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Grain size dependence of dielectric and field-induced strain properties of chemical prepared (Pb, La)(Zr, Sn, Ti)O_3 antiferroelectric ceramics

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Abstract

Dielectric and field-induced strain properties of (Pb, La)(Zr, Sn, Ti)O_3 antiferroelectric ceramics with average grain size ranging from 2.0 to 9.0 μm were investigated experimentally. PLZST powders were synthesized by a two-step wet chemical method using colloidal processing. Dense samples were prepared by tape-casting method and sintered from 1000 to 1250 °C for 2 h at 50 °C intervals to obtain various grain sizes. The dielectric constant of the samples show a maximum at an average grain size of 5 μm and the transformation temperature form antiferroelectric to paraelectric phase shifts to higher temperature with the increase of grain size. The field-induced strain is strongly dependent to grain size, showing a maximum longitudinal strain of 0.38% at an average grain size of 5 μm.

Keywords: Grain size dependence; Field-induced strain; Antiferroelectric; Lead lanthanum zirconate stannate titanate

1. Introduction

Lead lanthanum stannate zirconate titanate (PLZST) and its modifications, which field-induced structural changes at antiferroelectric to ferroelectric (AFE-FE) phase transformations (e.g. rhombohedral to tetragonal) lead to a maximum 0.85% longitudinal strain [1], have been studied for potential actuator applications [2–3].

The grain size is one important experimental variable affecting properties of polycrystalline ceramics. Extensive works have been made to investigate and explain the effect of the grain size on the dielectric, piezoelectric and pyroelectric property of ferroelectric ceramics [4–6]. For antiferroelectric ceramics, Uchino et al. reported the grain size dependence of permittivity in PLZT with an antiferroelectric composition [7], Yang et al. investigated the grain size dependence of phase transformation in Nb doped PZST [8].

In this work, the grain size dependence of dielectric and field-induced strain properties which are significant to the practical application of PLZST antiferroelectric ceramics were investigated experimentally. A wet chemical method using colloidal processing [9] which offers better homogeneity, finer grain and lower sintering temperature as compared to solid state reaction method were chosen for powder synthesis. Tape-casting method was used for sample preparation in order to achieve dense samples at possible low sintering temperature under normal sintering conditions.

2. Experimental procedure

The composition of $(Pb_{0.97}La_{0.02})(Zr_{0.65}Sn_{0.25}Ti_{0.10})O_3$ at the AFE to FE phase boundary in the PLZST ternary system was chosen in this work, as CC3 shown in Fig. 1. The powder synthesis was detailed in previous works [9].

The obtained powders were tape-casted using commercial polyvinyl butyral (PVB) binder with a powder to binder solid volume ratio of 60:40. The green tapes were then stacked, laminated and cut into square plate. After binder burn-out, the green plates were sintered from 1000 to 1250 °C at 50 °C intervals for 2 h in a lead rich atmosphere, obtaining samples with dimension of approximate 7×7×0.3 mm. Silver paste was screen printed onto the surfaces of the samples, which were then baked at 750 °C to form electrodes.

Relative density of the samples sintered at various temperatures was determined by the water displacement

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method. Scanning electron microscopy (Shimadzu EPMA-8705QH2 electron probe microanalyzer) was used to analyze the fracture surfaces of all the samples to look for changes in grain size and fracture behavior that may have occurred under different sintering conditions.

The temperature dependence of the dielectric constant of the samples was measured by a LCR meter (Hewlett Packard 4284A) combined with a programmable temperature chamber (UGU AI-708PA) from room temperature to 250 °C at a heating rate of 2 °C/min. Capacitance was tested

