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Grain oriented $CaBi_4Ti_4O_{15}$ piezoceramics prepared by the screen-printing multilayer grain growth technique

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Abstract

The grain oriented bismuth layer structure ferroelectric (BLSF) ceramics have superior ferroelectric and piezoelectric properties to the randomly oriented ceramics. The grain oriented $CaBi_4Ti_4O_{15}$ ceramics were prepared by the screen-printing multilayer technique without any template particles. The influences of sintering time, temperature, and the particle size of raw materials on grain orientation were studied. The degree of grain orientation and the grain morphologies were examined using XRD and SEM techniques. At sintering temperatures of 1000–1120 °C, orientation degree increases with sintering temperature and keep constant at temperatures of 1120–1150 °C. The orientation degree increases rapidly with sintering time at beginning and gradually reaches the highest value for 4 h at the sintering temperature. It was found that the particle size of starting materials is the important factor for grain orientation. Highly oriented ceramics can be obtained only when using nanosized starting materials. Without the use of template particles and pressure densification process, the screen-printing multilayer grain growth (MLGG) technique is a new approach to fabricate highly textured piezoceramics.

Keywords: Grain growth; Piezoelectric properties; Films; Layered perovskite; X-ray method

1. Introduction

Bismuth layer structure ferroelectrics (BLSFs) have a general formula $(Bi_2O_2)^{2+}(A_{m-1}B_mO_{3m+1})^{2-}$, and their crystal structure composed of pseudo-perovskite blocks $(A_{m-1}B_m O_{3m+1})^{2-}$ interleaved with bismuth oxide layers $(Bi_2O_2)^{2+}$ along *c*-axis.[1] BLSFs have potential use in high temperature applications because of their high Curie temperature (T_c) and low dielectric constant.

The BLSFs have peculiar anisotropy in ferroelectric properties. Their spontaneous polarization take place mainly in *a*(*b*) direction.[2–5] Conventionally prepared BLSF ceramics have low ferroelectric and piezoelectric properties for their randomly grain orientation. In order to improve the ferroelectric and piezoelectric properties of BLSF ceramics, grain orientation techniques have been studied.[6] Most of the work have been focused on the hot forging, templated grain growth (TGG)[7–9] and reactive templated grain growth (RTGG).[10] A pressure is necessary to aid the grain orientation during sintering process in hot forging method. For the TGG and RTGG processes, particular template particles play important roles that are usually obtained by molten-salt method. These techniques are complex for the processing, expensive for the equipments and not suitable for mass productions.

The screen-printing method has been widely used for fabricating thick films.[11,12] However, no ferroelectric ceramics have been reported yet by screen printing up to now. In this paper, the grain orientated BLSF ceramics were prepared by a novel screen-printing multilayer grain growth (MLGG) technique without the need of templates. The microstructure of grain oriented ceramics and the effect of sintering temperature, soaking time, and the size of starting materials on the grain orientation were discussed.

2. Experimental

$CaBi_4Ti_4O_{15}$ (CBT) ceramics were prepared by the screen-printing method. The starting materials were an-

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alytical grade oxide and carbonate powders, e.g. Bi_2O_3 (purity >99.9%. Changde Institute of Applied Chemistry), TiO_2 (purity >98.5%. Jiangsu Hehai Nanometer Science & Technology Co. Ltd.), and $CaCO_3$ (purity >99.9%. Henan Keli New Materials Co. Ltd.). The particle size of these powders was in nanometer scale (30–80 nm). Stoichiometric amounts of the starting powders were thoroughly mixed with alcohol in a ball mill for 4 h. The paste was obtained by mixing the powders with ethyl-cellulose and α-terpineol organic vehicles for 3 h. The paste was composed with 41 wt.% of the nanosized inorganic powders and 59 wt.% of the organic vehicles. The paste was screen-printed onto a glass substrate and then dried at 90 °C, and repeated the process 20 times until the multilayered thick film to be about 100 μm. The films was removed carefully from glass substrate and cut into 12 mm × 12 mm, then, stacked in layer of 20, and pressed uniaxially at 400 MPa. The binder was burned out by heating in air at 1 °C/min to 600 °C. The laminates were sintered at temperatures of 1000–1180 °C in air. The CBT powders prepared by solid-state reaction method using the same starting materials were prepared for comparison.

The crystalline phase and the degree of orientation were determined by X-ray diffraction (XRD) analysis (Rigaku, D/max 2550 V) using Cu Kα radiation with a scan speed of 4°/min and a step width of 0.02°. The microstructure of the ceramics was observed using scanning electron microscopy (SEM, model JSM-6700F) on the fracture surface.

