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Letter

Synthesis and formation mechanisms of high aspect ratio $KNb_5Bi_2O_{16}$ template via topochemical method

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ABSTRACT

Plate-like $Bi_5Nb_3O_{15}$ (B5N3) particles and rectangular $KNb_5Bi_2O_{16}$ (KN5B2) particles were synthesized by the molten salt process and topochemical microcrystal conversion (TMC), respectively. The effects of the synthesis parameters on the phase structure and morphology of B5N3 precursor and KN5B2 were investigated. Results indicated that the retro-synthesis process of the as-synthesized KN5B2 retained the morphology and structural feature of the B5N3 precursor. The prepared KN5B2 particles with high aspect ratio of 20–30 are promising templates for texturing bismuth-layer and alkali niobate based ceramics by (reactive) templated grain growth method. The same method can be applied to other perovskite-structured templates.

1. Introduction

$(K_{0.5}Na_{0.5})NbO_3$ (KNN) based ceramics are promising candidates for lead free piezoelectric ceramics. Comparing with the conventional lead based piezoelectric ceramics, KNN ceramics prepared by the conventional method exhibit worse piezoelectric properties because of the difficulty to obtain high density. Grain orientation techniques can significantly improve the properties of piezoelectric ceramics by changing their microstructure [1]. Templated grain growth (TGG) and reactive templated grain growth (RTGG) have received more attention recently because they can remarkably improve the piezoelectric properties of ceramics. These techniques depend on the preferentially oriented growth of large, anisotropic template grains consuming the matrix grains to yield high density textured ceramics. In TGG/RTGG process, the size and aspect ratio of the template particles (plate-like or needle-like) in the matrix powder are very important to improve the degree of orientation, so that they can be oriented by tape-casting and grown preferentially during sintering stage [2]. Thus, it is crucial to synthesize anisotropically shaped templates for fabricating textured ceramics. The characteristics of the template particles, including structure, shape and size are critical factors for the final product [3].

As regard to the synthesis of plate-like $KNbO_3$ particles, nanoneedles and nanoplatelets of pseudo-cubic $KNbO_3$ were reported by the polymerized complex method from $K_4Nb_6O_{17}$ precursor or soft-chemical method [4,5]. It is reported that the template with dimensions of 5–50 μm have been successfully used to fabricate textured ceramics. Saito and Takao successfully synthesized micrometer sized plate-like $KNbO_3$ from layer-structured $K_4Nb_6O_{17}$ precursor. Yan et al. also synthesized micrometer sized $NaNbO_3$ from layer-structured $Bi_{2.5}Na_{3.5}Nb_5O_{18}$ as precursor [6–10]. The synthesis of micronsized $KNbO_3$ and $NaNbO_3$ is both via topochemical microcrystal conversion method. However, there are still very few reports of the synthesis of micrometer templates of niobate system, which have the suitable size, shape, stability and crystal structure and could be applicable in fabricating textured $KNbO_3$(KN) or $(KNa)_{0.5}NbO_3$(KNN) based ceramics. Therefore, the synthesis of anisotropic templates with a proper scale is a key procedure in preparation of textured ceramics.

The $Bi_5Nb_3O_{15}$ is a mixed-layer Aurivllius-related phase, consisting of a $[Bi_2O_2]+[NbO_4]+[Bi_2O_2]+[BiNb_2O_7]$ stacking sequence, as illustrated in Fig. 1, and possesses orthorhombic structure [11]. In this study, plate-like layer-perovskite $Bi_5Nb_3O_{15}$(B5N3) particles were synthesized by molten flux method and platelet $KNb_5Bi_2O_{16}$ from $Bi_5Nb_3O_{15}$ precursor was synthesized via topochemical microcrystal conversion (TMC) method from the viewpoint of morphology inheritance. The effect of synthesis parameter soaking time on the morphology and phase structure of $Bi_5Nb_3O_{15}$ (B5N3) was investigated as well as the effect