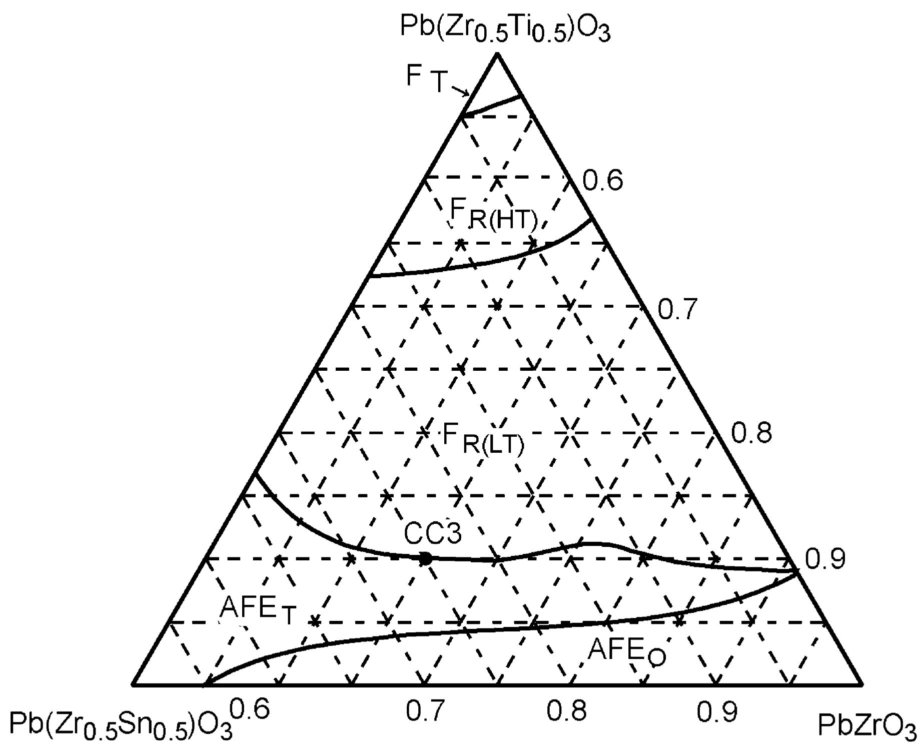

Fig. 1. Ternary phase diagram of $(Pb_{0.97}La_{0.02})(Zr, Sn, Ti)O_3$ showing composition in this work.

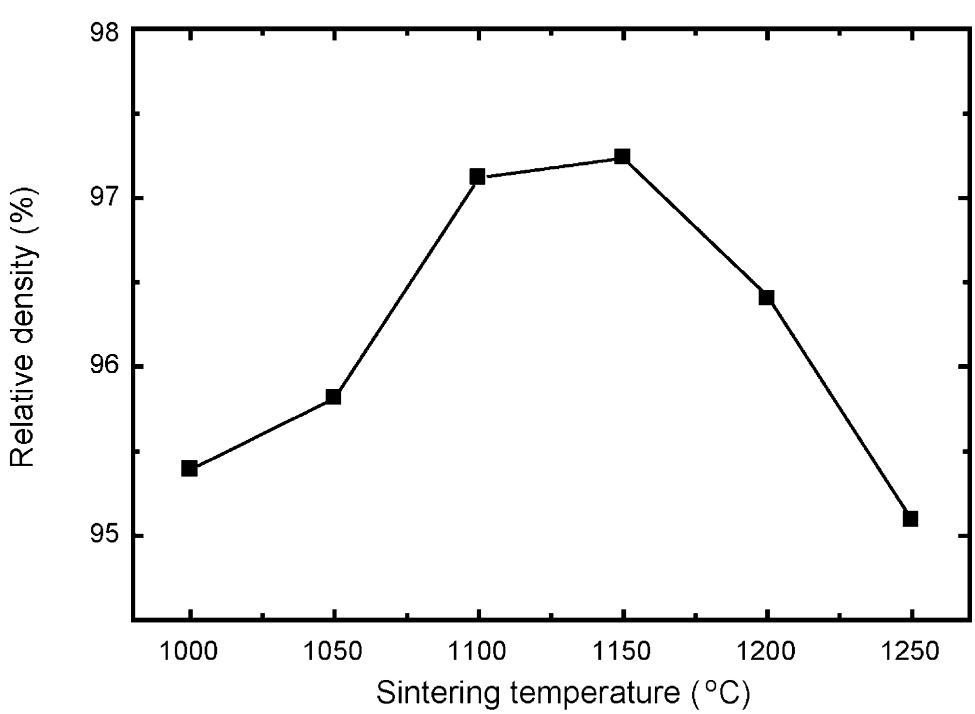

Fig. 2. Relative density of $(Pb_{0.97}La_{0.02})(Zr_{0.65}Sn_{0.25}Ti_{0.10})O_3$ samples sintered at various temperatures for 2 h.

