

Chemical prepared niobium modified PZT-95/5 antiferroelectric ceramics and the field-induced phase transformation properties

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Abstract A two step method by mixing the coprecipitated powder and oxide was developed to prepare the niobium doped PZT95/5 ceramic. The niobium was doped by adding the niobium pentoxide to the coprecipitated PZT powders. The crystalline phase, size and compositional homogeneity of powders were examined by XRD, SEM and XRF. The performances of phase transformation induced by electric fields and pressures in coprecipitate ceramic samples were measured. An antiferroelectric hysteresis loop in fresh specimen and the ferroelectric to antiferroelectric phase transformation pressure in poled ceramic specimen were measured for the composition of $\text{Pb}_{0.99}(\text{Zr}_{0.95}\text{Ti}_{0.05})_{0.98}\text{Nb}_{0.02}\text{O}_3$.

Keywords PZT95/5 · Coprecipitation · Antiferroelectric · Phase transformation

1 Introduction

The lead zirconate titanate (PZT) solid solution system particularly for ceramic with composition near the morphotropic phase boundary has been extensively studied

[1]. As the composition shifts to the lead zirconate rich region close to the ferroelectric (FE) and orthorhombic antiferroelectric (AFE) phase boundary, where the Zr/Ti ratio is 95/5, the crystalline structure changes to AFE phase [1]. External field such as electrical field or hydrostatic pressure which applied on the ceramic sample will lead phase transformation between AFE and FE. The characteristics of PZT close to the FE and AFE phase boundary can be used in important applications such as ceramic actuators [2, 3], and shock-wave power supplies [4, 5].

The purity, stoichiometry, grain size and second phase content which are controlled by the processing conditions, have remarkable affect on the properties and reliability of the devices [6]. PZT powders are traditionally synthesized by a solid-state reaction process using mixed oxides as starting materials [7]. This kind of method often leads to compositional fluctuation and structural inhomogeneities [8].

Wet chemical methods have more advantage in compositional and structural control than solid-states reaction methods [9–12]. The high cost of starting materials and the difficulties in densification caused by a high content of organic materials in the precursors make the Sol-gel method more suitable for the thin film preparation. Coprecipitation from solution is one of the wet chemical techniques that could produce stoichiometric electroceramic powders of high purity and fine particle size at a relatively moderate cost and is currently applied widely to make electroceramic powders in industry.

A two step method was designed, in which the PZT powder was prepared by coprecipitation and Nb was introduced by the form of niobium pentoxide. With relative low cost start materials being used, this method is suitable for bulk ceramic preparation.

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2 Experimental procedure

2.1 Powders preparation

The composition of $\text{Pb}_{0.99}(\text{Zr}_{0.95}\text{Ti}_{0.05})_{0.98}\text{Nb}_{0.02}\text{O}_3$ at the antiferroelectric to ferroelectric phase boundary was chosen for the powder preparation. Commercially available lead nitrate $\text{Pb}(\text{NO}_3)_2$ (99.9%+purity), zirconium nitrate $\text{Zr}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ (99.9%+purity), TiCl_4 (99.0%+purity) and niobium pentoxide Nb_2O_5 (99.9%+purity) were used as the starting materials with the nominal composition.

The flow diagram of the coprecipitation procedure is given in Fig. 1.

First, $\text{Pb}(\text{NO}_3)_2$ and $\text{Zr}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ were dissolved in the deionized water. These two kinds of prepared solutions were added into an acetic acid solution separately and then with TiCl_4 dripped into it. Transparent solution with homogeneous quality was achieved by this process. Soluble complex ion could be generated by first adding the lead nitrate into acetic acid solution, that could prevent the formation of the insoluble PbCl_2 and $\text{Pb}(\text{OH})\text{Cl}$ [9].

