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Preparation of *c*-axis-oriented $Bi_4Ti_3O_{12}$ thick films by templated grain growth

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Abstract

Highly *c*-axis-oriented $Bi_4Ti_3O_{12}$ thick films were successfully fabricated by templated grain growth. The effects of template particles and sintering conditions on grain orientation in thick films were investigated. SEM micrographs and X-ray diffraction (XRD) patterns exhibited that thick films were *c*-axis-oriented. The degree of grain orientation (Lotgering factor, *f*) increases with increasing sintering temperature and soaking time. Highly *c*-axis-oriented thick film (orientation degree of ~ 0.98) is obtained with the use of only 5 wt.% template particles by sintering at 1000 °C for 2 h. This film exhibits a better temperature-independent dielectric constant and a lower dielectric loss.

Keywords: Bismuth titanate; Dielectric properties; Microstructure

1. Introduction

Bismuth titanate, $Bi_4Ti_3O_{12}$ (BiT), has been intensively studied as a ferroelectric material for high-temperature piezoelectric applications, nonvolatile ferroelectric random access memory and electrooptic devices because of its high Curie temperature, exceptional fatigue endurance, and electrooptic switching behavior.[1–5] A spontaneous polarization vector lies in the *a*–*c* plane at an angle of 4.5° to the *a*-axis. As a result, BiT single crystal shows strong anisotropic properties, spontaneous polarization values of 4 and 50 μC/cm^2, coercive field values of 3.5 and 50 kV/cm, and dielectric constant of 130 and 160, along the *c*- and *a*-axis, respectively.[5] The small coercive field and dielectric constant make the *c*-axis-oriented BiT thin film a potentially useful capacitor material in destructive readout (DRO) ferroelectric random access memory (FRAM) or as a gate dielectric in nondestructive readout (NDRO) ferroelectric memory field-effect transistor (FET) designs.[6–9]

A problem that restricts the development of BiT-based high-temperature piezoelectric applications is their relatively high conductivity.[10] Electrical conductivity within BiT is also highly anisotropic, with a relatively low conductivity along the *c*-axis. It is therefore preferable to fabricate *c*-axis-oriented BiT materials, resulting in the requirement of lower switching voltages to be applied in a given thickness of materials and high resistivity, which are important for polarization of the materials and maintenance of efficiency at high temperatures. Although remanent polarization in *c*-axis-oriented BiT results in a relatively low output signal being generated by piezoelectric devices, in practice, this small signal can be enhanced by using electronic charge amplifiers.

Numerous applications require films that are several microns to several tens of microns thick, but much less attention has been paid to the processing of BiT thick films. As with thin films, thick films offer the advantages of miniature scale and direct integration into hybrid electronic packages. Screen printing methods have been widely applied to thick film fabrications due to their cost effectiveness and simplicity of the manufacturing process.[11,12]

Templated grain growth (TGG) is increasingly being employed to develop crystallographic and morphologic textures in BiT bulk ceramics.[13,14] In the templated grain growth process, small quantities of anisotropic particles (the template) are aligned in a fine powder matrix during forming (e.g., tape casting, extrusion, uniaxial pressing). After densification, the larger anisotropic templates grow by consuming the fine matrix grains, eventually developing a highly oriented ceramic material. However, there are as yet no reports on the preparation of BiT thick films using this technique.

In this study, we prepare highly *c*-axis-oriented BiT thick films using the TGG method and investigate the effects of tem-

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plate particles and sintering conditions on the orientation of BiT thick films.

2. Experimental procedure

A coprecipitation method was applied to synthesize the BiT precursor. Firstly, bismuth nitrate ($Bi(NO_3)_3{\cdot}5H_2O$, 99.5%, Wako Pure Chemical Industries, Ltd., Japan) was initially dissolved in HNO_3 solution (35%, Wako Pure Chemical Industries, Ltd., Japan) at pH >3 to produce a clear solution, after which titanium tetra-*n*-butoxide ($Ti(O\text{-}n\text{-}C_4H_9)_4$, 99%, High Purity Chemicals, Japan) in ethanol solution was slowly added while constantly stirring. Secondly, ammonia ($NH_3{\cdot}H_2O$, 25%, Wako Pure Chemical Industries, Ltd., Japan) was added dropwise to the clear mixture solution obtained above while vigorous stirring to produce a white precipitate at pH >8. Finally, the obtained precipitate was thoroughly washed with dilute ammonia and ethanol. After drying and grinding with a mortar and pestle, BiT precursors were calcined at a selected temperature of between 450 and 750 °C for 1 h.

