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Synthesis, sintering and characterization of PNZST ceramics from high-energy ball milling process

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Abstract

$Pb_{0.99}Nb_{0.02}[(Zr_{0.60}Sn_{0.40})_{0.94}Ti_{0.06}]_{0.98}O_3$ powders were synthesized from oxide mixtures of Pb_3O_4, Nb_2O_5, ZrO_2, SnO_2, and TiO_2 using a Fritsch P4^{TM} vario-planetary ball milling system. The perovskite structure of PNZST powder can be obtained well after 14 h milling and crystallite size of the powders greatly reduced to 20–30 nm. The resultant powders have better sinterability characteristics to obtain dense ceramic bodies at low temperature. The dielectric constant of samples shows a maximum at 1150 °C and the PE_{MC} to PE_{SC} transformation temperature shifts to higher temperature with an increase in grain size. The field-induced strain reaches maximum longitudinal strain of 0.32% and the *P–E* hysteresis loop shows much higher squareness at 1150 and 1200 °C. The measured dielectric and antiferroelectric properties of the PNZST ceramics were found to be comparable to those from other processing techniques.

Keywords: C. Dielectric properties; C. Ferroelectric properties; D. Perovskites; Ball milling

1. Introduction

Lead zirconate titanate stannate (PZST) ceramics and their modifications are recognized as prominent antiferroelectric materials due to their excellent electrical properties for practical applications [1–4]. Tin is fractionally substituted for zirconium to expand antiferroelectric phase region and reduce switching electric fields. Compared to PZT, an advantage of PZST is that it could produce double electric hysteresis at a suitable electric field. In larger tin modified lead zirconate titanate compounds $Pb_{0.99}Nb_{0.02}[(Zr_{0.60}Sn_{0.40})_{1-x}Ti_x]_{0.98}O_3$ (abbreviated as PNZST 2/40/x) family, a transitional paraelectric phase occurred between antiferroelectric (or ferroelectric) and simple cubic paraelectric phase [5,6]. This inserted paraelectric phase cut off the dielectric constant peak and formed a high dielectric hathpace. This compound has been investigated for applications including high charge storage capacitors, and large strain transducers and actuators.

Mechanical activation synthesis (MAS) was originally developed for production of alloys and intermetallic compounds in 1966 [7]. The major advantage is that the solid-state reaction is activated by the mechanical energy rather than by the calcination at elevated temperatures. The antiferroelectric lead ziconate titanate ceramics produced by high-energy ball milling had been reported by Kong et al. [8]. The measured dielectric and ferroelectric properties of PZST ceramics were found to be comparable to those from other processing techniques. Considering the importance of phase boundaries and double hysteresis, phase transition features with electric field and temperature variations are studied for larger tin modified lead zirconate titanate compounds $Pb_{0.99}Nb_{0.02}[(Zr_{0.60}Sn_{0.40})_{0.96}Ti_{0.04}]_{0.98}O_3$ in this work. The effect of sintering temperature on micro-structure and electrical properties of the PNZST ceramics will also be discussed.

2. Experimental procedure

Solid solutions of $Pb_{0.99}Nb_{0.02}[(Zr_{0.60}Sn_{0.40})_{0.94}Ti_{0.06}]_{0.98}O_3$ were prepared using high-energy ball milling. Reagent grade oxides Pb_3O_4 (99.9%), Nb_2O_5 (99.9%), ZrO_2 (99.9%), SnO_2 (99.9%), and TiO_2 (99.6%) were used as the starting materials. Hundred gram mixed oxides were ball milled for 4 h traditional milling with stabilized zirconia balls in alcohol then the mixture was dried and sieved.

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The milling operation was carried out in a Fritsch Pulverisette 4^{TM} vario-planetary high-energy ball milling system in air at room temperature for different times (0–14 h respectively). A 225-ml tungsten carbide vial and 50 tungsten carbide balls with diameter (D_B) of 10 mm were used as a milling medium. The milling speed of main disk was set at 400 rpm and the speed of each pair was set at −800 rpm, which means that the rotation speed ratio (R-ratio) was −2.0. The ball mass to powder mass ratio (M_B/M_P) varied between 10:1 and 20:1. The milling was stopped for 30 min for every 30 min of milling to cool down the system and was interrupted after each hour to decant samples for analysis. After 14 h milling, the milled powders were pressed into disks 12 mm in diameter and 1–2 mm in thickness at 200 MPa, and sintered in sealed crucibles at temperatures ranging from 1050–1250 °C for 1.5 h.