According to the solubility diagram for the Pb-Zr-Ti hydroxide system at 25 °C, the most appropriate pH to make these three kinds of ion to coprecipitate is 9. The solution was added to aqueous ammonia NH_4OH where the

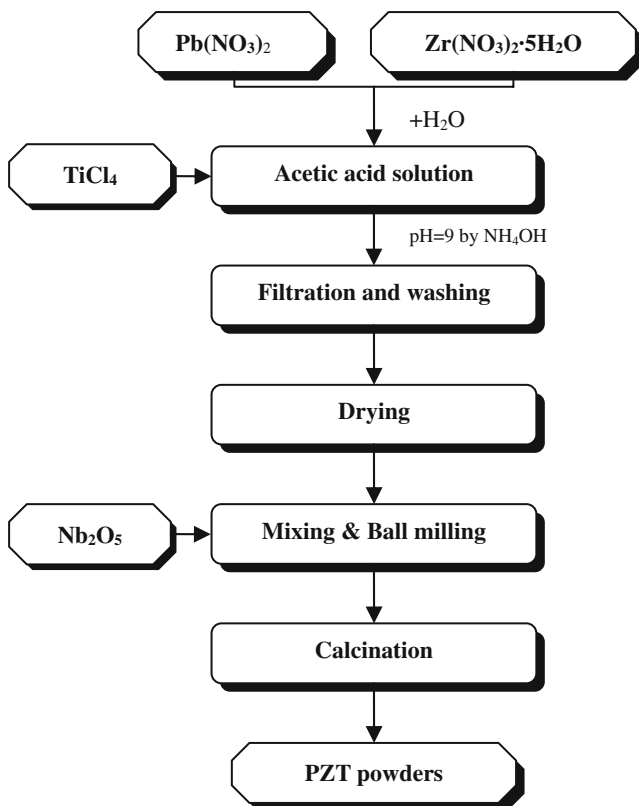


Fig. 1 Flow chart of chemical preparation of $\text{Pb}_{0.99}(\text{Zr}_{0.95}\text{Ti}_{0.05})_{0.98}\text{Nb}_{0.02}\text{O}_3$ ceramic powders

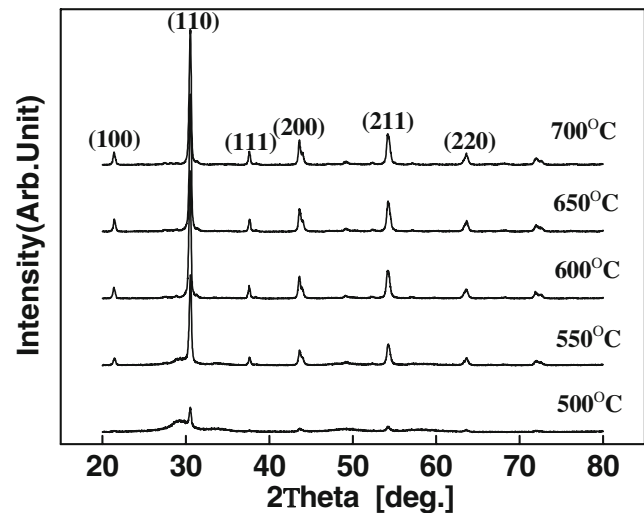


Fig. 2 XRD patterns of Nb_2O_5 doped PZT ceramics calcined at 500, 550, 600, 650 and 700°C

concentration had been adjusted to maintain the pH value of the mixture at 9.

The mixture was mixed for 90 min to ensure the ions in the solution absolutely precipitated. The precipitates were filtrated and then washed with the distilled water which the pH was adjusted to 9 by NH_4OH . Washing process was end until no residual Cl^- could be detected by silver nitrate. After dried at 110 °C for 3 h, the precipitates were mixed with Nb_2O_5 by planetary ball milling with ZrO_2 media for 4 h.

Fifteen hours planetary ball milling was then carried out to break the agglomerates formed during calcinations. Columniform specimen with diameter of 12 mm was formed by axial press. The specimens were sintered from 1100 to 1250 °C for 2 h in lead rich atmosphere. Specimen for measurement in disc shape with thickness of 1 mm was sliced from the columniform ceramic. Sliver paste was printed on the surface of the discs and baked at 550 °C to form the electrodes.

2.2 Powders and specimen characterization

X-ray diffraction analysis of the powders was performed using a Rigaku D/MAX-2400 X-ray diffractometer with $\text{Cu K}\alpha$ radiation by 0.02 with 20 steps width with 10° at 1 min.

The microstructure development of the sintered samples was characterized using a JSM-6460type scanning electron microscope. The stoichiometry of calcined powder was

Table 1 XRF analysis of the calcined PZT powder at 650°C for 2 h.