BiT platelike particles were prepared using the molten-salt method. The dried BiT precursor was mixed with an equimolar mixture of sodium chloride (NaCl, 99.5%, Aldrich) and potassium chloride (KCl, 99.5%, Aldrich). The eutectic temperature for this kind of chloride flux is 650 °C. Subsequently, mixture was then heated in a sealed alumina crucible at 900 °C for 0.5 h. The resulting powder was crushed and washed with hot deionized water several times to remove the chloride salts.

Thick film pastes were then prepared from the as-prepared BiT powders and 5 wt.% platelike particles with polyethylene glycol 300 (98%, Wako Pure Chemical Industries, Ltd., Japan). The BiT films were printed through a 200-mesh screen onto the 0.1 mm thick platinum (Pt) foils. A three times repeated thick-film printing process was used to obtain the desired layer thickness. Each printed layer was fired at 600 °C for 30 min. The final sintering was conducted at 950 °C and 1000 °C for 2 h or 4 h in a bismuth-rich atmosphere controlled by the calcined BiT powder. Finally, the silver top electrodes were screen-printed and fired at 600 °C for 10 min. Fig. 1 shows a flow chart of the thick film preparation. BiT thick films with and without 5 wt.% platelets are termed BiT_P and BiT_N, respectively, in the following text.

A scanning electron microscope (SEM, Hitachi S-4300, Tokyo, Japan) was applied to investigate the microstructure of the BiT powders, platelike particles and thick films. For phase characterization, an X-ray diffraction pattern was obtained using an automated diffractometer (RINT-2550, Rigaku Co., Tokyo, Japan) with Cu $K_{\alpha 1}$ radiation. The dielectric properties were characterized at a frequency of 100 kHz using an HP 4192A LF impedance analyzer.

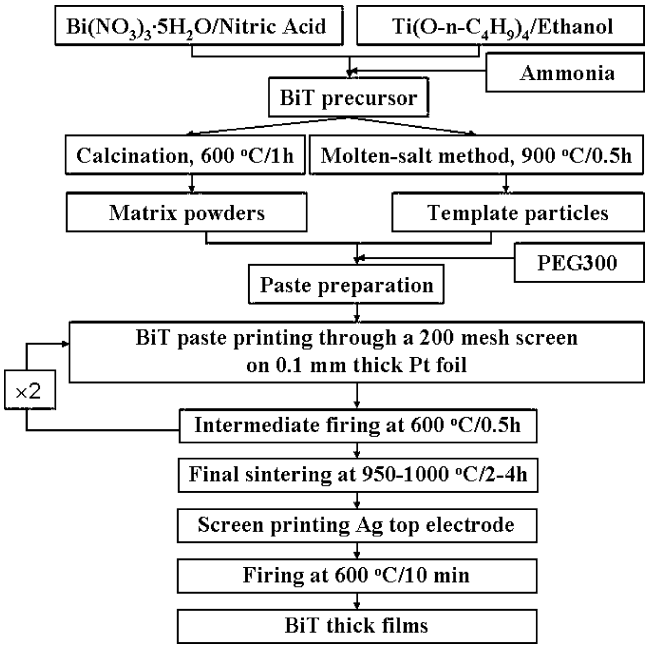

Fig. 1. Flow chart of preparation of BiT thick films.

3. Results and discussion

3.1. Characterization of BiT powders and platelets

Fig. 2 shows the X-ray diffraction patterns of the powder calcined at different temperatures. The BiT precursor after calcination at 450 °C is amorphous, as is the as-precipitated powder. When the heating temperature is increased to 600 °C, the amorphous powder is crystallized to form pure BiT phase. No other non-BiT phase is observed in the X-ray diffraction patterns. To ensure high sinterability, BiT powders calcined at 600 °C are selected as matrix powders for the preparation of thick films. As shown in Fig. 3(a), this powder shows equiaxed morphology, having an average diameter of approximately 100 nm.