Table 1
Average grain size and fracture characteristics of PLZST samples sintered under various conditions

Sintering condition	Average grain size (μm)	Fracture characteristics
1000 °C/2 h	2	Intergranular fracture
1050 °C/2 h	3.5	Intergranular fracture
1100 °C/2 h	5	Intergranular fracture with some transgranular fracture
1150 °C/2 h	6	Intergranular fracture with some transgranular fracture
1200 °C/2 h	9	Co-existence of transgranular and intergranular fracture
1250 °C/2 h	Not measurable	Transgranular fracture

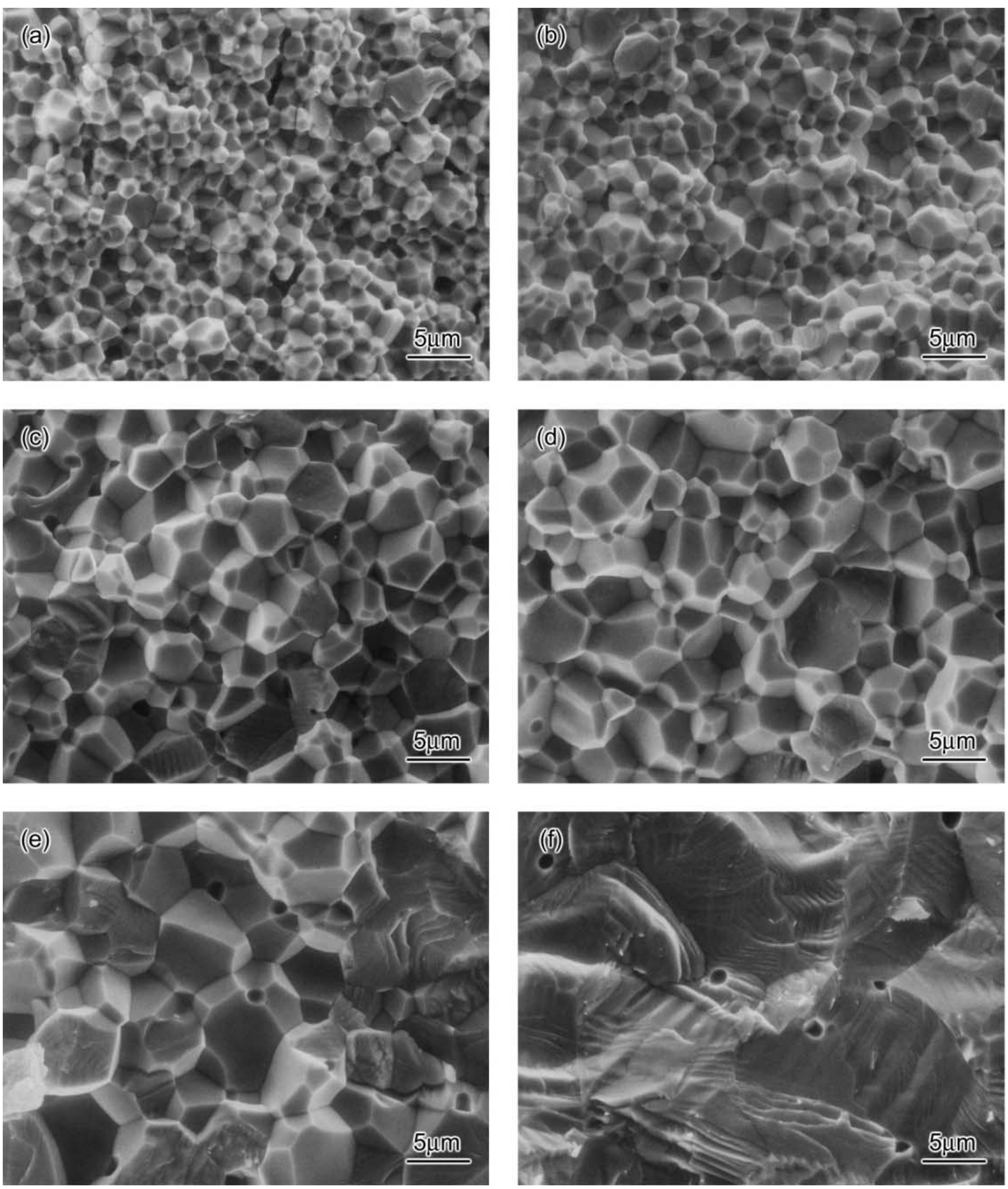

Fig. 3. SEM photograph of fractured surface from $(Pb_{0.97}La_{0.02})(Zr_{0.65}Sn_{0.25}Ti_{0.10})O_3$ samples sintered at: (a)1000C/2 h, (b) 1050 °C/2 h, (c) 1100 °C/2 h, (d) 1150 °C/2 h, (e) 1200 °C/2 h, (f) 1250 °C/2 h.

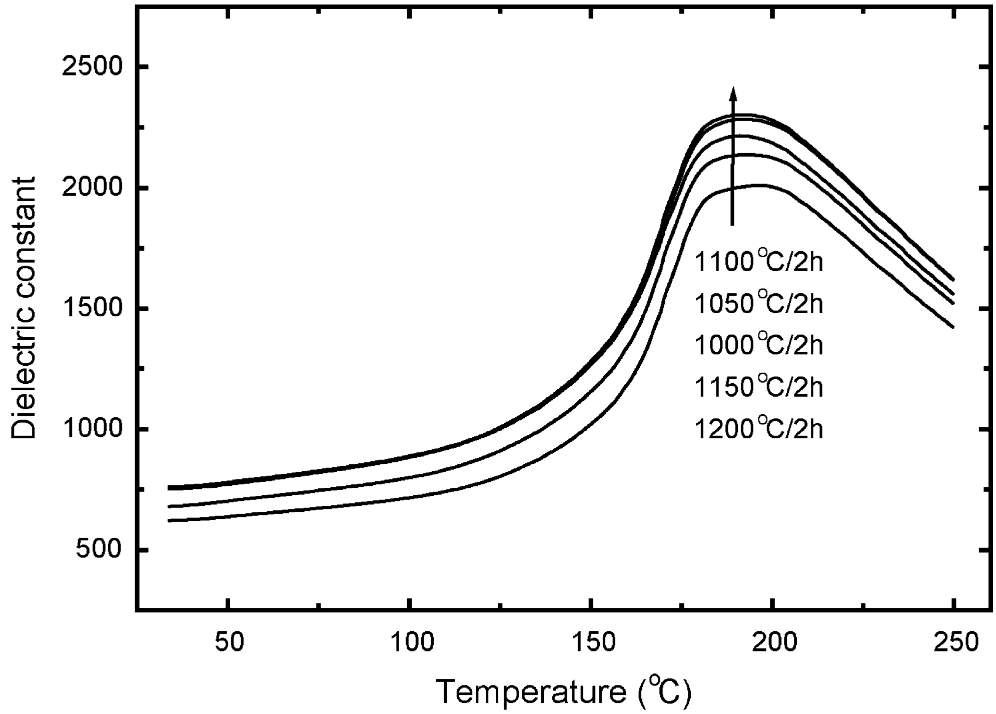

Fig. 4. The temperature dependence of dielectric constant of $(Pb_{0.97}La_{0.02})(Zr_{0.65}Sn_{0.25}Ti_{0.10})O_3$ samples sintered at various conditions.