	Nb_2O_5 (%)	TiO_2 (%)	ZrO_2 (%)	PbO (%)	Norm. (wt.%)
Composition	0.78	1.14	33.52	64.56	100.00
Analyzed value	0.75	1.13	34.10	63.91	99.89

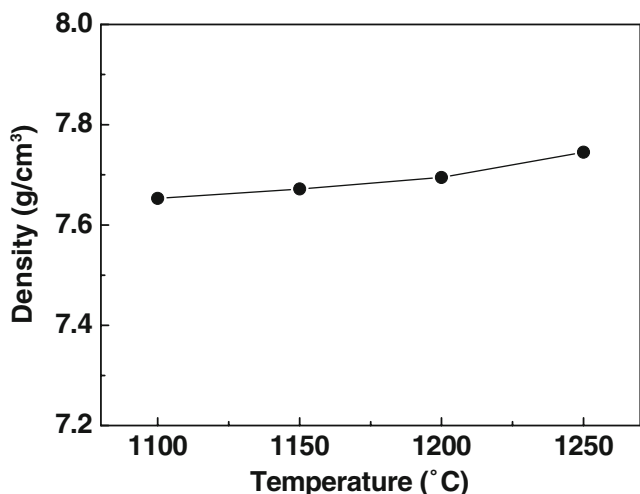


Fig. 3 Density of Nb₂O₅ doped PZT specimens sintered at 1100, 1150, 1200, 1250°C

analyzed by X-Ray fluorescence technique (Bruker, S4 pioneer).

The density of the PZT ceramics was measured using Archimedes method by balance AG245 and its accessory. Hysteresis loop was measured by TF analyzer 2000 FE-module system (aixacct). The effect of hydrostatic pressure on the phase transformation of FE and AFE was determined by measuring charge release of the specimen under pressure.

3 Result and discussion

The XRD patterns of the powder calcined at different temperature were shown in Fig. 2. The powder obtained was calcined in air for 2 h from 500 to 700 °C with step of 50 °C to determine the appropriate calcining temperature. The crystalline perovskite phase was obtained after being

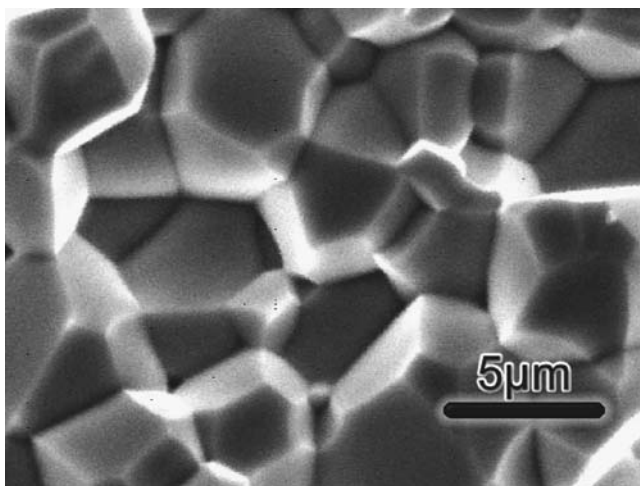


Fig. 4 SEM photograph of fractured surface from Nb₂O₅ doped PZT specimen sintered at 1250°C for 2 h

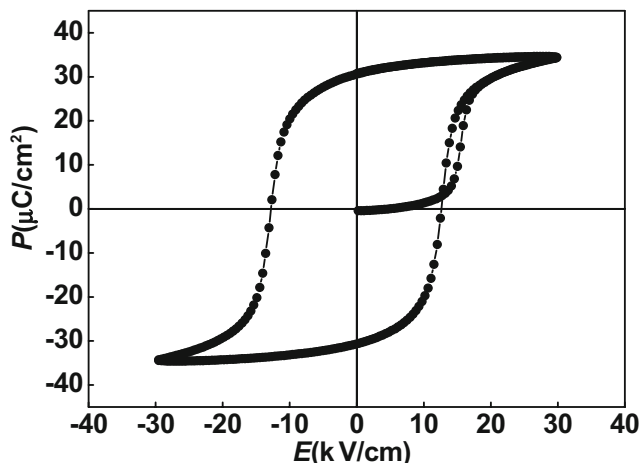


Fig. 5 Hysteresis loop of fresh Nb₂O₅ doped PZT antiferroelectric ceramic specimen

calcined at 550 °C for 2 h and the complete perovskite phase was obtained at the temperature of about 600 °C.