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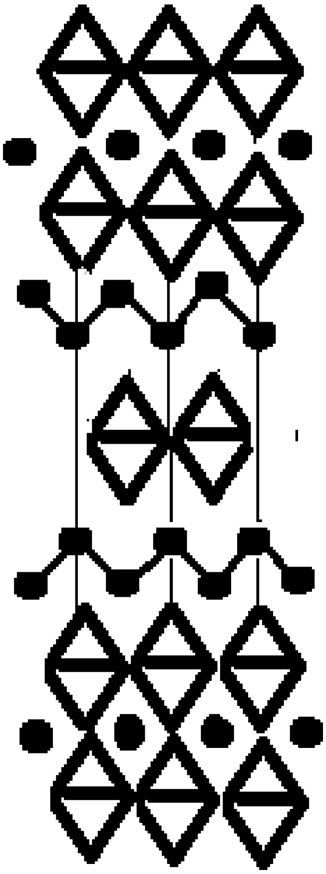


Fig. 1. structure of B5N3.

of different synthesis methods on the $KNb_5Bi_2O_{16}$ (KN5B2) particles. The formation mechanisms of $KNb_5Bi_2O_{16}$ were proposed.

2. Experimental procedures

2.1. Synthesis of plate-like $Bi_5Nb_3O_{15}$ via molten salt method

Plate-like $Bi_5Nb_3O_{15}$ (B5N3) particles were prepared by molten salt synthesis according to the following equation:

$$5Bi_2O_3 + 3Nb_2O_5 \rightarrow 2Bi_5Nb_3O_{15}$$

In this process, analytical grade Bi_2O_3 (99%) and Nb_2O_5 (99%) were used as raw materials and KCl (99%) was added as a flux. Bi_2O_3 and Nb_2O_5 were firstly weighted according to the stoichiometry of B5N3, and then they were mixed thoroughly with KCl for 3.5 h in the ethanol with media of agate balls. The weight ratio of oxide to salt (O/S) was 1:1 in the molten salt method. The milled slurry was dried at 80 °C in an oven.

In order to investigate the influence of soaking time on the crystal phase, a series of time points were set. Dried powders were calcined at 1050 °C for 2, 3 and 4 h. After the reaction, hot-water washing and decantation were repeatedly performed in order to remove the KCl flux during filtration.

2.2. Synthesis of $KNb_5Bi_2O_{16}$ via topochemical microcrystal conversion

Using plate-like B5N3 obtained in the molten salt method as precursors, the topochemical microcrystal conversion from B5N3 to the desired product KN5B2 was carried out at 1000 °C for 3.5 h in molten KCl flux salt according to the following equation:

$$2Bi_5Nb_3O_{15} + K_2CO_3 + 2Nb_2O_5 \rightarrow 2KNb_5Bi_2O_{16} + 3Bi_2O_3 + CO_2\uparrow$$

Excess amount of K_2CO_3 should be added appropriately to make up for the volatilization in the heating process. It can also enhance the conversion of precursor B5N3 to KN5B2. The product was washed with hot de-ionized water and HCl solution alternately for five to eight times. Byproduct Bi_2O_3 was removed via using HCl solution and KCl was washed away using hot de-ionized water. After being dried, the unagglomerated platelets preserved the morphology of the B5N3 precursor pretty well. To distinguish the difference between the TMC and the conventional molten method with respect to the particle morphology, KN5B2 particles were synthesized by the conventional flux method at 900 °C for 2 h with the weight ratio of 1:1 in a molten KCl flux according to the following equation:

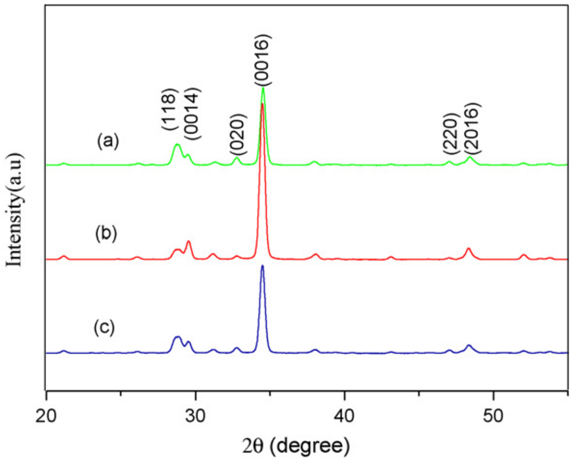


Fig. 2. XRD patterns of the B5N3 particles synthesized at 1050 °C for different soaking time: (a) 2 h, (b) 3 h, (c) 4 h.

$$K_2CO_3 + 2Bi_2O_3 + 5Nb_2O_5 \rightarrow 2KNb_5Bi_2O_{16} + CO_2\uparrow$$

X-ray diffraction (XRD, s-7000, Japan) using CuK_α radiation, was used for phase identification. The morphologies of the synthesized particles were investigated with field emission scanning electron microscopy (SEM, LEO1530) in combination with energy-dispersive X-ray spectrometry (EDS).