3. Results and discussion

3.1. X-ray diffraction analysis of grain oriented CBT ceramics

Fig. 1 shows the XRD patterns of three different samples, e.g. CBT powders by solid-state reaction, one ceramic sample of the surface parallel to screen-printing plane, and the other sample of the surface perpendicular to screen-printing plane. It can be seen that all (0 0 l) reflections increase in the parallel plane, and decrease in the perpendicular plane compared with the CBT powder diffraction patterns. The (1 1 9) peak is the most intense peak of $CaBi_4Ti_4O_{15}$ powder, while it remarkably decreases for the screen-printed sample in its parallel plane. This indicates that the ceramic grains were oriented align *c*-axe that is perpendicular to the screen-printing plane.

The degree of grain orientation can be calculated by Lotgering factor *f* which defined as: $f = (p - p_0)/(1 - p_0)$, where $p = \Sigma I(0\,0\,l)/\Sigma I(h\,k\,l)$, $p_0 = p$ for randomly oriented sample. *f* varies from 0 to 1. The diffraction lines between $2\theta = 10°$ and $2\theta = 50°$ were used to calculate *p* and p_0. The orientation degree *f* is calculated from the above equation to be 94.3% for CBT ceramics prepared by the MLGG process, which is competed with the piezoceramics fabricated by hot forge, TGG and RTGG.

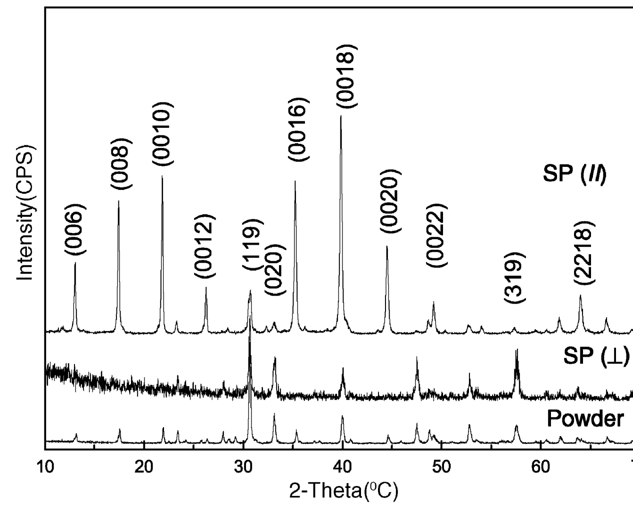

Fig. 1. The XRD pattern of the CBT ceramics prepared by screen-printing method on the surfaces parallel (//) and perpendicular (⊥) to the original sheet plane, compared to the XRD pattern of the CBT powder by conventional processing.

3.2. Effect of sintering temperature on the grain orientation

Fig. 2 shows X-ray diffraction pattern of the MLGG samples sintered at different temperatures of 1000–1120 °C. With the increase of sintering temperature, diffraction peaks of (0 0 l) planes progressively dominate the patterns, while the intensity of (1 1 9) peak decreases. Fig. 3 shows the microstructure of dewaxed ceramic sample. All particles are in nanosized scale and the layer interfaces are visible in some areas.

The microstructure of grain oriented ceramics sintered at 1000–1120 °C are shown in Fig. 4. The ceramic sintered at 1000 °C was porous with the grains partly oriented (Fig. 4a). There are several aligning directions in the sample, and the alignment angle of selected neighbor grains is large. Some

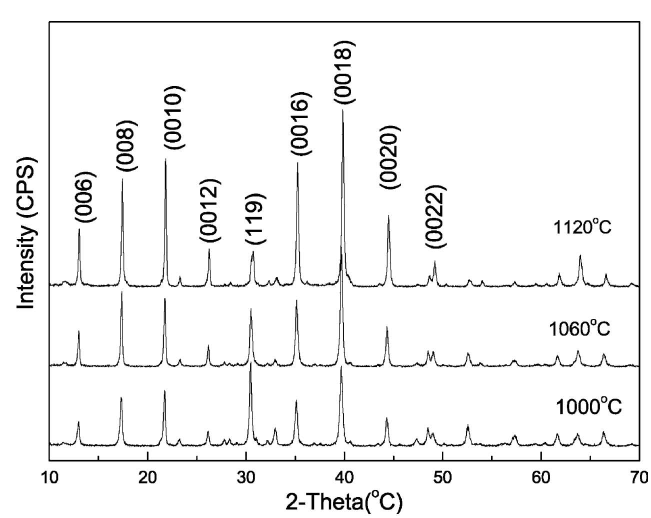

Fig. 2. XRD patterns of CBT ceramics sintered at various temperatures for 4 h.

