J = \int_0^{D_{max}} E\, dD \qquad (1)$$

where D_{max} is the maximum electric displacement, and E is the electric field [13]. Based on the *P–E* loop measured in Fig. 6, the energy storage density of the coprecipitation reaction ceramics (0.61 J/cm^3) is larger than that of the traditional one (0.03 J/cm^3), but the improved energy storage density is not high enough. However, our next work is to obtain slim *P–E* loops AFE materials by optimizing the ratio of Sn/Ti [14] via the hydroxide coprecipitation method.

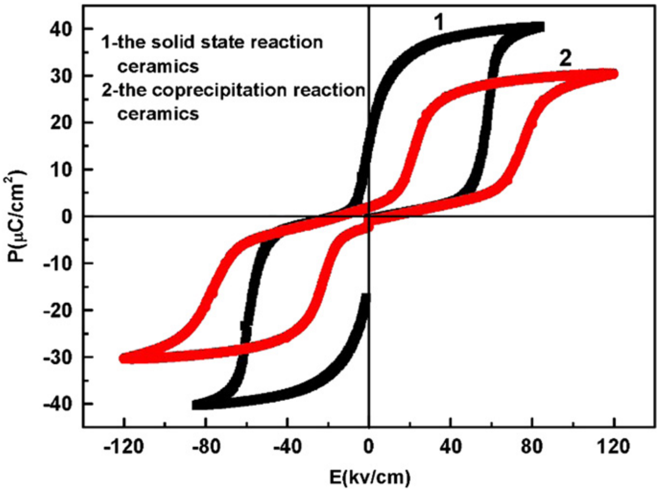

Fig. 6. *P–E* hysteresis loops for the solid state reaction ceramics and the coprecipitation reaction ceramics at room temperature.

4. Conclusions

The PLZST powders fabricated by hydroxide coprecipitation was in AFE phase as the calcined temperature is high 550 °C. The particle size decreases with increasing the concentration of metallic cations. By comparing the ceramics prepared without buffer solution and those prepared by conventional solid state reaction, both the particle size and electrical properties of samples with buffer solution were improved. Furthermore, the lower P_r and reinforcement of BDS of the ceramics are beneficial in improving the energy density.

Acknowledgments

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