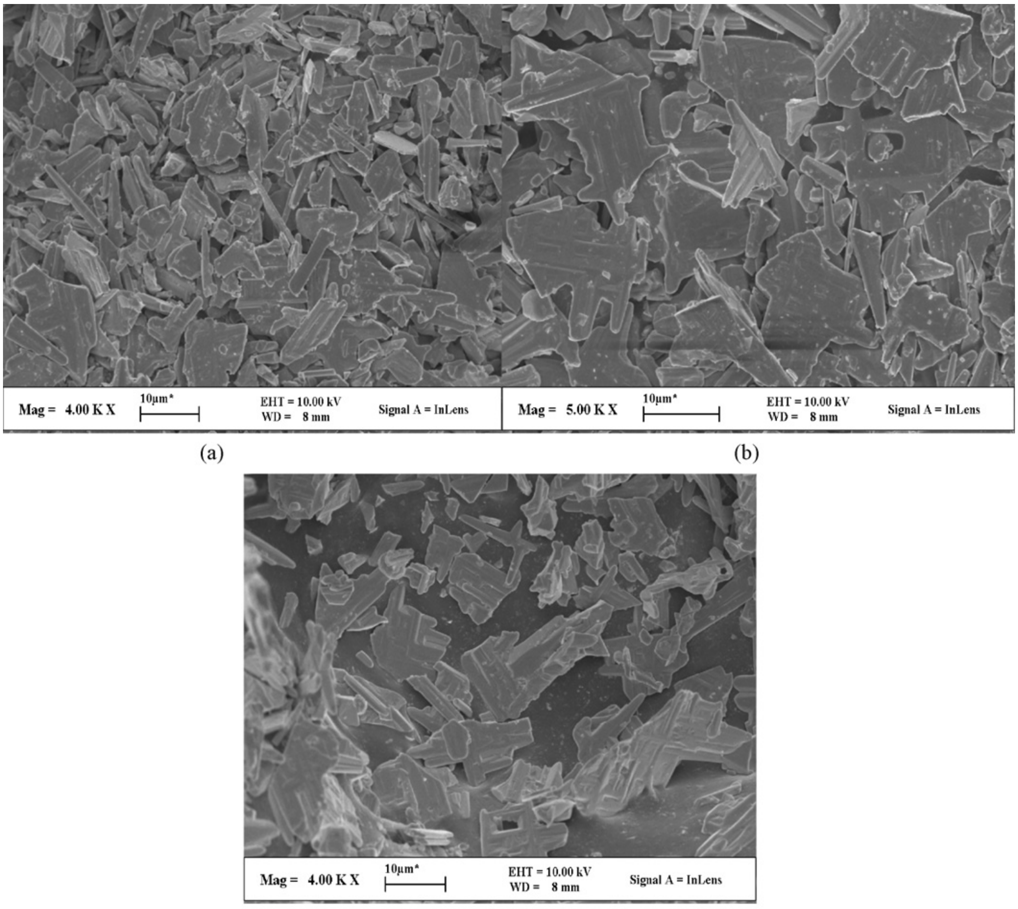
3. Results and discussion

3.1. Effects of synthesis parameter on the phase structure and morphology of $Bi_5Nb_3O_{15}$

Fig. 2 shows the XRD patterns of the B5N3 particles prepared at 1050 °C with different soaking time. The diffraction peaks are indexed according to JCPDS Card No. 39-0939. It can be seen that the major phase is B5N3. At the same time, with the increase of soaking time, intensity of the (0 0 l) peaks exhibited a trend of first ascending and then descending, especially the (0 0 1 4) and (0 0 1 6) peaks. The relative intensity of (0 0 l) reached the maximum value with 3 h, which was higher than that of other time points. This suggested that the B5N3 particles possess of a very high degree of orientation.