The powders synthesized by molten-salt method (Fig. 3(b)) show platelike rather than equiaxed morphology. The powders synthesized at 900 °C for 30 min are ~5–10 μm in diameter and ~0.2 μm thick. The high aspect ratio (~25–50) makes platelike particles easily aligned in slurry/paste.

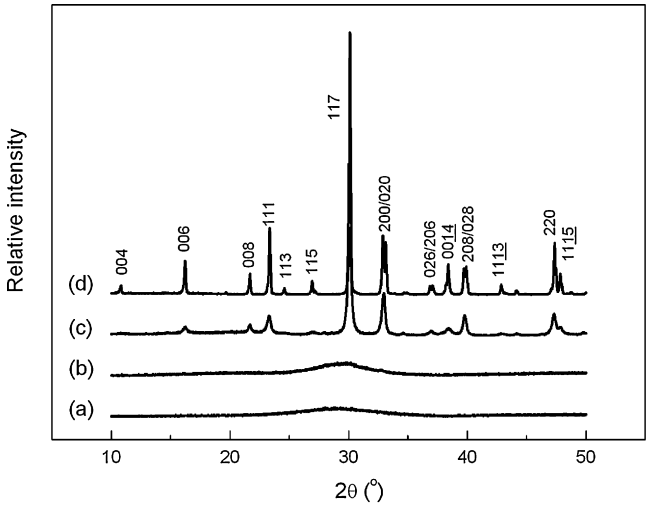

Fig. 2. X-ray diffraction patterns of BiT precursor (a) and BiT powders calcined at 450 °C (b), 600 °C (c) and 750 °C (d) for 1 h.

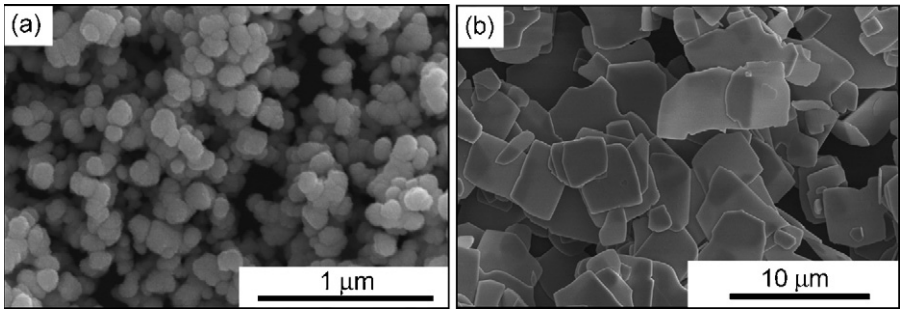

Fig. 3. SEM micrographs of BiT matrix powder calcined at 600 °C for 1 h (a) and BiT template particles synthesized by the molten salt method at 900 °C for 0.5 h (b).

