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Processing and property of textured lead-free $SrTi_4Bi_4O_{15}$ piezoelectric ceramics

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Abstract In this paper, textured $SrTi_4Bi_4O_{15}$(SBT) ceramics were produced by tape casting and hot-pressing to improve the piezoelectric property. Plate-like SBT powders were synthesized by a molten salt synthesis (MSS) method. Tape casting and hot-pressing were employed to obtain (00l) oriented SBT ceramics at 1,000°C with a density of 98.3%. Anisotropy characters of textured SBT were measured by piezoelectric coefficient and hysteresis loop. Compared with randomly oriented ceramics, textured SBT shown enhancements in the piezoelectric properties. Property of perpendicular to hot pressing direction (d_{33}=17 pC/N) was more eminent than that of parallel to hot pressing direction (d_{33}=1 pC/N).

Keywords Bismuth layer structure material · Textured · Tape casting

1 Introduction

With prominent ferroelectric properties such as negligible polarization fatigue, high Curie temperature and low leakage current, bismuth layered structure materials (BLSF) are proper to apply at high temperature and high frequency conditions and have attractive application in ferroelectric memory fields [1]. As the materials have relative inferior piezoelectric properties, heating treatment (heat-pressing, hot-forging), partly-order reaction (such as templated grain growth) and doped processing are some potential methods to resolve the problem [2–4].

Templated grain growth (TGG) enables the fabrication of textured ceramics with single crystal-like properties, as well as single crystals. In TGG, nucleation and growth of the desired crystal on aligned single crystal template particles results in an increased fraction of oriented material with heating. Initially, the template particles are randomly oriented but are then oriented during fabrication. To facilitate alignment during forming like tape casting and extrusion, template particles must be anisometric in shape.

In this paper we chose $SrBi_4Ti_4O_{15}$ (SBT) to produce textured ceramics to study its property. SBT, which contains four perovskite-like TiO_6 octahedron units stacked in between $(Bi_2O_2)^{2+}$ layers, has an orthorhombic symmetry with a=5.4507, b=5.4376, c=40.9841 Å [5, 6]. Textured $SrTi_4Bi_4O_{15}$ ceramics were produced by tape casting and hot-pressing to improve the piezoelectric property. Anisotropy characters of textured SBT were measured by piezoelectric coefficient and hysteresis loop.

2 Experimental procedure

To synthesize $SrBi_4Ti_4O_{15}$, reagent-grade oxide or carbonate powders of Bi_2O_3, TiO_2, $SrCO_3$ with 99% purity were used as the raw materials. Molten salt synthesis method was employed to synthesize plate-like $SrBi_4Ti_4O_{15}$ powder. The proportion of KCl and raw material was 1:1 (mol). The mixture was ball milled with alcohol for 24 h, dried, then calcined at 800 °C ~ 1,000°C for 2 h. The powder was washed in distilled water with 80°C temperature until the

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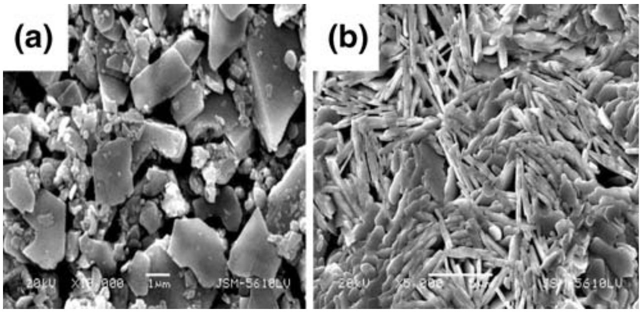

Fig. 1 Surface of sheets after calcined (**a**) and SBT ceramics (**b**) sintered by a conventional method

Cl^- ion could not be detected by $AgNO_3$ [7]. $SrBi_4Ti_4O_{15}$ powder was mixed with solvents ($C_2H_5COCH_3$ and C_2H_5OH) and dispersant (Glycerol trioleate) in a ball mill for 24 h and plasticizers (polyalkylene glycol) and binder (polyvinyl butyral (PVB)) were added and mixing for another 24 h to obtain the slurry. Tapes were cast about 200 μm thick on a glass surface at a blade speed of 7 cm/s and dried under ambient conditions. The tapes were stacked, cut and pressed into pellets [8]. Elevatory velocity of calcined temperature was controlled slowly (30~40°C/h). According to the decomposed temperature of organic additive, parameter of calcining was 240 °C for 0.5 h, 340°C for 0.5 h and 600 °C for 1 h. To eliminate defects in the SBT body after calcined, cool isostatic pressing and hot pressing sintering should be utilized to produce high-oriented textured SBT ceramics.