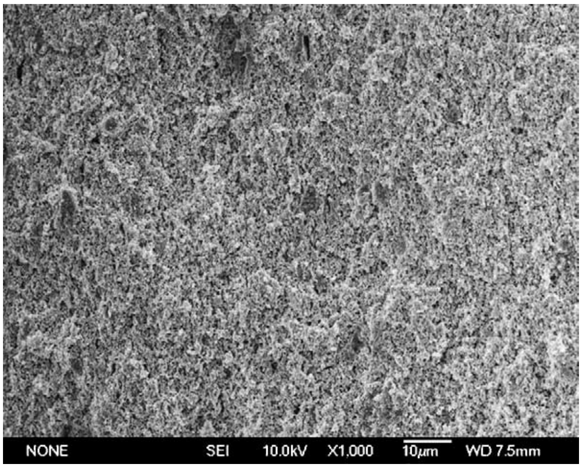

Fig. 3. SEM image of dewaxed CBT sample.

grains align with *ab* plane can be seen clearly. The ceramic sintered at 1120 °C has much higher density (Fig. 4b). Most of the plate-like grains with the thickness about 100–500 nm and the length of several micrometers align along screen-printing direction (*c*-axis) and no *ab* plane can be seen. Therefore, the ceramics sintered at higher temperature have higher degree of grain orientation.

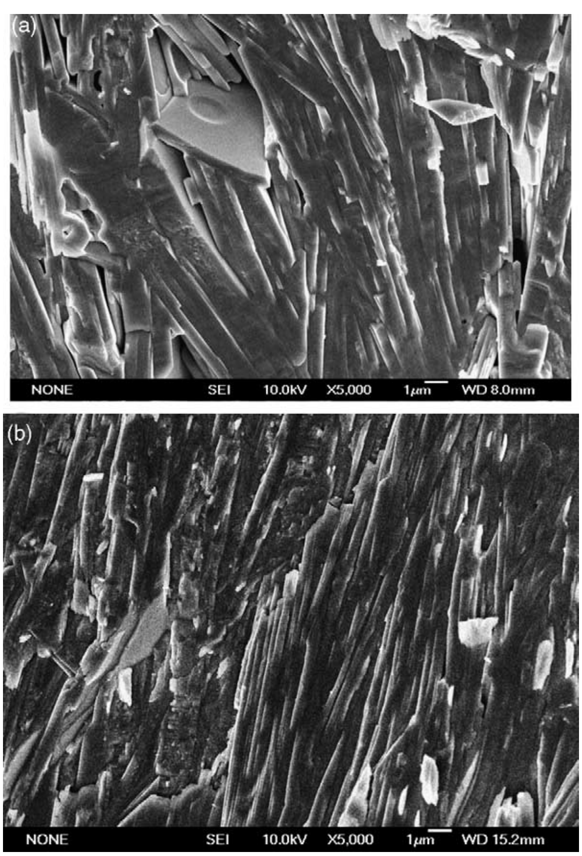

Fig. 4. SEM images of CBT ceramics sintered at: (a) 1000 °C and (b) 1120 °C.

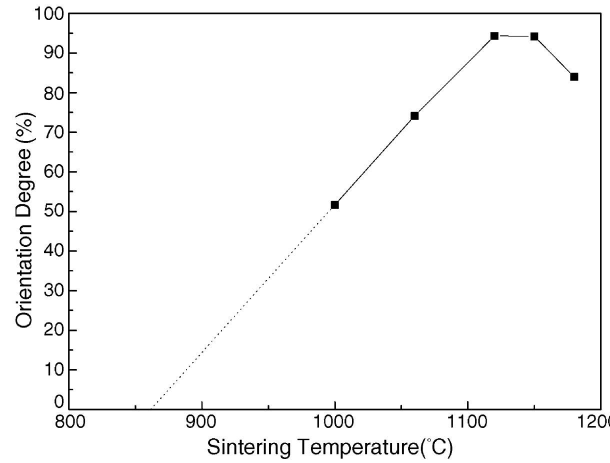

Fig. 5. Effect of the sintering temperature on the degree of orientation of CBT ceramics.