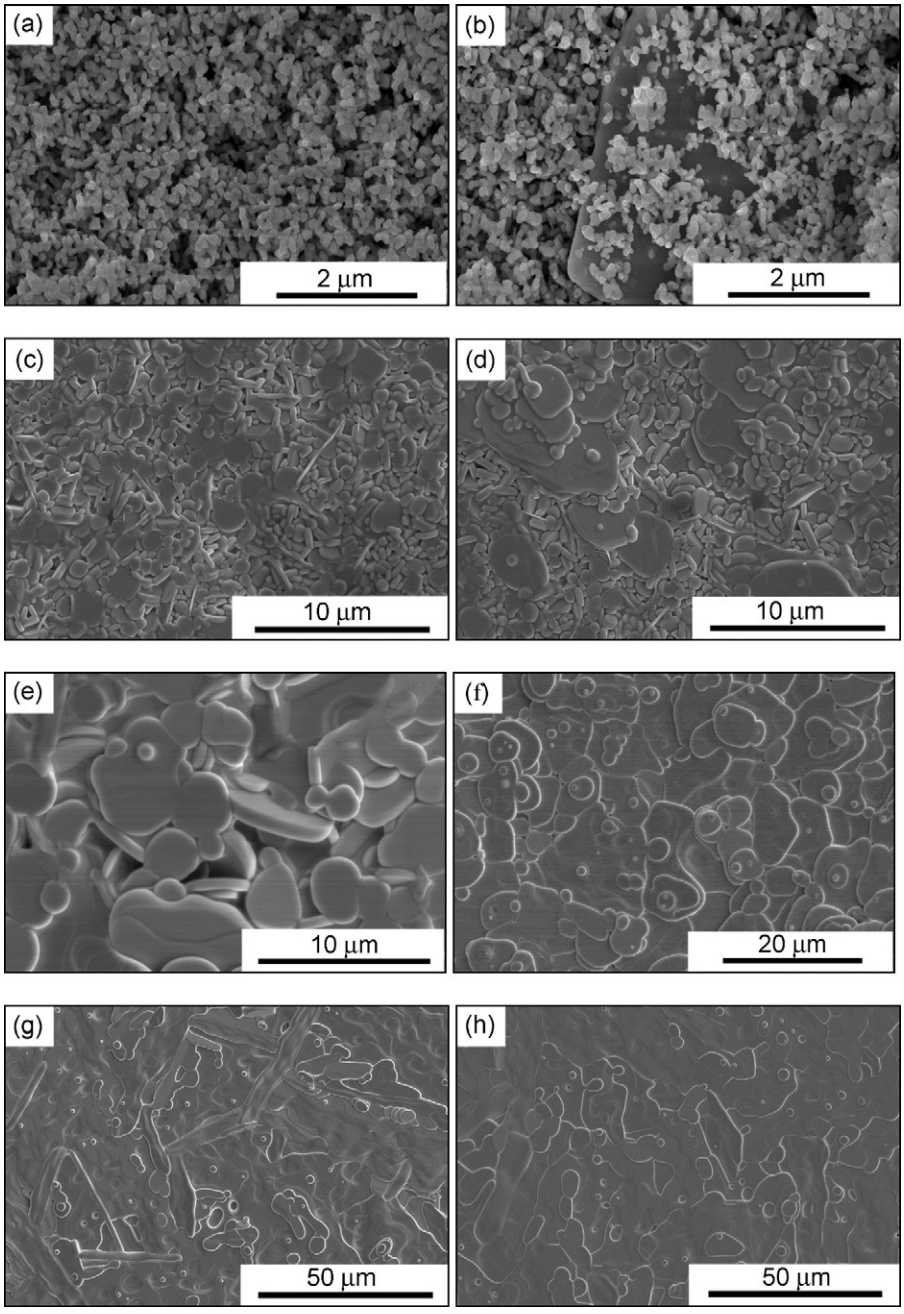

Fig. 4. SEM micrographs of major faces of BiT_N (a, c, e, and g) and BiT_P (b, d, f, and h) thick film before sintering (a, and b) and after sintering at 950 °C/2 h (c, and d), 1000 °C/2 h (e, and f), 1000 °C/4 h (g, and h).

3.2. Grain growth and texture development in BiT thick films

Fig. 4(a) and (b) are SEM micrographs of the surfaces of as-dried BiT thick films at 600 °C. In Fig. 4(b), it is obvious to see that the BiT platelets are aligned in the equiaxed ultrafine powder matrix, with their major surface planes oriented in parallel to the Pt substrate. The main reasons for the alignment of the platelets are the high aspect ratio of the BiT template particles and the shearing force exerted during screen printing. This shearing force is similar to that produced when the blade passes over the surface of the slurry during tape casting.

SEM micrographs of the surfaces of BiT_N and BiT_P thick films sintered under different conditions are also shown in Fig. 4. It can be seen that the ultrafine BiT particles grow up to approximately 1–2 μm in diameter and adopt a platelike morphology after sintering at 950 °C for 2 h (Fig. 4c). However, there is no appreciable growth of BiT template particles at this temperature, due to the low sinterability of BiT platelets (Fig. 4c). When the temperature is increased to 1000 °C, the microstructure of BiT_P thick film consists almost entirely of platelike grains approximately 5–20 μm in diameter, aligned in the substrate. The template particles can no longer be identified, indicating that the primary platelets have grown by consuming the fine matrix grains. The typical microstructure of a cross-section of BiT_P sintered thick film shows a well-developed textural structure (Fig. 5). The platelike grains, approximately 0.5 μm in thickness, are oriented with their *c*-axis perpendicular to the substrate. The thickness of the designed thick films is approximately 5 μm.

