

Bulk dense fine-grain $(1-x)\text{BiScO}_3-x\text{PbTiO}_3$ ceramics with high piezoelectric coefficient

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High density fine grain $(1-x)\text{BiScO}_3-x\text{PbTiO}_3$ ceramics were successfully prepared by two-step sintering and their ferroelectric properties were investigated. Experimental evidence indicates the existence of a morphotropic phase boundary at the composition $x=0.635$, which exhibits a piezoelectric coefficient d_{33} of 700 pC/N at room temperature, significantly higher than the reported values to date. Furthermore, a higher electromechanical coupling factor $Kp=0.632$ and a larger remnant polarization $P_r=47.3 \mu\text{C}/\text{cm}^2$ were obtained. The paraelectric-to-ferroelectric phase transition occurs at 446 °C, slightly lower than in the coarse grain ceramics with a similar composition, suggesting a grain size effect. The local effective piezoelectric coefficient d_{33}^* was estimated to be 795 pC/N at 2.29 V, measured by scanning probe microscopy. Further atomic force microscope observation revealed the existence of 90° domains of about 60–70 nm in width, confirming the previous results that small domain structure enhances the piezoelectric properties. © 2008 American Institute of Physics. [DOI: 10.1063/1.2995861]

Recently, $(1-x)\text{BiScO}_3-x\text{PbTiO}_3$ (BSPT) ceramics have received increasing attention as a promising candidate for high temperature actuator and transducer material due to their considerably higher Curie temperature (T_C) for ferroelectric-paraelectric transition than conventional ceramics such as lead zirconate titanate (PZT). Like PZT, the best piezoelectric activity is found near the morphotropic phase boundary (MPB) between the tetragonal phase and the rhombohedral phase. According to Eitel *et al.*,¹ the piezoelectric coefficient d_{33} of BSPT ceramics reaches 450 pC/N and the T_C is around 450 °C in the region of $x=0.64$, which was designated as the MPB composition. Shimojo *et al.*² independently determined the phase diagram for $x>0.55$ and suggested that the MPB occurs at $x=0.625$. Inaguma *et al.*³ observed a peak electromechanical coupling factor and a minimum coercive electric field in the vicinity of $x=0.63$. While these findings confirmed the outstanding properties of BSPT near the MPB, first-principles studies of Iniguez *et al.*⁴ suggested even better piezoelectric properties. Moreover, in our previous work we showed that two-step sintering can enhance the BSPT properties with d_{33} reaching 520 pC/N at $x=0.64$.⁵ The present study aims to locate the composition for optimum piezoelectric properties and use the improved processing method including two-step sintering to further improve BSPT's piezoelectric properties. An excellent d_{33} of 700 pC/N is found for $x=0.635$. This and other piezoelectric properties and their characterization are described here.

Fine powders were synthesized by a citrate sol-gel method⁶ using a procedure for gel preparation described elsewhere.⁵ The gel was calcined and the powder ball milled, then sieved. The powders were next pressed into pellets with a diameter of 10 mm and a thickness of 1 mm. The

pellets were first heated to a higher temperature $T_1 = 1000\text{--}1050$ °C at a heating rate of 4 °C/min, then immediately cooled to a lower temperature $T_2=800$ °C and held for 4 h. The cooling rate from T_1 to T_2 was 20 °C/min.

X-ray diffraction (XRD) with Cu $K\alpha$ radiation at 40 kV was used for phase analysis. The microstructures of the sintered pellets were examined by scanning electron microscopy to determine the average grain size by a linear intercept method using surface micrographs. The densities of the sintered pellets were measured by the Archimedes method using distilled water. Before piezoelectric measurement, sintered pellets were electroded by a silver paste, then polarized under an electric field of 50–60 kV/cm for 15 min in a silicone bath at 120 °C. The hysteresis loop was measured using a ferroelectric test system (RT6000HVS, Radiant Technology Incorporation, New Mexico, USA). Dielectric spectra and T_C were measured using an impedance analyzer (4294A, Agilent, Palo Alto, CA) at 10 and 100 kHz. Planar electromechanical coupling factor (Kp) was measured using an impedance/grain-phase analyzer (HP Hewlett 4194A) and calculated from the resonance frequency f_r and the antiresonance frequency according to Ref. 7,

