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Synthesis and properties of high aspect ratio $SrBi_4Ti_4O_{15}$ microplatelets

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ABSTRACT

(001) oriented $SrBi_4Ti_4O_{15}$ (SBT) microplatelets with Aurivillius-type crystal structure were fabricated by molten salt synthesis. The effects of flux type selection and salt-to-oxide ratio variation on crystallization habit and morphology of the product were investigated. The sodium salt fluxes facilitate the formation of $Sr_2Bi_4Ti_5O_{18}$ large size platelets ($\geq 17\ \mu m$ in length), while potassium salt fluxes create favorable condition for the growth of small size $SrBi_4Ti_4O_{15}$ platelets ($\leq 5\ \mu m$ in length). When using KCl flux, a higher salt-to-oxide ratio is beneficial to produce smaller SBT platelets with relatively narrow size distribution. The ferroelectricity and piezoelectricity of an individual SBT platelet were examined by piezoelectric force microscopy. These microcrystals are suitable template candidate to achieve highly textured ceramics for high temperature applications.

1. Introduction

Among several bismuth layer-structured ferroelectrics (BLSF), lead-free $SrBi_4Ti_4O_{15}$ (SBT) has been recently extensively studied for high temperature pyro- and piezoelectric applications, due to its high Curie temperature (≥ 500 °C), appropriate ferroelectric polarization and fatigue-free property [1–3]. This Aurivillius-type structure consists of insulating $(Bi_2O_2)^{2+}$ layers and pseudo-perovskite $(A_{n-1}B_nO_{3n+1})^{2-}$ blocks stacked along *c*-axis, where A represents the mixture of Sr^{2+} and Bi^{3+}, B represents Ti^{4+} and $n=4$ is the number of TiO_6 octahedrons in SBT formula. Because of the highly anisotropic crystal structure, the electrical properties of SBT based ceramics prepared by conventional method are relatively low as grains show random orientations [2,3]. The textured ceramics formation allows reconstruction of these directionally dependent properties [4–6] and may significantly enhance the electrical properties of SBT. Texture development by templated grain growth (TGG) is based on the epitaxially preferential growth of anisotropically shaped templates distributed in a fine-grained matrix. It has been demonstrated that the template particles' composition, morphology and their alignment in matrix powders have significant influences on the texture quality of the resulting ceramics [6,7]. Therefore, the ability to synthesize anisotropic SBT crystals and tailor their sizes to control their orientation is crucial to the texture formation in SBT by TGG.

Several techniques have been developed to prepare anisotropic crystals with high aspect ratios [8–13], such as hydrothermal synthesis, chemical precipitation, two-step chemical approach, vapor–solid process, and molten salt synthesis. Among them, molten salt synthesis (MSS) is a relatively simple, inexpensive and effective method for fabricating inorganic microcrystals with anisotropic morphology and has been widely used to prepare $NaSr_2Nb_5O_{15}$, $Bi_{3.25}La_{0.75}Ti_3O_{12}$, etc. [7,14,15]. In MSS, it takes advantage of the much higher mass transport rate attained in a flux, thereby enabling the synthesis completed in a lower temperature and a shorter time. In addition, the unstrained growth environment in the flux promotes the formation of anisotropic crystals according to crystal structure. In order to synthesize high-quality SBT single-crystal particles with tailored particle sizes, several critical factors need to be carefully considered, such as the type and amount of the fluxes. Moreover, it is highly desired to test the ferroelectricity and piezoelectricity of an individual SBT particle. However, few reports on such studies were available in the literature. In this work, molten salt synthesis of SBT microplatelets was described, and the effects of flux type selection and salt-to-oxide ratio variation on crystallization habit and morphology development of the product were studied. Besides, local amplitudes of piezoelectric and ferroelectric responses of an individual SBT platelet were determined by piezoelectric force microscopy.

2. Experimental

In order to synthesize $SrBi_4Ti_4O_{15}$ particles, $SrCO_3$, Bi_2O_3, and TiO_2 were mixed in a 1:2:4 M ratio and ball milled in ethanol for 12 h.

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Then, a salt of either NaCl, Na_2SO_4, KCl or K_2SO_4 was added in a salt-to-oxide weight ratio of 1:1, and the mixture was ball milled for 12 h. The dried powder mixtures were heated at 1100 °C (heating rate 6 °C/min) for 6 h. To investigate the effect of salt-to-oxide weight ratio on the SBT morphology, KCl was chosen as the salt and mixed with oxide in salt-to-oxide weight ratios of 0.50:1, 0.75:1, 1:1, and 1.50:1. Then the mixtures were treated by the same procedure listed above. The flux was removed from the products by repeated washing with hot deionized water. The products were dispersed by ultrasonicating and rinsed several times with deionized water.

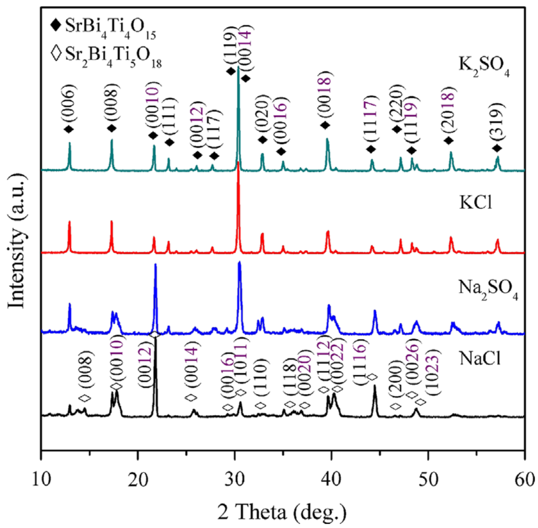

Fig. 1. XRD patterns of specimens synthesized in different fluxes.