Fig. 6 shows the X-ray diffraction patterns of BiT thick films. It can be seen that BiT_N thick film exhibits stronger (00*l*) diffraction peaks, as do BiT_P thick films, after sintering at 1000 °C. On doping with 5 wt.% platelets, the strongest diffraction peak (1 1 5) in randomly oriented sample becomes markedly weakened and (00*l*) reflections come to dominate X-ray diffraction pattern. These observations demonstrate that a highly *c*-axis-oriented microstructure has developed in BiT thick films. To determinate the degree of orientation of oriented BiT thick films, Lotgering factors (*f*)[15] are calculated using the following equation from X-ray diffraction data recorded over a 2θ range of 10°–60°.

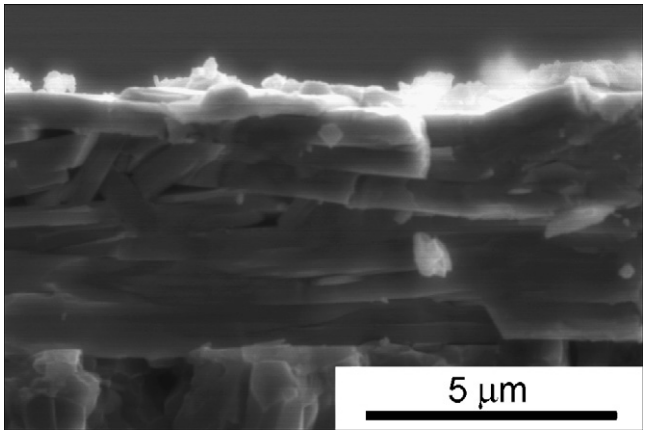

Fig. 5. SEM micrographs of cross-section of BiT_P thick film sintered at 1000 °C for 2 h.

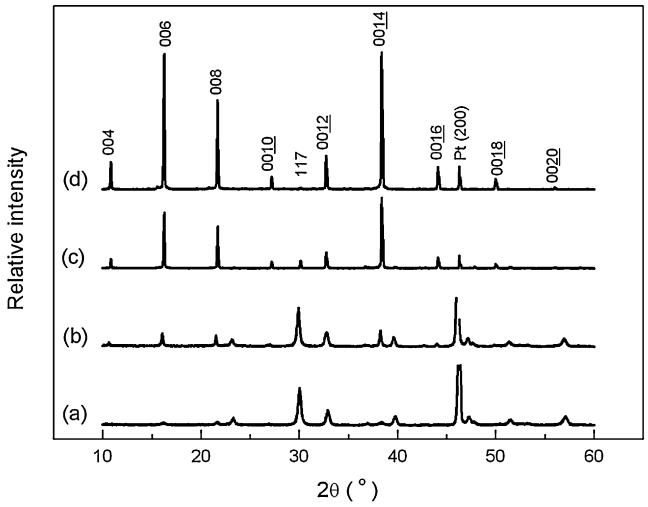

Fig. 6. X-ray diffraction patterns of BiT_N (a, and c) and BiT_P (b, and d) thick film before sintering (a, and b) and after sintering at 1000 °C/2 h (c, and d).

$$f = \frac{(P - P_0)}{1 - P_0} \quad (1)$$

where $P = \sum I(00l)/\sum I(hkl)$ for grain-oriented samples and P_0 is P for a randomly oriented powder. Lotgering factors (*f*) show values of 0.52, 0.98, and 0.98 for BiT_P thick films sintered at 950 °C/2 h, 1000 °C/2 h, and 1000 °C/4 h, respectively. The values of BiT_N thick films sintered under different conditions are 0.27, 0.82, and 0.9, respectively. This result indicates that the degree of orientation increases with sintering temperature and holding time. However, due to bismuth evaporation, a small amount of non-BiT phase is present in BiT thick films sintered at 1000 °C for 4 h.