The grain orientation factor *f*, was calculated using the Lotgering method

$$f = \left(\frac{p - p_0}{1 - p_0}\right)$$

P is the ratio of the sum of intensities of the oriented peaks to the sum of intensities of all the peaks including oriented peaks for the grain-oriented pellet. P_0 is the similar ratio referring to the non-oriented polycrystalline powder. SEM was employed to observe the microstructure of the powder synthesized by different methods and to make it certain that pellets sintered by MSS powder should have the grain-orientation. The density of the sintered pellet was measured via the Archimedes method, using distilled water and a balance with precision of $\pm 10^{-4}$. The relative density of the samples was the ratio of density to theory density (ρ=7.45 g/cm^3, obtained from X-ray measurements).

Piezoelectric properties of samples were poled on polished disks electroded with Ag paste by applying a direct-current (dc) electric field of 3~4 kV/mm for 30 min, in silicopne oil, at 170 °C. The piezoelectric constant(d_{33}) was measured using a d_{33} meter Model ZJ-2. The hot-pressing samples were electroded in two ways: (1) by applying an electrical field perpendicularly to the pressing axis, and (2) by applying an electrical field parallel to the axis. Hysteresis loop was measured by Radient precision work station.

3 Results and discussion

After calcination, organic composition was removed from body, which resulted the loosen microstructure (Fig. 1(a)). Plate-like $SrBi_4Ti_4O_{15}$ grain almostly lined along the direction of blade movement at sheet. Conventional sintering could not eliminate these defects and also could not get high-oriented just randomly orientated ceramics (Fig. 1(b)). Though some region of the ceramics surface had (00l) oriented, most of plate-like grain was disorder and the relative density of it was only 84.3%.

To improve the microstructure and produce high-oriented ceramics, some other processing should be employed such as cool isostatic pressing and hot-pressing sintering, which could help to elevate the density of the tape body and ceramics. During hot-pressing sintering, grains were prior

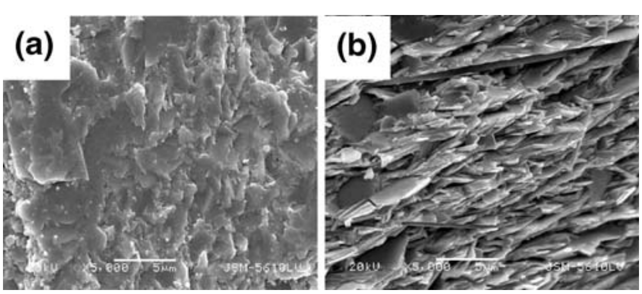

Fig. 2 Surface (**a**) and fracture (**b**) micrographs of samples produced by tape casting forming and hot-pressing sintering

