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Plate-like $Na_{0.5}Bi_{0.5}TiO_3$ particles synthesized by topochemical microcrystal conversion method

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Abstract

In this work, plate-like $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) particles were successfully synthesized from a bismuth layer-structured ferroelectric $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ (NBT4) precursor by a topochemical microcrystal conversion (TMC) method. Because of the high anisotropic structure, plate-like NBT4 particles were first synthesized by molten salt process. After topochemical reaction with the complementary reactants (Na_2CO_3) and TiO_2 at 950 °C for 4 h in NaCl flux, the layer structure of the NBT4 particles was transformed into a simple perovskite NBT template. The resulting large NBT templates had plate-like shape, an average size of 10–15 μm and retained the morphological features of the NBT4 precursor. The large as synthesized plate-like NBT particles were utilized to fabricate textured 99.40 $Na_{0.5}Bi_{0.5}TiO_3$-0.60$BaZrO_3$ (NBT-BZ) ceramics via the templated grain growth (TGG) method.

Keywords: Lead-free ceramics; Molten salt synthesis; Topochemical microcrystal conversion; NBT template

1. Introduction

Over the past two decades, lead-free piezoelectric ceramics have been focused as alternative materials for the replacement of lead-based ceramics in piezoelectric industry.[1,2] Unfortunately, most of the lead-free piezoelectric ceramics exhibit substandard performances when compared with lead-based piezoelectric ceramics.[3] Several research works have been conducted to investigate new materials and methods to improve the piezoelectric properties of lead-free ceramics. In general, two methods are considered very effective: (1) development of new ceramics through compositional modification of the morphotropic boundary (MPB) solid solution[4–8]; (2) fabrication of textured ceramics, i.e., ceramics having a uniform grain orientation.[9–12] Grain orientation techniques, such as the templated grain growth (TGG) method have been commonly used to prepare textured ferroelectric and piezoelectric ceramics with perovskite structure.[13–15] In the templated grain growth process, anisotropic particles play a very important role. For the grain-oriented NBT-based ceramics, plate-like $SrTiO_3$ (ST) particles or bismuth layer-structured ferroelectric (BLSF) $Bi_4Ti_3O_{12}$ (BIT) templates have been frequently utilized.[9] However, although $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) based ceramics textured by ST templates exhibit a high degree of orientation, but the paraelectric phase of ST in ceramics may have adverse effects on the electromechanical properties, causing a decrease in the depolarization temperature.[16] On the other hand, a large volume fraction of BIT templates is required to obtain highly textured ceramics,[17] which makes the ceramic densification difficult. In principle, it is more advantageous to use plate-like NBT particles for the fabrication of textured NBT-based ceramics. The resulting textured ceramics are expected to exhibit a high degree of grain orientation, while the high depolarization temperature remains almost unchanged.

NBT has a perovskite structure with high symmetry. It is difficult to obtain large anisotropic NBT particles by conventional

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methods, such as mixed oxide route,[18] sol–gel[19] or hydrothermal methods.[20] $Na_{0.5}Bi_{4.5}TiO_{15}$ (NBT4) has a layered structure in which the A site is co-occupied by Na^+ and Bi^{3+}. It is experimentally well known that BLSFs can easily form plate-like particles during the molten-salt process. Thus, owing to the structural similarity in the between NBT and NBT4, it is possible to convert the layer-structured NBT4 into a simple perovskite NBT by the topochemical microcrystal conversion method. In this paper, we report the topochemical synthesis of NBT templates from NBT4 particles and its direct comparison with the simple perovskite NBT particles synthesized by a conventional mixed oxide (CMO) routes. Furthermore, the as synthesized NBT particles by TMC method were used as a template to fabricate highly textured 99.40 $Na_{0.5}Bi_{0.5}TiO_3$-0.60$BaZrO_3$ (NBT-BZ) ceramics via templated grain growth method.

2. Experimental method

Plate-like $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ (NBT4) precursors were first prepared by molten salt synthesis (MSS). Reagent-grade Bi_2O_3, TiO_2 and Na_2CO_3 powders of purity (99.9%) were initially mixed following the stoichiometry of $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ (NBT4) and NaCl (99.95%) was then added to the NBT4 mixture in weight ratio (1.5:1) and ball-milled for 24 h. After removal of balls and drying, the dried powder was put in a tightly covered Al_2O_3 crucible and heat treated at 1100 °C for 4 h. When the reaction was completed, the NaCl was removed from the as-synthesized product by washing thoroughly with hot de-ionized water. NBT4 platelets, Na_2CO_3 and TiO_2 were then weighed to provide a total NBT composition in accordance to the chemical equation (1). NaCl salt was added to the mixture with 1:1.5 weight ratios and then mixing was carried out in an ethanol solution with magnetic stirrer for 5 h. After drying the slurry, a heat treatment (950 °C for 4 h) was performed in a tightly covered Al_2O_3 crucible. Finally, hot de-ionized water was used to remove NaCl from the product and HCl was utilized to eliminate the bismuth oxide (Bi_2O_3) by-product. For comparison NBT particles were also produced by a conventional mixed oxide route.[18]

$$Na_{0.5}Bi_{4.5}Ti_4O_{15} + 2Na_2CO_3 + 5TiO_2 \rightarrow 9Na_{0.5}Bi_{0.5}TiO_3 + 2CO_2 \quad (1)$$