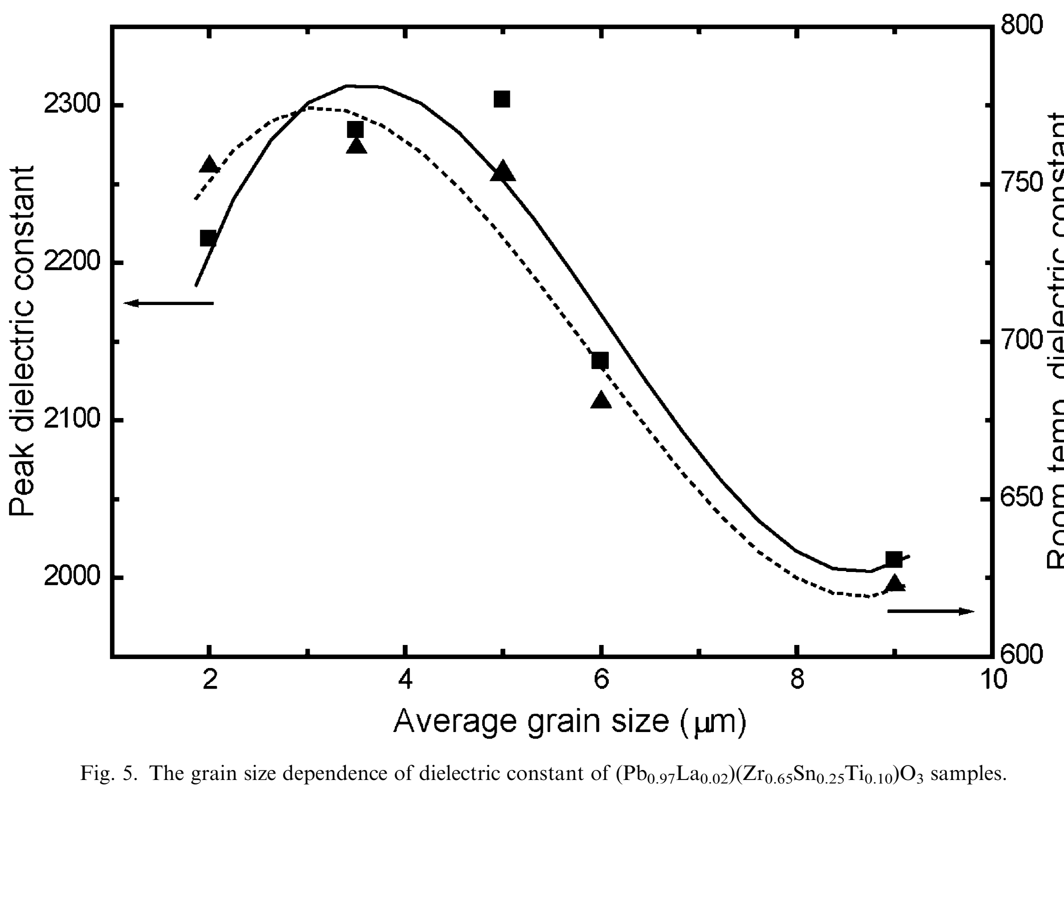

Fig. 5. The grain size dependence of dielectric constant of $(Pb_{0.97}La_{0.02})(Zr_{0.65}Sn_{0.25}Ti_{0.10})O_3$ samples.

under 1 V rms at 1 kHz, and converted to dielectric constant according to the sample geometry.

The double P–E hysteresis and field-induced longitudinal strain curves were measured using a computer controlled system comprised of a modified Swayer-Tower circuit, a high voltage source (Trek, 609A) and a linear variable displacement transformer (LVDT) at room temperature. The samples were submerged in silicon oil to prevent arcing. Electric fields as high as 6 kV/mm with triangular waveform at 0.7 Hz were applied.

3. Results and discussions

Fig. 2 shows the relative density of samples sintered from 1000 to 1250 °C for 2 h. Dense samples with relative density greater than 95 % were obtained at a sintering temperature as low as 1000 °C.

The SEM photographs of the fractured surfaces from the samples are shown in Fig. 3. The average grain size and fracture characteristics are summarized in Table 1. With an increase in grain size, the fracture characteristics of the samples change from intergranular to transgranular fracture.