The milled powders were analyzed by Rigaku D/MAX-2400 X-ray diffraction with Cu Kα radiation at room temperature. Microstructures of ceramics were analyzed by scanning electron microscopy (JEOL JSM-6460). TEM images of the powders were obtained using a JEOL JEM3010 transmission electron microscopy. A HP4284A impedance analyzer in conjunction with a furnace was used to measure the dielectric constants as a function of temperature on heating at frequencies of 0.1 kHz to 100 kHz. The P–E hysteresis loops were measured using TF analyzer 2000 FE-module system (AIXACCT).

3. Results and discussion

The XRD pattern of the milled powder mechanochemically treated is shown in Fig. 1. The peak of perovskite phase in $2\theta = 54.92°$ and $21.70°$ emerged after 3 h and 7 h milling respectively. It may indicate that powder are significantly refined and partially synthesized in this experiment, so that there are some powders of PNZST synthesized and other oxides waiting for synthesis. The perovskite phase can be observed clearly after 10 h milling, especially at 14 h. The peak is so sharp that can be comparable to peaks from calcined powder, which is synthesized by traditional reaction. Diffraction peaks of PbO are also observed because of the presence of unreacted PbO. Our work in synthesizing the PNZST reduces the milling time and shows sharp peaks compared with previous report [8]. In a word, high-energy ball milling is a suitable method to replace solid-state reaction.

Fig. 2 is a bright-field TEM micrograph that shows the particle size and morphology of PNZST particles after 14 h milling. Nano-size particles 20–30 nm in size are observed clearly, although they have aggregated together to form irregularly shaped particle agglomerates.

To examine the sinterability of the PNZST nano-size powders produced by high-energy milling, Fig. 3 shows SEM micrographs of the PNZST sintered at 6 different temperature from 1000 to 1250 °C for 1.5 h. Samples sintered at lower temperatures contain smaller grains, whose size ranged from 300 to 500 nm. The grain size of the ceramics increases with an increase in sintering temperature. The samples exhibit grain growth behavior, showing a sharp increase in grain size from 1100 to1150 °C. Moreover, the density increases from 1000 to 1150 °C, reaches a maximum value 8.255 g/cm^3 at 1150 °C and decreases a little after further sintering at higher temperature.

Fig. 4 shows the temperature dependence of the dielectric constant of the sample, which was sintered at 1150 °C. It is typical of the PNZST2/40/x family in that a multiple cell paraelectric phase exists between the antiferroelectric phase and the simple cubic phase. It can be observed that there is a hathpace, which means a flat curve and moderate change between 135 and 166 °C in the dielectric curve of PNZST2/40/6 resulted from a transitional paraelectric phase. In order to investigate this occurrence corresponding electric hysteresis was measured. Electric hysteresis of PNZST on heating

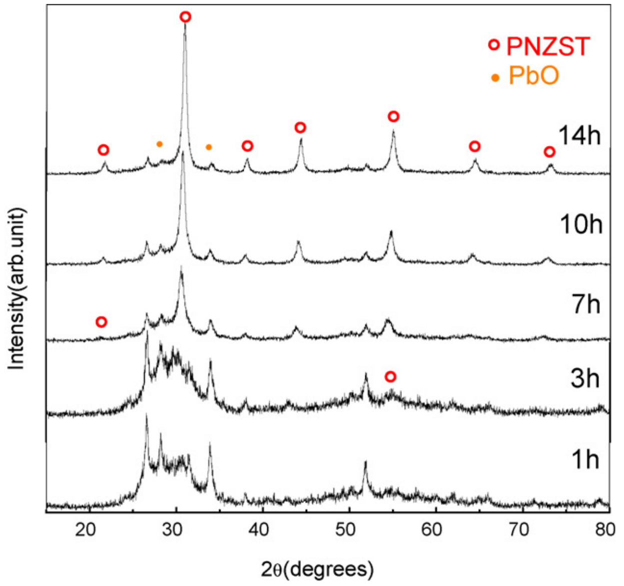

Fig. 1. XRD patterns of PNZST powder mixture treated for various times ranging from 1 to 14 h.