Morphological characterization was performed using scanning electron microscopy (SEM, Quanta 200 FEG, FEI Corporation, OR, USA) with energy-dispersive spectroscopy (EDS). Phase purity and structure were determined by X-ray diffraction (XRD, D/max 2400, Rigaku Corporation, Tokyo, Japan). To study the transformation during a heating process, differential thermal analysis (DTA) and thermogravimetric analysis (TG) of the powder mixtures were performed using Thermoanalyzer Systems (Q600SDT, TA instruments, USA). Local ferroelectric and piezoelectric properties of the final products were evaluated nearly along the large face direction by piezoelectric force microscopy (MFP-3D, Asylum Research, USA) using switching spectroscopy mode (SS-PFM) via a conductive Pt/Ir coated tip and a conductive Pt substrate as the top and bottom electrodes, respectively.

3. Results and discussion

XRD patterns of specimens synthesized in different fluxes are shown in Fig. 1. The main phase of microcrystals obtained in NaCl flux was identified to be $Sr_2Bi_4Ti_5O_{18}$, and a tiny amount of $SrBi_4Ti_4O_{15}$ coexists. Both $SrBi_4Ti_4O_{15}$ and $Sr_2Bi_4Ti_5O_{18}$ phases were detected when using Na_2SO_4 flux, and the amount of $SrBi_4Ti_4O_{15}$ is much larger than that obtained by using NaCl flux. The microcrystals obtained in KCl and K_2SO_4 fluxes were all identified as single phase $SrBi_4Ti_4O_{15}$ with strong (001) orientation. The XRD results indicate that sodium fluxes facilitate $Sr_2Bi_4Ti_5O_{18}$ formation while $SrBi_4Ti_4O_{15}$ phase formation is preferable in potassium fluxes. This may be due to the solubility differences of SrO and TiO_2 in fluxes, since the solubility relation between a given oxide and a flux is critical in dictating phase formation of seeds [16].

SEM micrographs of specimens synthesized in different fluxes are shown in Fig. 2. Microcrystals synthesized in NaCl flux consist

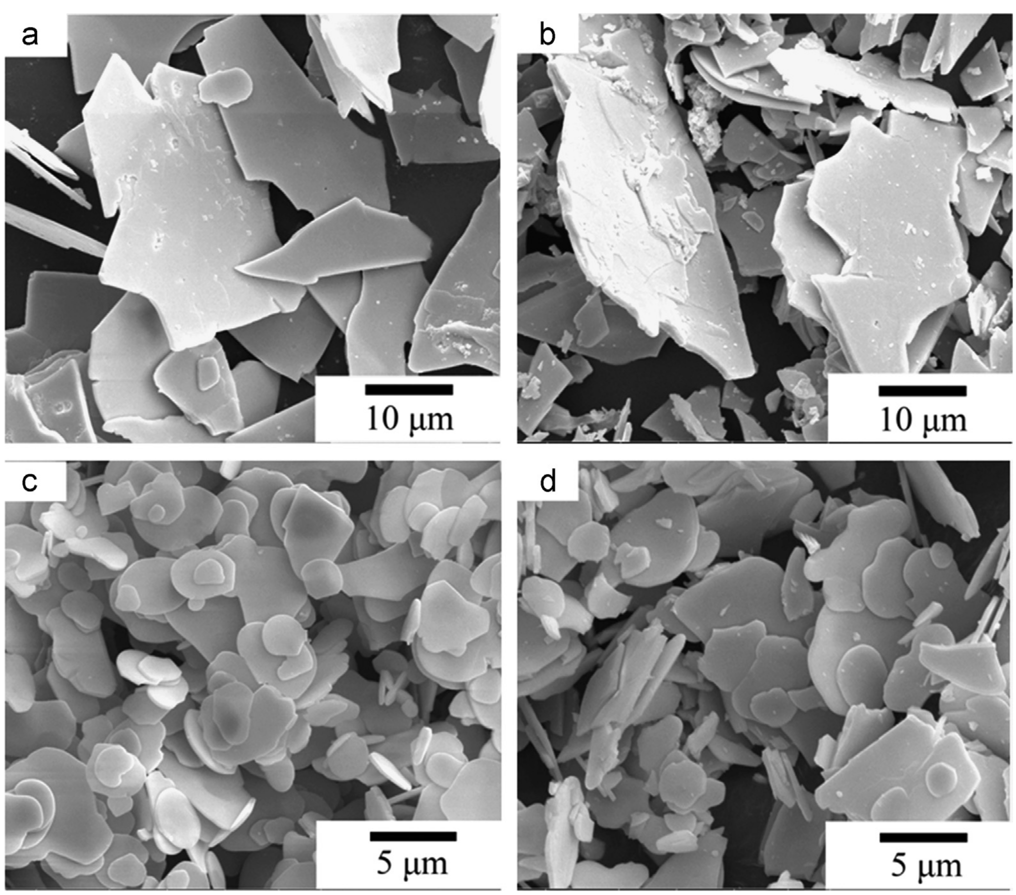

Fig. 2. SEM micrographs of specimens synthesized in (a) NaCl, (b) Na_2SO_4, (c) KCl and (d) K_2SO_4 fluxes, respectively.