In Fig. 2 the strong intensities of (0 0 1 4) and (0 0 1 6) peaks indicate that B5N3 prefers to orient to the (0 0 l) planes.

The effects of soaking time on the morphology of B5N3 particles are shown in Fig. 3. In these images the synthesized particles presented plate-like morphology and the aspect ratio of product was high. The size of the B5N3 increased with soaking time, and reached the maximum at the soaking time of 3 h, then decreased when the soaking time was above 3 h. When the soaking time was 3 h, the size of the B5N3 particles was more homogeneous and the shape was irregular plate-like as shown in Fig. 3(b). The length of B5N3 was 10–30 μm, and the thickness was 0.5–1 μm. The aspect ratio of length to thickness varied from 20 to 60. In liquid molten salt surroundings, the growth of particles involved dissolution and precipitation processes, which accelerated the growth rate of B5N3. At the same time, due to a free circumstance in liquid, particles were apt to grow according to their growth habits. For mixed bismuth-layer-structure, many particles of this kind structure usually grow in [0 0 1] direction and exhibit a plate-like appearance with high aspect ratio. The synthesis of $Bi_4Ti_3O_{12}$, $Bi_{2.5}Na_{3.5}Nb_5O_{18}$, $SrBi_4Ti_4O_{15}$ and $Bi_{2.5}Na_{0.5}Ta_2O_9$ can support this point [7,12–14].



(a) (b)

(c)

Fig. 3. SEM images of B5N3 particles by the conventional molten method at 1050 °C with different soaking time: (a) 2 h, (b) 3 h, (c) 4 h.

In the molten flux method, the volatility of the reactant and KCl flux would be worse with the increase of soaking time. Therefore, the solubility and mobility of the reactant oxides in molten KCl would be affected in turn and had a tendency of descending. The ion exchange reaction would be partly forbidden because of the reduction of molten flux media and the slowdown of the development of crystal. Soaking time for 2 h was not adequate for the thorough development of B5N3 crystals, so the intensity of (0 0 l), the size and the aspect ratio would be not as good as those in the soaking time for 3 h. According to the Ostward ripening mechanism, the bigger crystal particles would lick up small particles and become larger as the soaking time increases. Because of the consumption of fine B5N3 particles by the larger ones, the size distribution of the particles obtained for long soaking time became relatively broad. As soaking time increased from 3 h to 4 h, the size of B5N3 particles became inhomogeneous and some of them were larger than 30 μm which would be worse for practical applications and would break into small pieces during the process of tape-casting in the TGG/RTGG.

Due to different atomic bonds and corresponding surface energy of crystal planes, the growth rates depend upon the crystallographic direction. This phenomenon translates into a specific morphology (or crystal habit) for each individual crystal. The platelet morphology of B5N3 indicated that the growth rate in ⟨0 0 l⟩ direction was slower than that in the other directions, leading to the expansion of (0 0 l) planes or major faces of the platelets. As a result, BNN particles developed into plate-like morphology.

3.2. *Effect of different methods on the as-synthesized $KNb_5Bi_2O_{16}$ particles*

Fig. 4 shows the XRD patterns of as-synthesized $KNb_5Bi_2O_{16}$ particles, in comparison with JCPDS patterns of $KNb_5Bi_2O_{16}$ (No. 53-1258). Fig. 4(a) shows XRD pattern of $KNb_5Bi_2O_{16}$ grown on $Bi_5Nb_3O_{15}$ core particles for platelet morphology. It appeared that the dwell time in molten KCl was adequate for the conversion of $Bi_5Nb_3O_{15}$ particles to $KNb_5Bi_2O_{16}$.