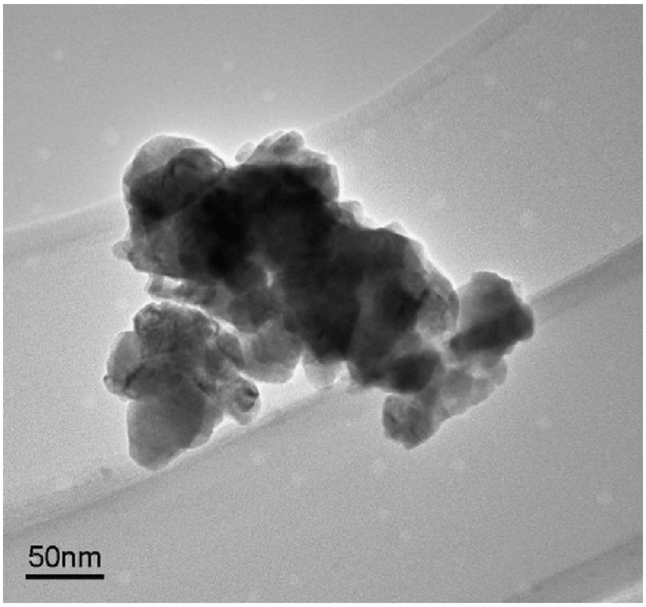

Fig. 2. A bright field electron micrograph of the 14-h milled sample.

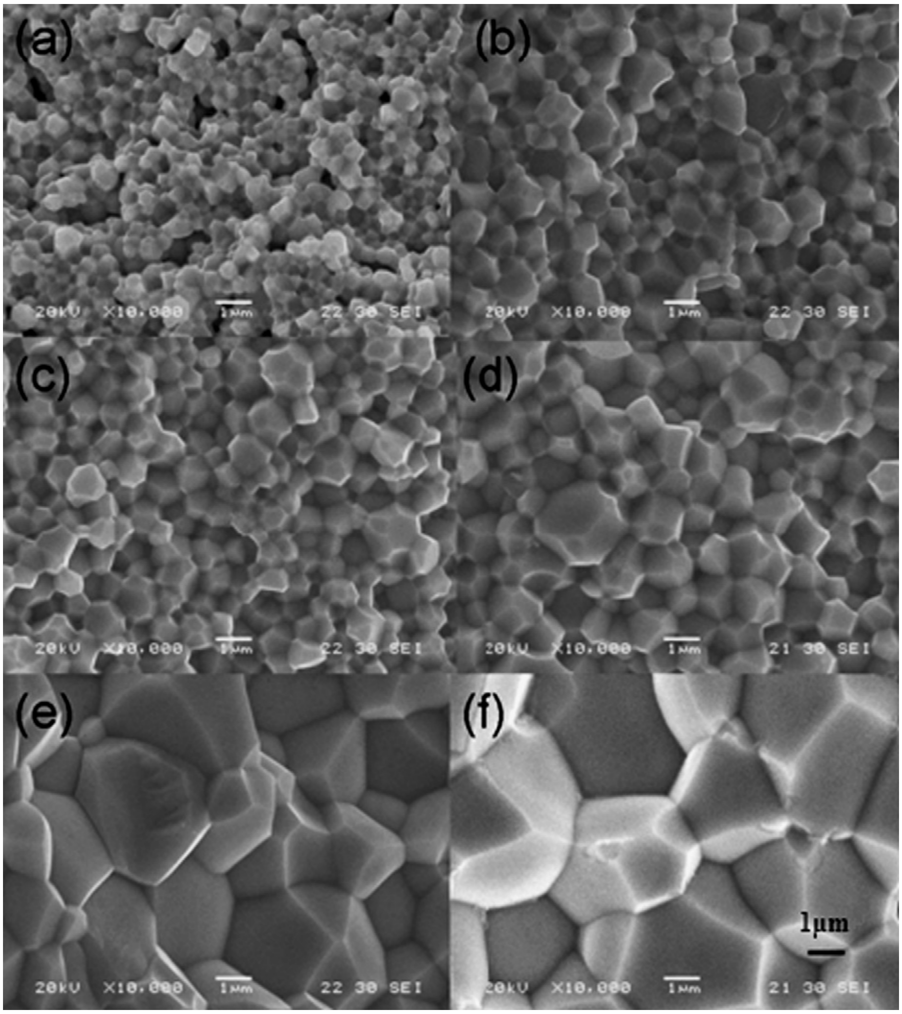

Fig. 3. SEM photograph of fractured surface from PNZST samples sintered at: (a) 1000 °C/1.5 h, (b) 1050 °C/1.5 h, (c) 1100 °C/1.5 h, (d) 1150 °C/1.5 h, (e) 1200 °C/1.5 h, (f) 1250 °C/1.5 h.

