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Preparation and electrical properties of $NaNbO_3$ ceramics synthesized by topochemical microcrystal conversion

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Abstract

$NaNbO_3$ (NN) ceramics were successfully synthesized from bismuth layer-structured $Bi_{2.5}Na_{3.5}Nb_5O_{18}$ (BNN) particles by a topochemical microcrystal conversion method. Plate-like BNN particles were first synthesized by molten salt synthesis (MSS) technique. After topochemical reaction with complementary reactant sodium carbonate (Na_2CO_3) in sodium chloride (NaCl) flux, the layer structure of BNN particles were transformed to NN perovskite structure. The crystal structure and microstructure of the synthesized particles were examined through XRD and SEM analysis, respectively. Dielectric, complex impedance and conduction behaviors of the sintered NN ceramics were investigated in the frequency range of 100 Hz–1 MHz at different temperatures (50–550 °C).

Keywords: A. Grain growth; B. Platelets; C. Electrical properties; D. Perovskites

1. Introduction

(K, Na)$_{0.5}$NbO$_3$ (KNN) based ceramics have become the focus of much research interest since Saito et al. [1] obtained high piezoelectric properties (d_{33}=416 pC/N and k_p=0.61) by reactive template grain growth (RTGG) method. However, KNN-based ceramics prepared by conventional solid state reaction (SSR) show poor piezoelectric properties (d_{33}=80 pC/N, and k_p=0.36) due to difficulty in obtaining high density ceramics [2,3].

$NaNbO_3$ (NN) is considered one of the most promising materials for texturing KNN-based ceramics. However, NN particles prepared by conventional mixed-oxide (CMO) method have equiaxial morphology which cannot satisfy the requirement as template in the RTGG process. Molten salt synthesis (MSS) is a well established technique to prepare particles with anisotropic morphology [4,5]. Another useful approach to prepare perovskite templates is topochemical microcrystal conversion (TMC) synthesis, which involves replacing or modifying the interlayer cations but retaining the morphological and structural features of plate-like layered-perovskite precursors by ion exchange and intercalation reactions at low temperatures [6,7].

In view of the importance of the NN templates for high performance lead-free textured KNN-based ceramics the present study is carried out to prepare and study the structure and electrical properties to better understand the underlying conduction mechanism.

2. Experimental procedure

Plate-like $Bi_{2.5}Na_{3.5}Nb_5O_{18}$ (BNN) precursors were prepared by MSS. Reagent-grade Bi_2O_3, Nb_2O_5 and Na_2CO_3 powders of purity (99.9%) were first mixed according to the formula of $Bi_{2.5}Na_{3.5}Nb_5O_{18}$ (BNN) for 12 h. The mixture was then mixed thoroughly with NaCl (99.95%) in the weight ratio of oxide to salt 1:1.5 for 12 h. After drying, the mixture was placed in a sealed alumina crucible, heated to 1125 °C for 4 h. After the completion of reaction, the as-synthesized product was washed several times with hot de-ionized water to remove NaCl salt. BNN platelets and Na_2CO_3 were weighed in molar ratio of

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BNN/Na_2CO_3 1:1.5, NaCl salt was added to them with 1:1.5 weight ratios, and then mixed with a magnetic stir bar for 6 h. The mixture was placed in a sealed alumina crucible, and heated at 950 °C for 4 h. The product was washed several times with hot de-ionized water. The NN template was separated using HCl to remove the by-product, Bi_2O_3. Finally, the obtained plate-like NN ceramics were pressed into pellets and sintered at 1250 °C for 4 h.

Crystallographic phases and surface morphology of the prepared samples were confirmed by XRD and SEM, respectively. For the measurements of the electrical properties, a 0.5 mm thick disk-shaped sample was covered with a thin layer of silver-palladium paste as electrodes and was fired at 700 °C for 30 min. The dielectric and the complex impedance data of the NN template ceramics were measured by an impedance analyzer (HP4192A) in the frequency range of 0.1 kHz to 1 MHz over a temperature range of 50–550 °C.

