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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.

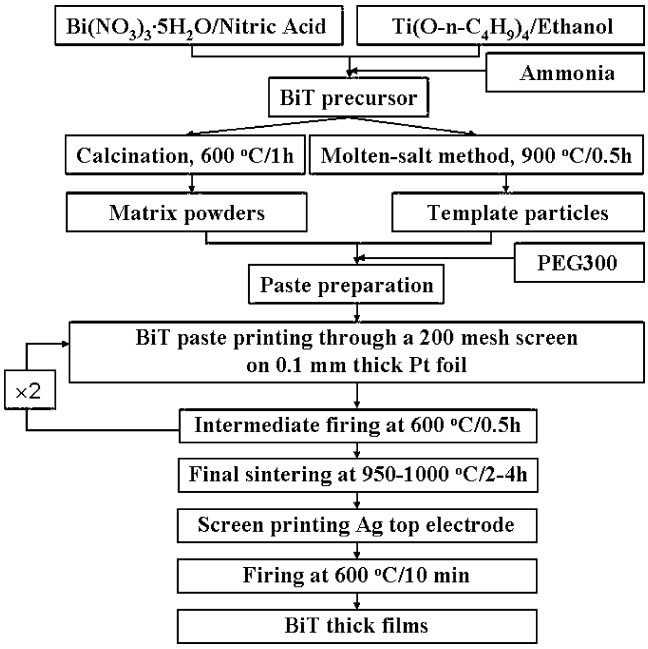

Fig. 1. Flow chart of preparation of BiT thick films.

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.

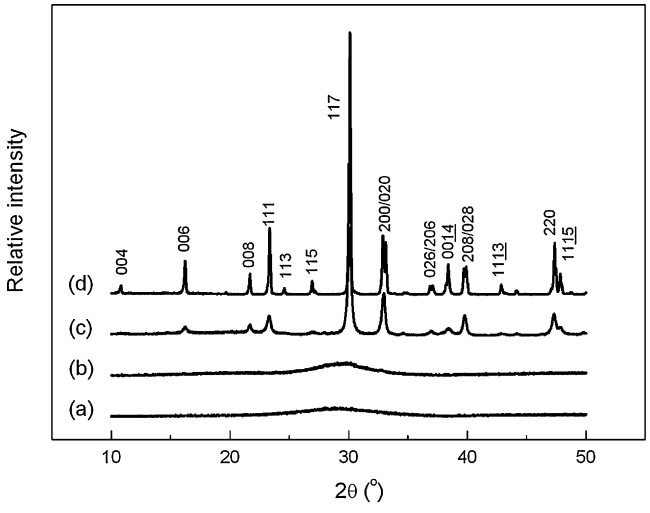

Fig. 2. X-ray diffraction patterns of BiT precursor (a) and BiT powders calcined at 450 °C (b), 600 °C (c) and 750 °C (d) for 1 h.