It is interesting to note that BiT_N thick film sintered at 1000 °C/2 h also shows a high degree of orientation (∼ 0.82) and most platelike grains in the BiT_N sample are aligned with their major face parallel to the substrate, as shown in Fig. 4(e). Although the Pt foil substrates used in this study show a high degree of (1 0 0) orientation, the formation of oriented BiT thick film cannot be attributed to the (1 0 0)-oriented Pt foil, since *c*-axis-oriented BiT thick films are also obtained on fused quartz substrates. Clearly, the lattice matching mechanism is not the dominant factor in grain alignment in BiT thick films. For thick films, the interaction of sintering and anisotropic grain growth of BiT crystals becomes stronger due to their thinness in comparison with the bulk materials. Since the thickness of films in the present study is small at approximately 5 μm, we assume that the sintering shrinkage stress between platelets relaxes in the direction parallel to the substrate due to the faster growth in the *ab*-plane of the BiT grains. As a result, *c*-axis-oriented BiT thick films are obtained independently of type of substrate. Additionally, much less substance in the thickness direction than in the direction parallel to the substrate is also considered to have contributed to the development of the *c*-axis-oriented structure. With the addition of 5 wt.% platelets, the Lotgering factor of BiT_P thick films increases to 0.98. This enhancement in degree

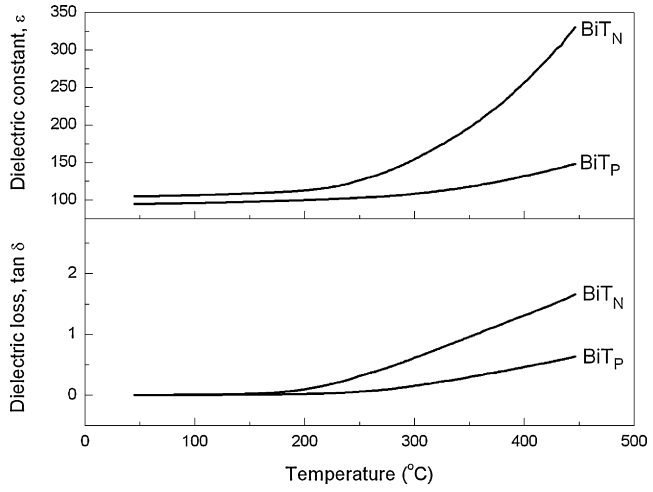

Fig. 7. Variation of dielectric properties at 100 kHz of BiT_N and BiT_P thick films sintered at 1000 °C/2 h as a function of temperature.

of orientation can be attributed to mechanisms involving an Ostwald ripening process, which have been shown to satisfactorily explain texture development in BiT bulk ceramics.[13,14] As seen in Fig. 4e and f, the much larger grain size in the BiT_P thick films (~5–20 μm) than that in BiT_N sample (~2–10 μm) partly demonstrates an Ostwald ripening process, in which the templates consume the fine matrix grains and grow during sintering.

3.3. Dielectric properties of BiT thick films

The dielectric properties of BiT_N and BiT_P thick films sintered at 1000 °C/2 h are measured as a function of temperature at 100 kHz (Fig. 7). It is noted that BiT_P thick film exhibits a better temperature-independent dielectric constant and a lower dielectric loss: these are useful characteristics for high-temperature applications. The different dielectric properties shown in BiT_N and BiT_P thick films can be attributed to different degree of orientation.

4. Conclusions

Using templated grain growth, highly *c*-axis-oriented $Bi_4Ti_3O_{12}$ thick films were successfully prepared on Pt foils by screen printing. Without any template particles, BiT thick film sintered at 1000 °C for 2 h shows an obvious grain orientation with a Lotgering factor (*f*) of approximately 0.82. With doping of only 5 wt.% temperate, the degree of orientation (*f*) increases to approximately 0.98. The development of a highly *c*-axis-oriented microstructure can be attributed to interaction between sintering and anisotropic growth of BiT grains and an Ostwald ripening process. This highly *c*-axis-oriented thick film possesses improved dielectric properties. Further study is needed to investigate the ferroelectric properties of oriented thick films and to reduce the sintering temperature to make them compatible with silicon micromachining and thus more useful in practical applications.

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