3. Results and discussion

Fig. 1(a), (b) shows the SEM micrographs of BNN and NN particles, respectively. The particles show an anisotropic platelet microstructure with pseudocubic or pseudotetragonal surface with high aspect ratio and high degree of orientation. The BNN particles prepared by the MSS method were used as precursor for NN templates through TMC method. It can be observed from Fig. 1(b) that the converted product preserve the morphology of BNN precursor and develop a (00l)-oriented tetragonal perovskite. These NN particles are believed to possibly be easily orientated in a matrix of fine powders by a shearing process (e.g. tape casting), resulting in well textured microstructure found in products obtained by TGG or RTGG processing.

The XRD pattern of NN particles transformed from the BNN precursor are shown in Fig. 2(a). It has a single phase perovskite structure with tetragonal symmetry. The perovskite type materials with intensity peak (200) at 2θ angle of 46.5° is characterized as a cubic phase, however the splitting of (200) into (002) and (200) at 2θ angle of 46.5° is the characteristic of tetragonal phase, which is identified by JCPDS nos. 75–2102 and 74–2455, respectively. The difference between the cubic phase and tetragonal phase is that in cubic phase Na^+ locates in the center of eight NbO_6 octahedra, while in tetragonal phase Na^+ deviate from the center of eight NbO_6 octahedra. At the higher soaking temperature, Na^+ of cubic NN deviates the center of eight NbO_6 octahedra because of

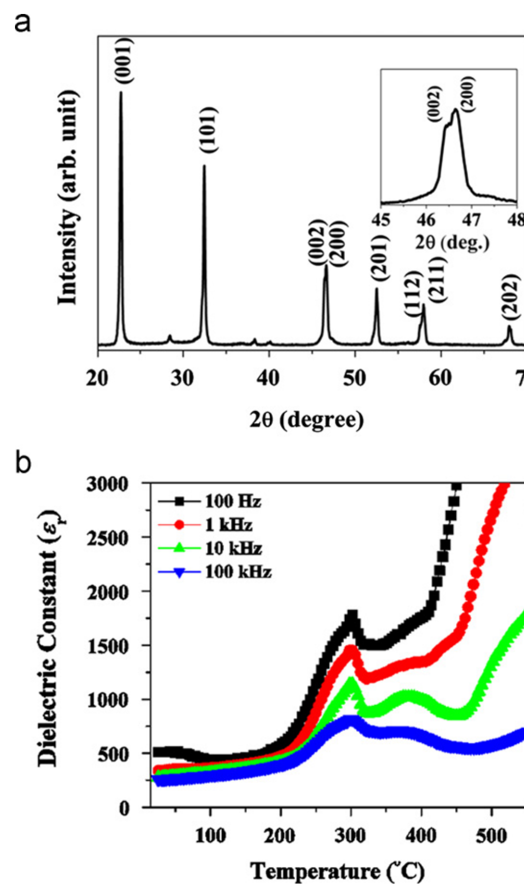

Fig. 2. (a) XRD patterns of plate-like NN particles synthesized from BNN precursor. (b) Temperature dependence of dielectric constant of NN ceramic at different frequencies.

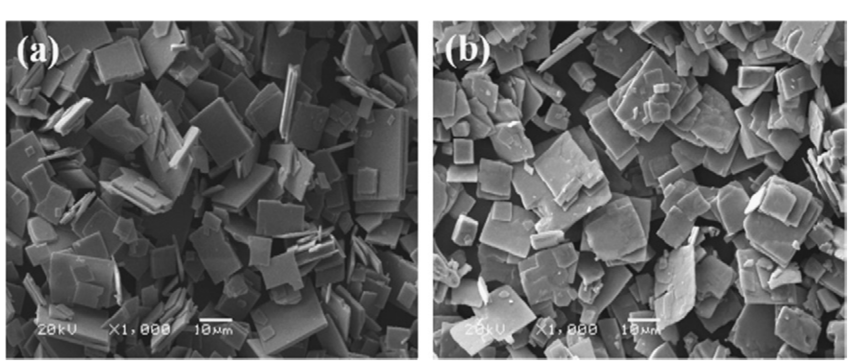

Fig. 1. SEM micrographs (a) BNN precursors synthesized by MSS. (b) NN templates synthesized by TMC.