$$1/(Kp)^2 = 0.398 f_r/(f_a - f_r) + 0.579.$$

Local nanoscale piezoresponse [atomic force microscopy (AFM) and piezoelectric force microscopy (PFM)] was measured using a scanning probe microscopy (SPM) system (AFM, SPI3800N&SPA400, Seiko, Tokyo, Japan) by inducing mechanical oscillations with an ac voltage (10.0 V_{rms}) at 5.0 kHz applied to the tip of a microcantilever (SI-DF3-R, Rh coated) with a spring constant of 1.9 N/m and a free resonance frequency of 28 kHz. In this measurement, the sample was polished and glued to a conductive substrate serving as a bottom electrode connected to the ground.

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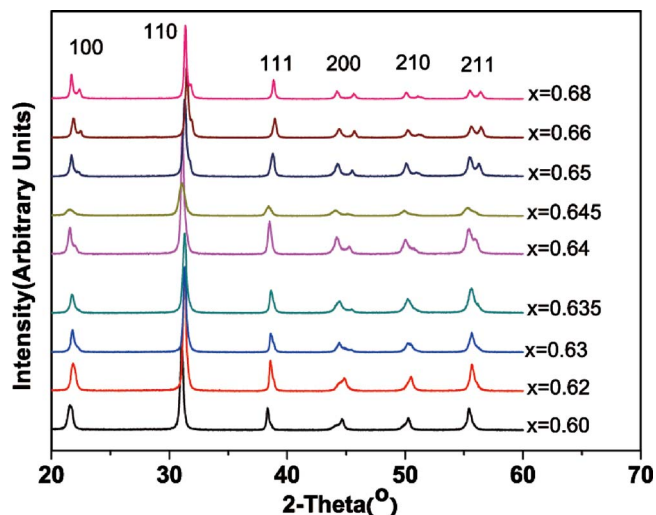


FIG. 1. (Color online) XRD pattern of BSPT ceramics with different compositions.

The ceramics with $x=0.60-0.68$ show the XRD patterns in Fig. 1. The sample of $x=0.60$ is rhombohedral and the sample of $x=0.68$ is tetragonal. The MPB is located near $x=0.64$ and $x=0.635$, for which the XRD patterns feature splitting of $\{100\}$ and $\{110\}$ peaks and a broad $\{111\}$ peak. This is consistent with the piezoelectric coefficient in Fig. 2, which shows a peak at $x=0.635$, reaching 700 pC/N . This value is significantly higher than the reported values (460^1 and 520 pC/N^5) to date. The electromechanical coupling factor Kp also shown in Fig. 2 again reaches its maximum at $x=0.635$ with a $Kp=0.632$, which is significantly higher than the one reported by Inaguma *et al.* (0.425).³ The sample of peak d_{33} exhibits a dense uniform microstructure with a grain size average of $1.47 \mu\text{m}$ (Fig. 3) with a relative density of 96.8% . In short, the coincidence of maximum Kp and d_{33} at $x=0.635$ strongly suggests the existence of a MPB at or near this composition.

The T_C of the $x=0.635$ ceramic is $446 \text{ }^\circ\text{C}$, $2-4 \text{ }^\circ\text{C}$ lower than that observed in bulk ceramics with the same composition.¹ Kanzig⁸ reported that for sintered BaTiO_3 ceramics with high densities, the T_C decreases with increasing grain size from 1 to $5 \mu\text{m}$. A similar trend was also reported recently for BaTiO_3 ceramics of even smaller grain sizes.⁹

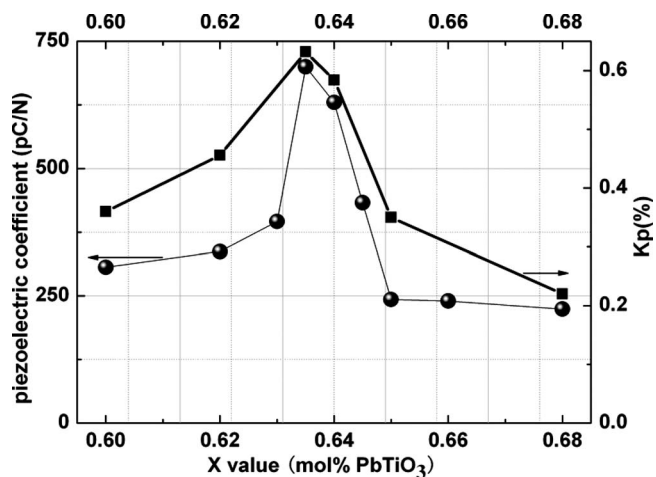


FIG. 2. Piezoelectric coefficient and electromechanical coupling factor of BSPT ceramics with different compositions.