is shown in Fig. 5 which revealed that below 150 °C behavior was antiferroelectric, and above 150 °C polarization was linear with electric field increasing which is typical a paraelectric phase. This transitional paraelectric phase of a multiple cubic crystal structure (PE_{MC}) intervened between tetragonal antiferroelectric phase (AFE_T) and simple cubic paraelectric phase (PE_{SC}). Thus it was confirmed certain that first dielectric inflexion at 135 °C was related to an AFE to PE_{MC} transition and that the second inflexion at 166 °C was related to a PE_{MC} to PE_{SC} transition. The intrusion of the multiple cell paraelectric phase drastically reduces the dielectric constant peak usually associated with the Curie point. The gradually increasing stability of the additional paraelectric phase with composition ‘‘cuts off the top’’ of the dielectric constant peak, cause the raising the cubic inversion temperature and lowering the antiferroelectric inversion temperature [1].

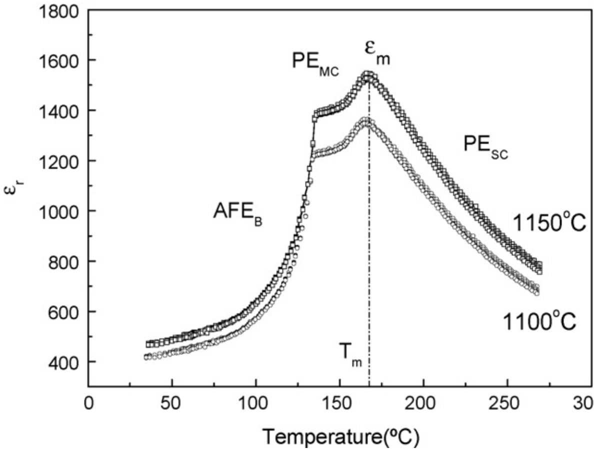

Fig. 4. The temperature dependence of dielectric constant of PNZST samples sintered at 1100 and 1150 °C from 0.1 kHz to 1 MHz.

The peak dielectric constant and the transformation temperature of the samples are shown in Fig. 6. The peak dielectric constant increases with an increase of the sintering temperature and shows a maximum at 1150 °C. As the grain size increases, the volume fraction of the grain boundaries will be reduced and then the restriction can be decreased. Therefore, the dielectric constant of ferroelectric ceramics increases with increasing grain size. A further increase in the sintering temperature leads to a slight decrease in the peak

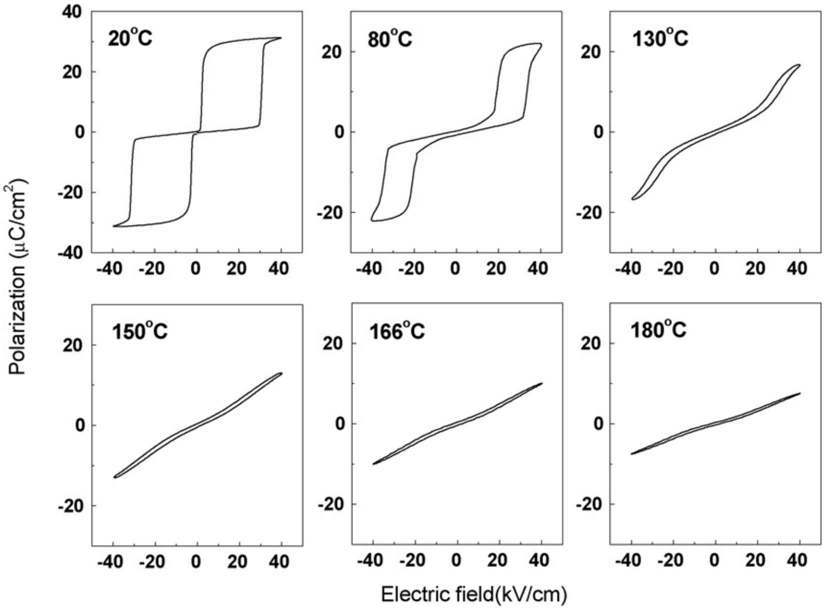

Fig. 5. *P–E* hysteresis loops of PNZST on heating from 20 to 180 °C.

dielectric constant, which may be due to the volatilization of PbO and the formation of a porous microstructure. Also the transformation temperature varies with different sintering temperature. In order to show the change clearly, the temperature T_m, which is the point of PE_{MC} to PE_{SC} transition, is selected. The transformation temperature shifts towards higher temperature from 163.1 to 166.3 °C as the sintering temperature increased. This change may be attributed to variation of these samples in microstructures, grain size and densities.