The actual composition of the PZT powder calcined at 650 °C for 2 h in air atmosphere was analyzed by XRF. The result listed in Table 1 shows the composition of the niobium doped PZT powder. The PbO component was 0.7% weight lower than the preestablished value. It needs about excess Pb(NO₃)₂(1 wt.%) to compensate the lead evaporation during the sintering process. The measured error percentage of the components was not beyond the precision of the instrument which is 1%.

The measured density of PZT ceramics is illustrated in Fig. 3. It shows a nearly linear increment of density with the increment of sintering temperature. The average percent theoretical densities of sintered PZT 95/5 ceramics ranged from 95.5% to 96.7%(or 7.65 g/cm³–7.75/cm³). Figure 4 shows the microstructure of the fracture surfaces of PZT ceramics sintered at 1250 °C for 2 h. The ceramic is well

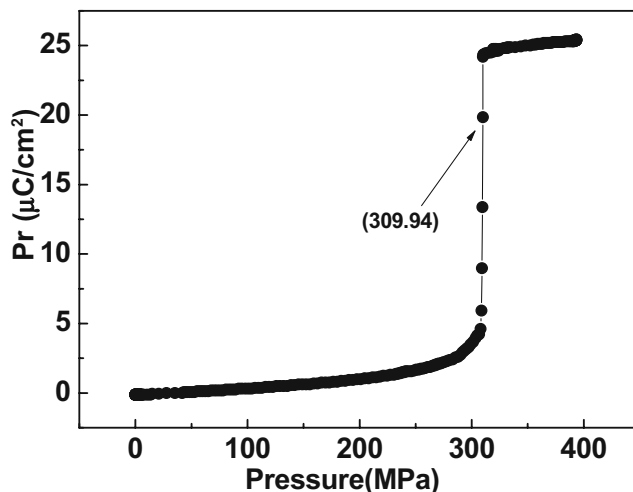


Fig. 6 Phase transformation induced by hydrostatic pressure of Nb₂O₅ doped PZT ceramic prepared by coprecipitation method

densified when sintered at this temperatures and the average grain size is about 5 μm .

The hysteresis loop of the fresh specimen sintered at 1250 °C for 2 h is measured at room temperature and shown in Fig. 5. The hysteresis loop illustrate that the fresh sample remains antiferroelectric state. The increasing electric field induced the phase transformation from the antiferroelectric state to the ferroelectric metastable FE state. The phase transformation field from AFE to FE ($E_{\text{AFE-FE}}$) is 15 kV/cm. With electric filed increased to 30 kV/cm, the polarization of the specimen had reached its max value which is about 35 $\mu\text{C}/\text{cm}^2$. The hydrostatic depoling behavior of FE to AFE phase transformation was investigated at room temperature. Pressure was measured by a calibrated manganin sensor and increased at a rate of 10 MPa/s. A 10 μF capacitor was used to collect the charges from the poled ceramics. The depoling process was studied and is shown in Fig. 6. The metastable ferroelectric state in poled ceramic specimen transformed to antiferroelectric state when the hydrostatic pressure reach the transformation pressure. The polarization released in the hydrostatic pressure is about 80% of the remanent polarization values. The pressure that induced FE-AFE phase transformation in poled chemical prepared ceramic specimen was about 310 MPa, where the transformation pressure was defined as the pressure where a half of the total charge has been released.

4 Conclusion

A two step method using coprecipitated powder and niobium pentoxide was developed for preparation of the $\text{Pb}_{0.99}(\text{Zr}_{0.95}\text{Ti}_{0.05})_{0.98}\text{Nb}_{0.02}\text{O}_3$ antiferroelectric ceramic. Niobium pentoxide was added to the previous coprecipitate powders and mixed by planetary ball milling. The complete perovskite phase was obtained at 600 °C for 2 h. The high

sintering temperature is required to form the pure perovskite phase when using the oxide as the starting material in the solid-state method. Powders from coprecipitate method need relative low sintering temperture to form the pure perovskite phase. This result shows that the calcining temperature of the coprecipitate PZT powders was not affected by the introduced niobium pentoxide. Precise control of the relative rare component could be acquired by this method and low calcining temperature could still be achieved. By using this method, an antiferroelectric to ferroelectric $E_{\text{AFE-FE}}$ transformation field which is 15 kV/cm was obtained in the ceramic specimen. The hydrostatic pressure needed for phase transformation in poled ceramic specimen prepared by this method was about 310 MPa.

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