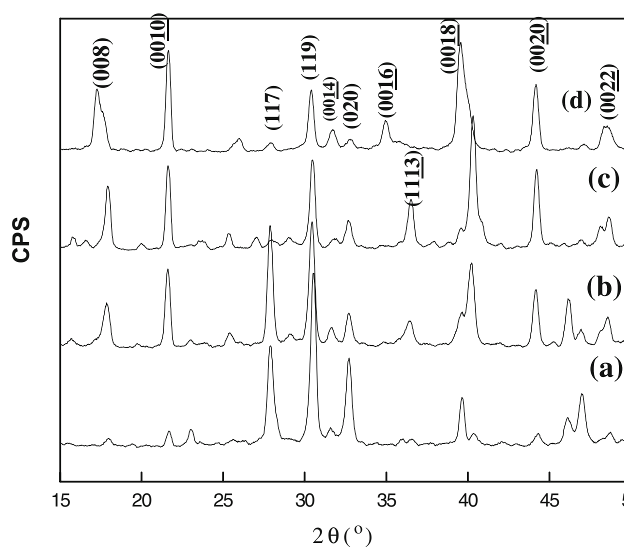

Fig. 3 X-ray diffraction patterns of $SrBi_4Ti_4O_{15}$ ceramics

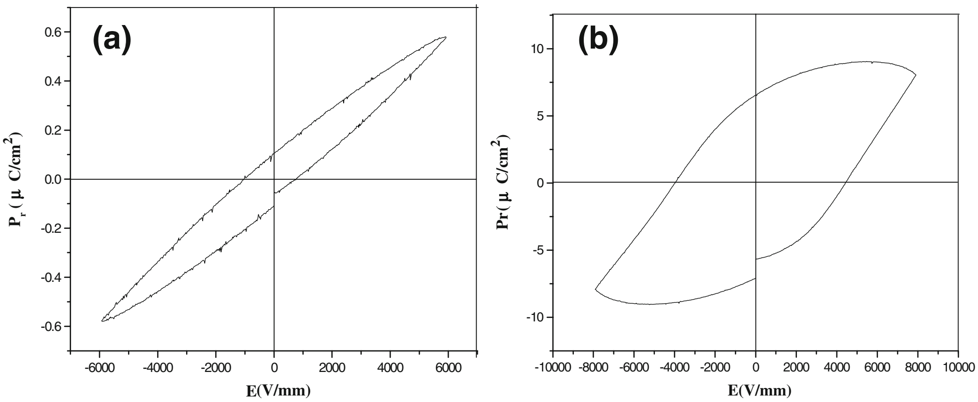

Fig. 4 Hysteresis curves of SBT (**a**) parallel (**b**) perpendicular to pressing direction

to grow at perpendicular to pressing direction. As shown in Fig. 2, the microstructure of ceramics had distinct (00l) orientation with relative density 98.3%.

Molten salt synthesis method could synthesize plate-like powder. If it followed by conventional solid sintering (sample b), there was a little increase in (00l) orientation relative to randomly-oriented sample. The sample followed by tape-casting forming and hot-pressing sintering (Fig. 3(d)) got distinct (00l)-orientation.

Figure 4 shows the *P–E* hysteresis loops of the HP samples at different direction. A high ferroelectric anisotropy was found in the HP sample. The remanent polarization of perpendicular to pressing direction (P_r) was 6.54 μC/cm^2 and coercive field value (Ec) was 4.433 kV/mm, while remanent polarization of parallel to pressing direction was only 0.105 μC/cm^2 with Ec=0.76 kV/mm and piezoelectric coefficient at this direction was only 1 pC/N. The purpose of texturing is to access physical properties that are directly related to crystallographic orientation (like thermal conductivity, dielectric permittivity, piezoelectricity, electrical conductivity, etc.). It is preferable if the template axis matches the desired crystallographic orientation. The experimental results shown that the polarization could be reoriented only in the plane parallel to the Bi_2O_2 layer (ab plane of orthorhombic structure)[9]. This plane was usually perpendicular to pressing direction. HP sample have relative high orientation at this direction compared to CS sample. Piezoelectric coefficient (d_{33}) of randomly-oriented (CS sample) sample was only 8 pC/N and d_{33} of textured ceramics (HP sample testing at perpendicular to pressing direction) was 17 pC/N [10, 11].

4 Conclusion

Salt synthesis method was employed to synthesized plate-like $SrBi_4Ti_4O_{15}$ powder. Textured lead-free $SrBi_4Ti_4O_{15}$ ceramics was produced by tape-casting and hot-pressing sintering. Anisotropy of textured $SrBi_4Ti_4O_{15}$ ceramics was distinct. Property of perpendicular to hot pressing direction (d_{33} was 17 pC/N) was more eminent than that of parallel to hot pressing direction (d_{33}=1 pC/N).

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