Fig. 5 shows the Lotgering factor varies with the sintering temperature. The ceramics have been partly orientated below the sintering temperature of 1000 °C. The orientation degree increases proportionally in the temperature range of 1000—1120 °C, then reaches the highest value and keeps constant between 1120 and 1150 °C. It decreases slightly as the sintering temperature up to 1180 °C. The decreased orientation might be caused by low density of the sample sintered at higher temperature. Extrapolating the line to *X*-axis (sintering temperature), the cross point is at 860 °C, which coincides with the calcinating temperature of CBT ceramic. Therefore, it can be proposed that when the solid-state reaction takes place from the raw materials to form CBT ceramic, some of the grains begin to grow along the screen-printing direction. The most possible sites for this grain growth are in the multilayer interfaces.

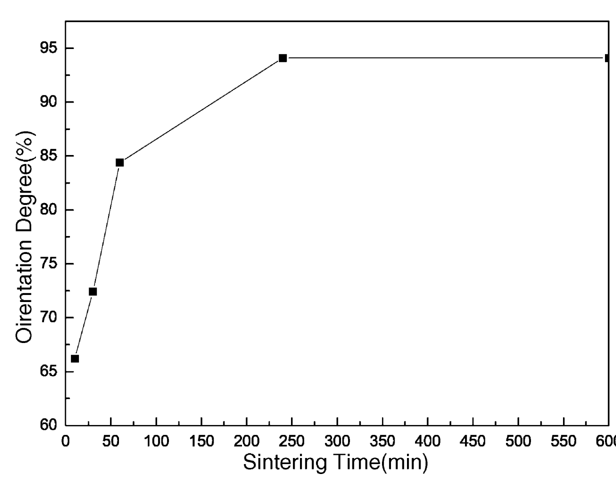

Fig. 6. Effect of sintering time on the degree of orientation of CBT ceramics heated at 1120 °C.

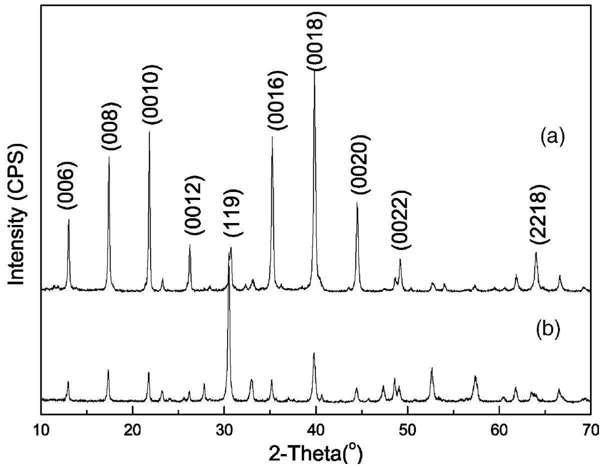

Fig. 7. XRD patterns of different raw material grain sizes: (a) nanosized and (b) micrometer sized.

3.3. Effect of sintering time on the grain orientation

Fig. 6 shows the effect of soaking time on the degree of grain orientation at 1120 °C. A large degree of orientation was obtained by soaking only for 10 min. The orientation degree increases rapidly with the soaking time within a period of 1 h, and reaches the highest of orientation slowly for sintering 4 h. Further increase of sintering time did not enhance the orientation degree for more than 4 h.

3.4. Effect of the powder size of starting materials

CBT ceramics were also prepared by screen-printing using ordinary starting materials (Bi_2O_3, TiO_2, $CaCO_3$) with large size (>5 μm). Fig. 7 shows the X-ray diffraction pattern of CBT ceramics prepared by different size of starting materials. Using nanosized raw materials, highly oriented CBT ceramics was obtained ($f = 94.3\%$). When using ordinary raw materials with micrometer sizes a low degree of orientated CBT ceramics was prepared by this technique ($f = 15.0\%$). This indicates the particles size of the starting materials plays significant role to fabricate grain orientated piezoelectric ceramics by the novel technique (MLGG). The mechanisms of the crystallization and the grain growth by the MLGG technique are undertaking in our group and will be published elsewhere.

4. Conclusions

A novel screen-printing multilayer grain growth technique was proposed. A CBT piezoelectric ceramic with a high grain orientation of 94.3% was obtained without the template particles. The XRD patterns of the grain oriented ceramics showed prominent difference in two directions of parallel and perpendicular to screen-printing plane. The degree of orientation increased with the sintering temperature and soaking time. The powder size of raw materials is a crucial factor to the grain orientation growth process. Higher degree orientation can be obtained by using nanosized raw materials. Compared to the hot forge and the templated grain growth (TGG and RTGG), the screen-printing multilayer grain growth (MLGG) technique is promising to fabricate high quality textured piezoelectric ceramics with a simple process. More importantly, the mechanism for this type grain growth is different from that of TGG and RTGG. The key factor is the interface between nanosized layers and further study is needed.

Acknowledgements

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