In Fig. 5(a) and (b) it was observed that KN5B2 particles preserved the plate-like morphology of B5N3 precursor particles and the shape of synthesized product was more regular

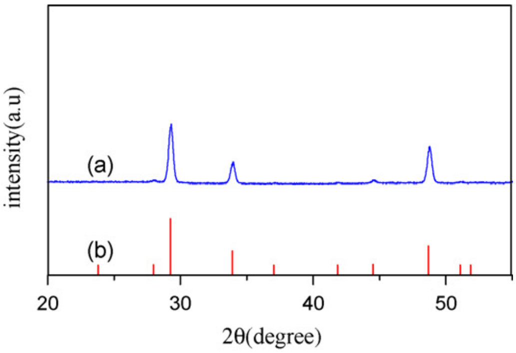


Fig. 4. XRD patterns (a) KN5B2 particles topochemical microcrystal conversion (TMC); (b) KN5B2 particles synthesized by conventional molten salt synthesis (MSS); (c) KN5B2 pattern of JCPDS powder diffraction file # 53-1258.

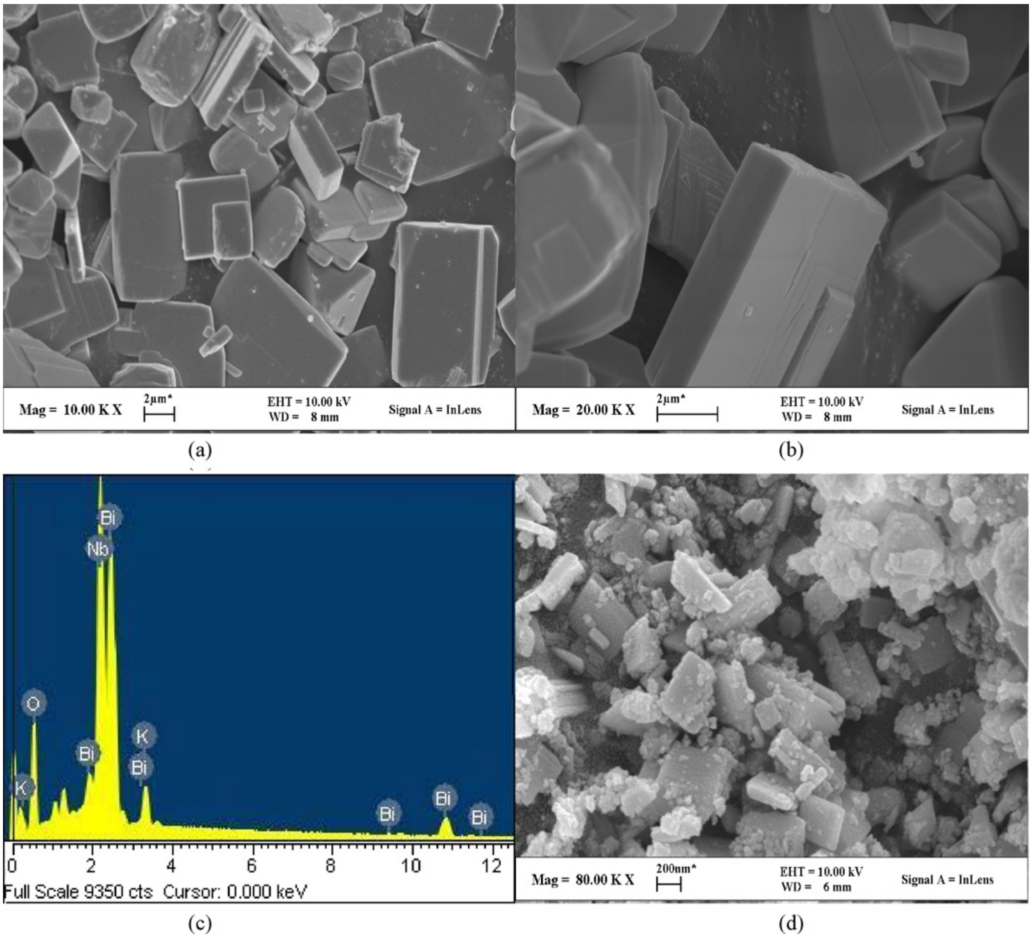


Fig. 5. SEM photographs of KN5B2 particles synthesized by different methods. (a) and (b) KN5B2 synthesized by topochemical microcrystal conversion (TMC); (c) EDS of KN5B2 in (b); (d) KN5B2 synthesized by molten salt synthesis (MSS).

and homogeneous than B5N3. In the TMC process the platelet B5N3 acted as nucleation centers and reacted with K_2CO_3 without altering the plate-like shape. EDS file showed that after the topochemical crystal conversion K^+ diffused into the lattice of B5N3 and the conversion from B5N3 to KN5B2 was accomplished.