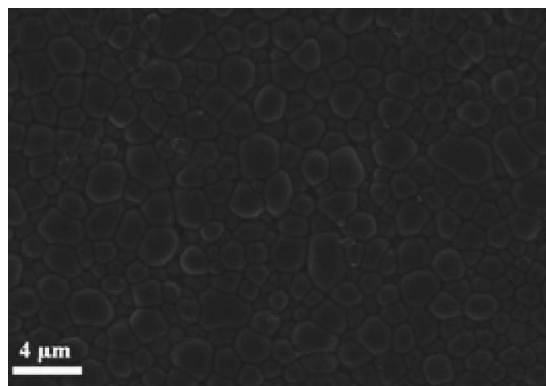


FIG. 3. Surface micrograph of the surface for BSPT ceramic ($x=0.635$).

Thus the decrease in T_C may be related to the relatively smaller grain size compared with those (several to dozens of micrometers) in the previous studies. Since the decrease in T_C is rather small whereas the increase in piezoelectric properties is substantial, this trade-off is “worth the price.” Moreover, the T_C of $446 \text{ }^\circ\text{C}$ of BSPT is still some $60 \text{ }^\circ\text{C}$ higher than that of conventional PZT.

Figure 4(a) depicts the polarization-field hysteresis loop for the $x=0.635$ ceramic measured in a silicon oil bath at room temperature. The loop has a regular shape with a large remnant polarization (P_r) of $47.3 \mu\text{C/cm}^2$ compared with the reported values of $32 \mu\text{C/cm}^2$ in the literature.¹ Accord-

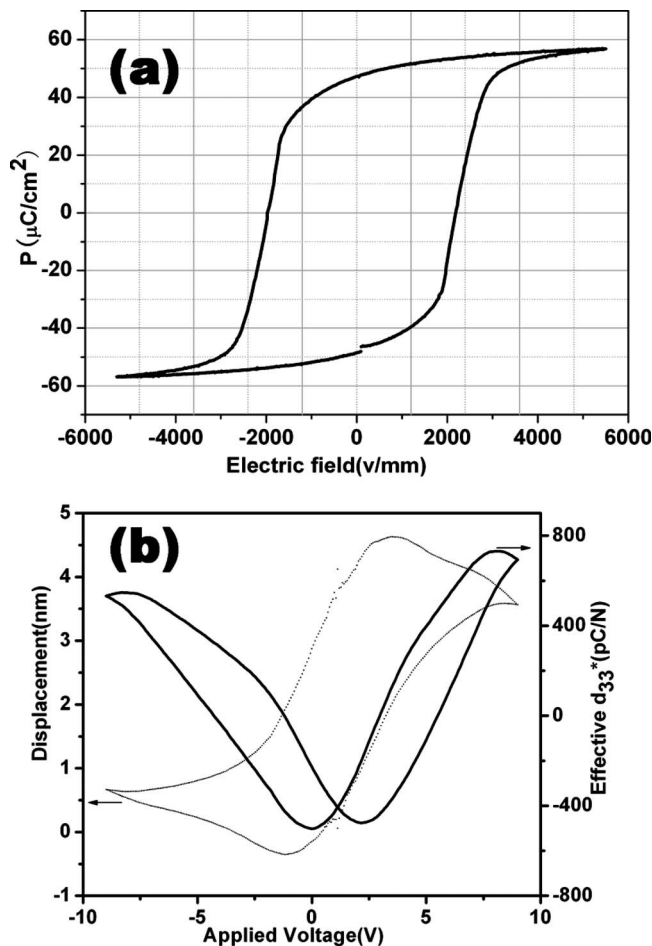


FIG. 4. (a) Hysteresis loop of BSPT ceramics ($x=0.635$), (b) local piezoelectric response vs applied voltage of the grain marked by a cross in Fig. 5(a).