Fig. 7 shows the room temperature double *P–E* hysteresis loops and field-induced strain curves of the PNZST samples sintered at 1150 and 1200 °C. There is no distinct difference in the polarization properties of the samples including the maximum polarization (31.2 μC/cm²), the transformation field form AFE to FE $E_{AFE\text{-}FE}$ and the reverting field $E_{FE\text{-}AFE}$. The field-induced strain varies with different sintering temperature are also shown in Fig. 7. The maximum longitudinal strain under 40 kV/cm reaches to a maximum of 0.32% at 1150 °C, and then decreases with further grain size increase. This trend may be explained by the relationship between antiferroelectric domain and grain size.

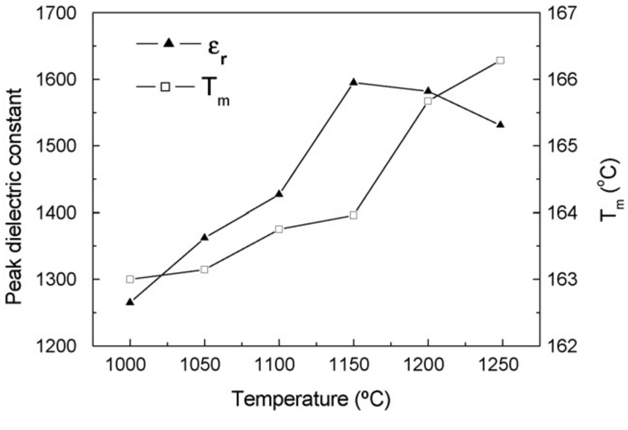

Fig. 6. The peak dielectric constant and the transformation temperature (T_m) of the samples as a function of sintering temperature.

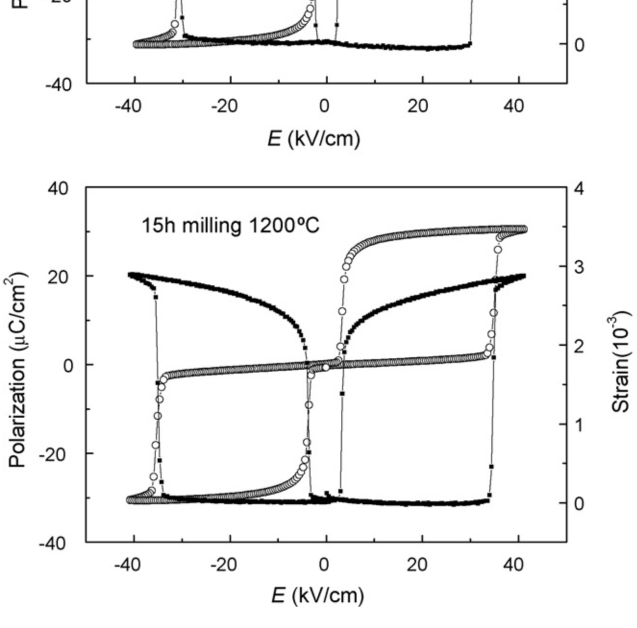

Fig. 7. The double *P–E* hysteresis and field-induced strain curves of PNZST samples sintered at: (a) 1150 °C, (b) 1200 °C.

4. Conclusions

The high-energy ball milling technique was successfully applied to synthesize $Pb_{0.99}Nb_{0.02}$ $[(Zr_{0.60}Sn_{0.40})_{0.94}Ti_{0.06}]_{0.98}$ O_3 powder and to decrease its sintering temperature by 100 °C. The sinterability enhancement of PNZST powder through this technique was evidenced by experimental results. The dielectric constant of samples shows a maximum at 1150 °C and the PE_{MC} to PE_{SC} transformation temperature shifts to higher temperature with an increase in grain size. The field-induced strain reaches maximum longitudinal strain of 0.32% and the *P–E* hysteresis loop shows much higher squareness at 1150 °C. The measured dielectric and antiferroelectric properties of the PNZST ceramics were found to be comparable to those other processing techniques, which indicate that the high-energy ball milling is a suitable method to synthesize antiferroelectric ceramics.

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