In Fig. 5(d) the direct molten salt synthesis could also yield products with regular-square shape. It was clearly observed that the size of synthesized particles was small and a great number of crystals strongly agglomerated together with low dispersibility. The particles synthesized by the MSS method had a similar morphology with KN5B2 particles prepared by TMC, whereas they were considerably smaller than latter in size. The crystalline phase of these particles was a cubic perovskite KN5B2 structure, as determined by XRD.

It is evident that the KN5B2 particles can be fabricated by TMC method as rectangular plate-like particles with a width of 10–15 μm, a thickness of 0.5 μm and aspect ratio of 20–30. According to the 4S standards the TMC-synthesized KN5B2 particles are more suitable for the application in TGG/RTGG ascribing to its rectangular plate-like shape and high aspect ratio.

In the microstructure of B5N3, due to the alternation of Bi_2O_2 layer and perovskite layer an inner strain will be brought by this kind of lattice mismatch. And this strain could not be overcome thoroughly by the spinning of oxygen octahedral [13]. The more the amount of perovskie layer is, the greater this strain will be. The compound will not be stable because of the existence of the inner strain. Under certain appropriate temperature, K^+ ions diffuses into the lattice of B5N3 and substitutes all $Bi3^+$ ions in oxygen octahedral and some $Bi3^+$ ions in the Bi_2O_2 layer. Because the X-ray diffraction pattern of KN5B2 is a representative of bismuth-layer-structure, it can demonstrate that the topochemical reaction just replaces part of the $Bi3^+$ ions of in the Bi_2O_2 layer. Then we can get the product KN5B2, and the Bi^{3+} substituted by K^+ will appear in terms of Bi_2O_3 in the reaction product. Accordingly, the transformation from the layered B5N3 to KN5B2 may contain two processes: one is the decomposition of Bi_2O_2 layers, and the other is the diffusion of K^+ into the lattices and the substitution of residual $Bi3^+$ by K^+.

Both $Bi_5Nb_3O_{15}$ and $KNb_5Bi_2O_{16}$ are mixed bismuth-layer compound belonging to Aurivillius phases. In general, the bond between interlayer and adjacent oxygen octahedral is very weak, and during TMC the interlayer can be replaced by other cations under certain temperature. Then new compound with the morphology of precursor can be gained. By using layered perovskites as templates, it is possible to retrosynthetically design new perovskites that retain the structural features of the precursor layered phases. In this process topochemical method is widely used and the morphology of reagent could be retained. Therefore, TMC is suitable for synthesis of template in TGG/RTGG. Through this well-designed reaction route, almost any kind of metastable shape and structure could be expected.

In the following experiment, we will place more effort on the application of KN5B2 as nucleation sites for epitaxial growth of KNN in TGG process. Due to the existence of Bi_2O_2 layer in the structure of KN5B2, the synthesis of another template derived from KN5B2 also is concerned.

4. Conclusions

High aspect ratio plate-like $Bi_5Nb_3O_{15}$ particles were successfully synthesized by the molten salt process, and $KNb_5Bi_2O_{16}$ with regular rectangle morphology was prepared via TMC using $Bi_5Nb_3O_{15}$ as precursor. During the TMC process, plate-like $KNb_5Bi_2O_{16}$ particles that preserved the shape of the precursor particles, were synthesized at 1000 °C for 3.5 h with the weight ratio of O/S 1:1. The length of $KNb_5Bi_2O_{16}$ template varied from 10 to 15 μm, and the thickness varied from 0.6 to 1 μm. The aspect ratio of length to thickness was in the range of 10–25. The two kinds of plate-like particles could be both expected to be applied for the synthesis of textured bismuth-layer and alkali niobate based ceramics.

The effect of soaking time on the size and morphology of $Bi_5Nb_3O_{15}$ precursor was investigated as well as the synthesis methods on the grain growth of $KNb_5Bi_2O_{16}$. The formation mechanisms of the conversion from $Bi_5Nb_3O_{15}$ to $KNb_5Bi_2O_{16}$ were proposed.

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