The temperature dependence of the dielectric constant of the samples is shown in Fig. 4. All the samples show antiferroelectric (AF) to paraelectric (PE) phase transformation with diffusive characteristics different form the simple antiferroelectric pervoskites, e.g. $PbZrO_3$ and. $PbHfO_3$, in which AF to PE phase transformation results sharp dielectric constant peak [10].

The grain size dependence of room temperature and peak dielectric constant of the samples is shown in Fig. 5. For both curves, the dielectric constant shows a maximum at the average grain size of 5 μm. Fig. 6 shows the shift of AF to PE phase transformation temperature of the samples. The transformation temperature shifts towards higher temperature from 190.9 to 196.4 °C as the average grain size increases from 2 to 9 μm. This shift may be attributed to confined elastic strain energy [11].

The double P–E hysteresis loops and field-induced strain curves of the samples are illustrated in Fig. 7. There is no distinct difference in the polarization properties of the samples including the maximum polarization, the transformation field form AFE to FE $E_{AFE\text{-}FE}$ and the reverting field $E_{FE\text{-}AFE}$, excepting that the degree of loop squareness lowers while the average grain size decreases to 2 μm.

The field-induced strain varies with grain size remarkably. The dependence of maximum longitudinal strain under 6 kV/mm to average grain size is shown in Fig. 8. The strain increases to the maximum of 0.38% with the grain size up to 5 μm, and then decreases with further grain size increase.

The decrease of strain as the grains become finer in range of 2–5 μm may be explained as: by the decreasing grain size, antiferroelectric domain walls become difficult to form in the grain, and the domain rotation contribution to the strain becomes smaller [12]. The decrease of strain with the grain size greater than 5 μm is attributed to the grain boundary which could clamp the transformation strain.

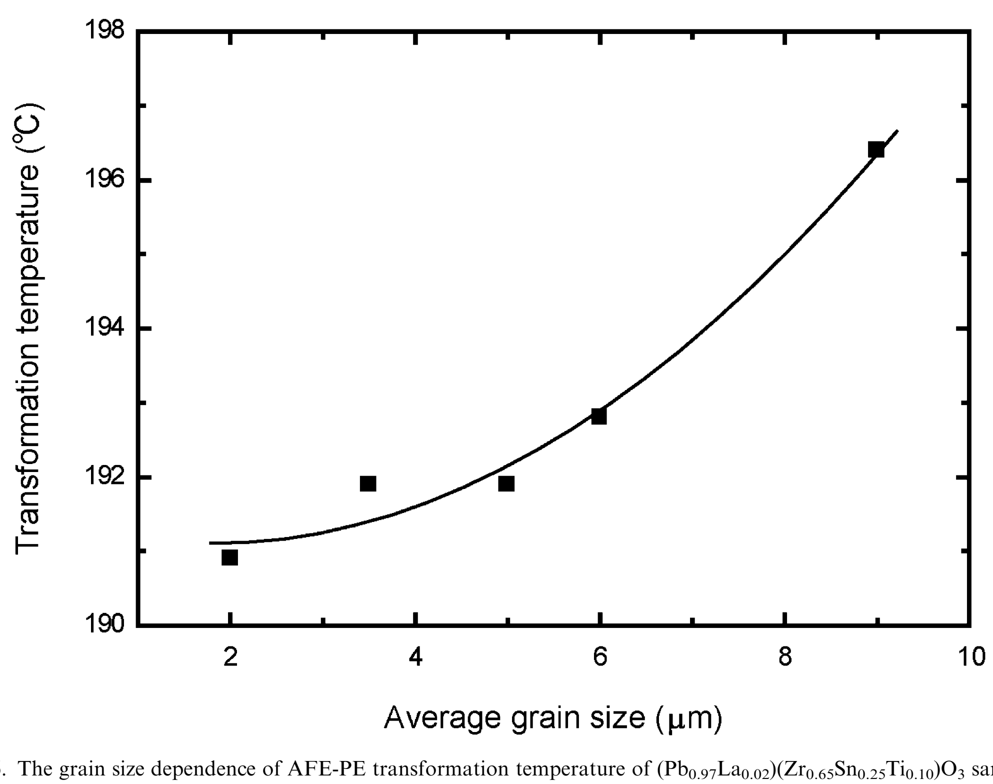

Fig. 6. The grain size dependence of AFE-PE transformation temperature of $(Pb_{0.97}La_{0.02})(Zr_{0.65}Sn_{0.25}Ti_{0.10})O_3$ samples.