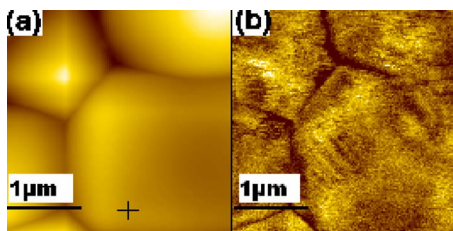


FIG. 5. (Color online) (a) AFM topography of the surface of BSPT ceramic ($x=0.635$), (b) PFM image corresponding to (a).

ing to Haertling,¹⁰ a high remnant polarization relates to high internal polarizability, strong electromechanical coupling, etc. Moreover, the piezoelectric coefficient is the product of remnant polarization, dielectric constant, and electrostrictive constant. Therefore, the high P_r itself may at least partially explain the high peak values of d_{33} (700 pC/N) and Kp (0.632) of this ceramic. Besides, the coercive field E_c is around 22 kV/cm, which is consistent with the reported value for near MPB compositions.¹

The enhanced piezoelectric activity at the MPB is usually explained in terms of its structure intermediate between the rhombohedral and the tetragonal phases. As a result, there may be more crystallographic directions suitable for polarization, facilitating piezoelectricity. On the other hand, nanosized domains have also been suggested to contribute to enhanced piezoelectricity.^{11–13} Observations of domain structures are provided in Figs. 5(a) and 5(b) showing an AFM micrograph together with a PFM image depicting the domain structure in the $x=0.635$ specimen with an average grain size of 1.47 μm . Using computer simulation, Ahluwalia *et al.*¹¹ investigated the domain-size dependence of the piezoelectric properties of a model ferroelectric, and their results showed that the piezoelectric coefficient is enhanced by reducing the domain size. Supporting experimental evidence was observed by Wada *et al.*¹² in barium titanate single crystals and Takahashi *et al.*¹³ in microwave sintered BaTiO₃ ceramics, correlating superior piezoelectric properties to small domain sizes. In our study, the PFM micrograph reveals a fine domain structure probably composed of 90° domains of 60–70 nm in width. These observations are in accord with the previous results mentioned above. Therefore, the superior piezoelectric properties of the $x=0.635$ ceramic could be a result of both the MPB composition and the small domain size, although further experiments separating these two effects are required to verify this hypothesis.

Finally, we investigated the local piezoelectric response using SPM. The region of interest is marked in Fig. 5(a) by a cross. The measurement was achieved by keeping the SPM tip at a fixed height above the grain and applying a dc voltage from -9 to 9 V while recording the response signal (displacement). As shown in Fig. 4(b), the piezoelectric hysteresis loop (dotted line) can be calculated from the displacement, which has the typical “butterfly” loop (solid line). The effective piezoelectric coefficient d_{33}^* thus estimated is 795 pC/N at 2.29 V. Due to the grain size distribution in the sample and the intragranular interactions during domain formation, variations in the local piezoelectric re-

sponse among different regions are expected. Considering these variations, the above local d_{33}^* value is in reasonable agreement with the bulk piezoelectric coefficient obtained from macroscopic measurements.

In conclusion, dense bulk $(1-x)\text{BiScO}_3-x\text{PbTiO}_3$ ceramics were successfully prepared using two-step sintering. The composition corresponding to optimum piezoelectric properties was located at $x=0.635$. The d_{33} value reaches 700 pC/N at this composition for a ceramic of an average grain size of 1.47 μm . The electromechanical coupling factor and remnant polarization are $Kp=0.632$ and $P_r=47.3 \mu\text{C}/\text{cm}^2$, respectively. At the same composition, the ferroelectric to paraelectric phase transition occurs at 446 °C. Local AFM investigation revealed ferroelectric domain of a width of 60–70 nm, which may contribute to the enhancement of the piezoelectric responses. Local SPM measurements also recorded well-formed butterfly-shaped displacement-voltage loops with an effective d_{33}^* of around 795 pC/N at 2.29 V, which are in accord with the macroscopic piezoelectric hysteresis loop. The discovery of large d_{33} in 0.365 BiScO₃–0.635 PbTiO₃ bulk ceramics via a low-cost process is of great practical and scientific interest, as it furthers the possibility of using strongly piezoelectric materials at higher temperatures.

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