Textured ceramics with composition 99.40 $Na_{0.5}Bi_{0.5}TiO_3$-0.60$BaZrO_3$ (NBT-BZ) were prepared by templated grain growth (TGG) method using NBT templates. Commercially available carbonate powders: Na_2CO_3 and $BaCO_3$ (99.95%, Sigma Aldrich), and metal oxides: Bi_2O_3, TiO_2 and ZrO_2 (99.9% Junsei Co., Limited) were first mixed by ball milling and then calcined at 850 °C to form a perovskite structure. The calcined powders were mixed thoroughly with a solvent (60 vol.% ethanol and 40 vol.% methyl-ethyl-ketone, MEK) and triethyl phosphate (dispersant) in a ball mill for 24 h. Polyvinyl butyral (binder) and polyethylene glycol/diethyl-ophthalate (plasticizer) were added before ball milling the mixtures again for 24 h. NBT templates of 15 wt% were then added to the mixture and ball milled with a slow rotation for another 12 h to form a slurry for tape casting. The slurry was tape cast to form a green sheet with a thickness of ~100 μm on a SiO_2 coated polyethylene film by a doctor blade apparatus. After drying, a single layer sheet was cut, laminated and hot-pressed at a temperature of 45 °C and a pressure of 50 MPa for 2 min to form a 2 mm thick green compact. The compacts were further cut into small samples of about 1 cm × 1 cm and then heated at 600 °C for 12 h with intermediated steps of 250 and 350 °C for 6 and 8 h and to remove organic substances prior to sintering. The samples were sintered at 1150 °C for 15 h in air atmosphere and were then brought to room temperature at cooling rate of 5 °C/min. Non-textured NBT-BZ ceramics were also prepared through conventional solid state reaction for comparison.

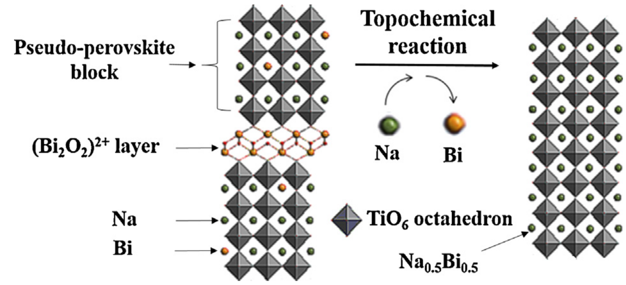

Fig. 1. Schematic illustration of the conversion of layered structure perovskite $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ into a simple perovskite $Na_{0.5}Bi_{0.5}TiO_3$ by a topochemical microcrystal conversion.

Crystal structure and purity information of the as synthesized NBT particles were checked by X-ray diffraction machine (XRD, RAD III, Rigaku, Japan) using CuKα radiation (λ = 1.541 Å) at room temperature. The XRD patterns were collected in the Braggs–Brentano configuration operated at 10 mA and 20 kV with a step size of 0.02°. The particle size and shape was observed through field emission scanning electron microscope (FE-SEM, JP/JSM 5200, Japan). Selected area electron diffraction (SAED) pattern and high-resolution transmission electron microscopy (HRTEM) images were obtained by transmission electron microscope (TEM) using a FE-TEM (JEOL/JEM-2100F version) operated at 200 kV. The upper and the lower extensive surfaces of the samples were polished and coated with a silver-palladium paste to form electrodes for electrical properties measurements. The specimens were poled at room temperature by immersion in silicon oil under a dc electric field of 4 kV/mm for 30 min. The dielectric constant and loss response were measured through an impedance analyzer (HP4194A, Agilent Technologies, Palo Alto, CA). Field-induced strain response was measured using a contact-type displacement sensor (Model 1240; Mahr GmbH, Göttingen, Germany) at 50 mHz.

3. Results and discussion

Plate-like NBT templates were synthesized by a topochemical reaction from bismuth layered structure ferroelectric NBT4 precursor. Fig. 1 demonstrates a schematic diagram of the formation of a simple perovskite structure from the layered-perovskite by a topochemical conversion. A bismuth layered structure compounds with a chemical formulation $Bi_2O_2(A_{m-1}B_mO_{3m+1})$ (A-sites contain Na^+ and Bi^{3+}, while B-sites contain Ti^{4+}, m