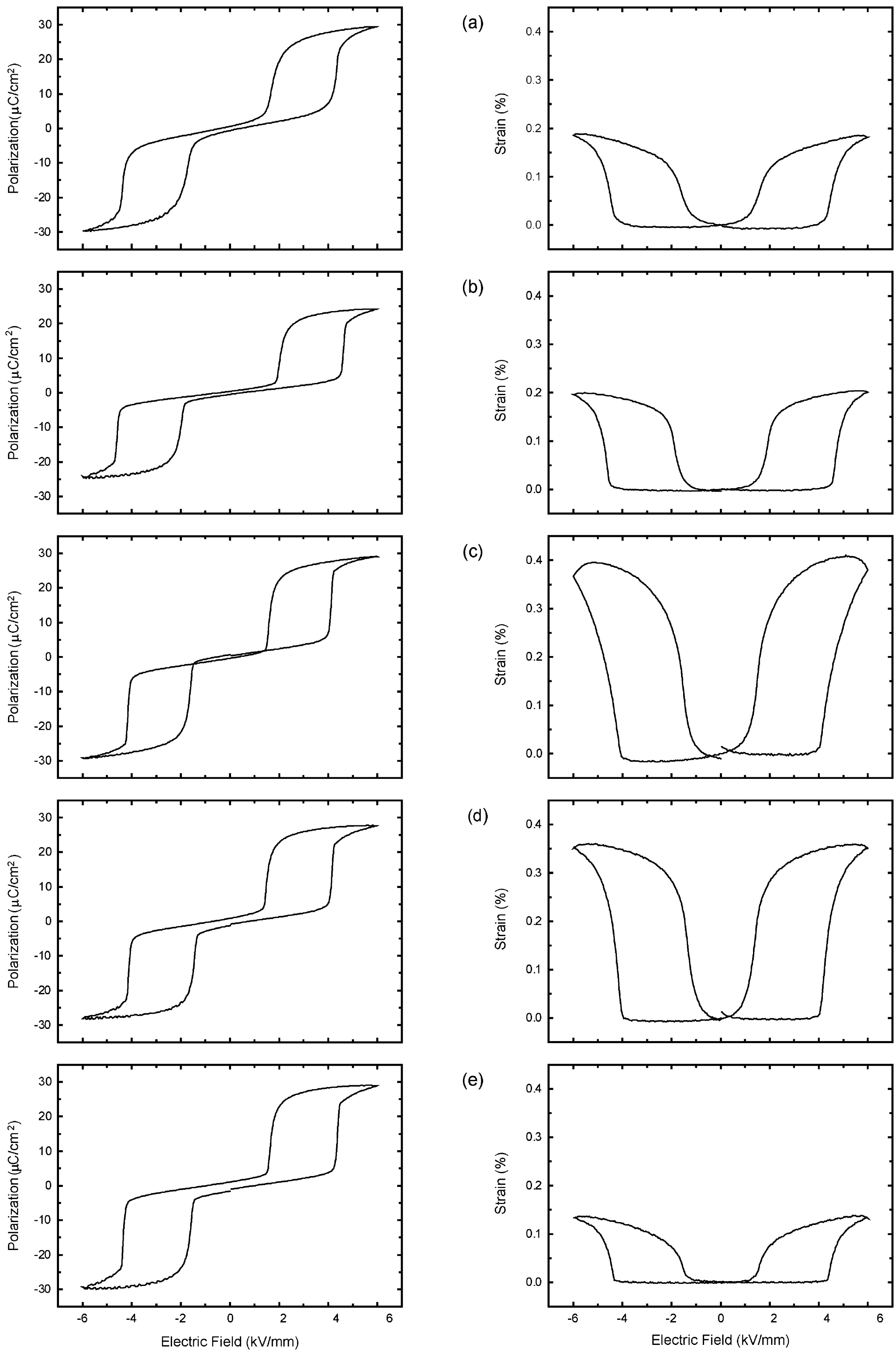

Fig. 7. The double P–E hysteresis and field-induced strain curves of $(Pb_{0.97}La_{0.02})(Zr_{0.65}Sn_{0.25}Ti_{0.10})O_3$ samples sintered at: (a)1000 °C/2 h, (b) 1050 °C/2 h, (c) 1100 °C/2 h, (d) 1150 °C/2 h, (e) 1200 °C/2 h.

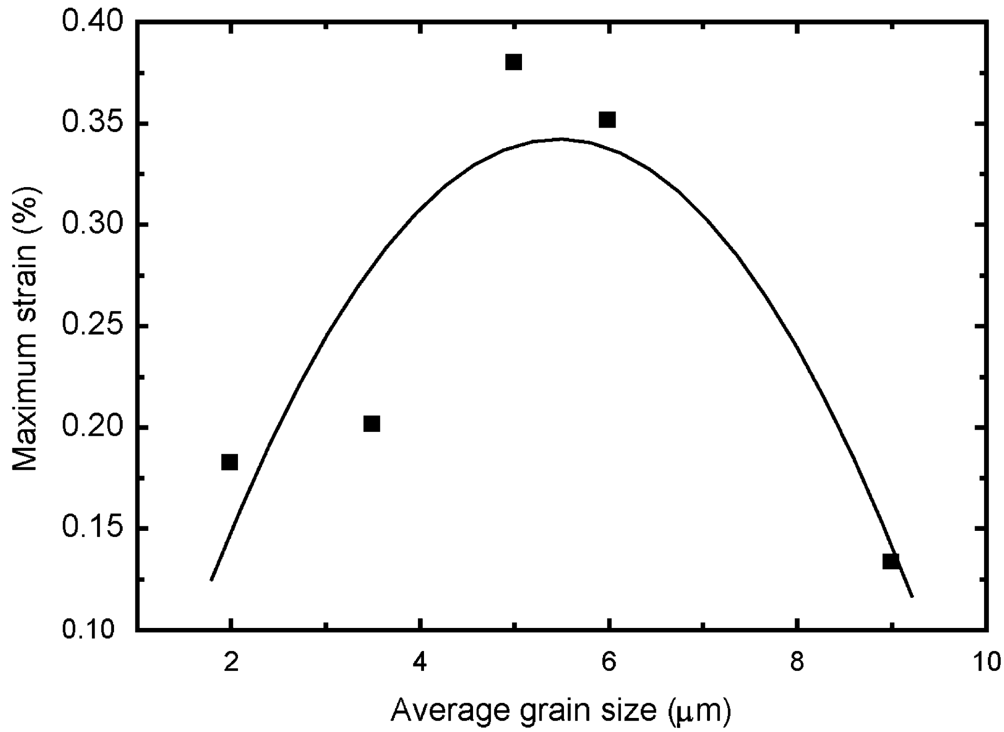

Fig. 8. The grain size dependence of maximum longitudinal strain of $(Pb_{0.97}La_{0.02})(Zr_{0.65}Sn_{0.25}Ti_{0.10})O_3$ samples under 6 kV/mm applied field.

4. Conclusions

Dielectric and field-induced strain properties of $(Pb_{0.97}La_{0.02})(Zr_{0.65}Sn_{0.25}Ti_{0.10})O_3$ ceramics with average grain size ranging from 2.0 to 9.0 μm were investigated experimentally. Sub-micron powders were prepared by the two-step wet chemical method using colloidal processing. Dense samples (relative density >95%) with various grain size were prepared by the tape-casting method and normal sintering method from 1000 to 1250 °C at 50 °C intervals for 2 h. The dielectric constant of samples show a maximum at average grain size of 5 μm, and the AF to PE transformation temperature shifts to higher temperature with the increase of grain size. The field-induced strain shows strong dependence to grain size, and maximum longitudinal strain of 0.38% was measured from the sample with an average grain size of 5 μm.

Acknowledgements

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