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Preparation of textured $Ba_2NaNb_5O_{15}$ ceramics by templated grain growth

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Abstract

Acicular $Ba_2NaNb_5O_{15}$ (BNN) single crystals were synthesized by the reaction of $BaCO_3$ and Nb_2O_5 in molten NaCl at 1200 °C for 4 h. Using these single crystals as seeds and V_2O_5 as additive, textured BNN ceramics were successfully prepared via templated grain growth (TGG). The degree of grain orientation for textured BNN ceramics increased with sintering temperature and reached 80.1% texture degree at 1300 °C. Most of the rod-like grains arranged along the tape-casting direction at higher temperature since the seeds grew at the expense of fine-grained matrix grains.

Keywords: Barium sodium niobate ($Ba_2NaNb_5O_{15}$); Templated grain growth (TGG); Texture; Seeds

1. Introduction

Barium sodium niobate ($Ba_2NaNb_5O_{15}$, abbreviated as BNN) has a filled tungsten bronze structure, in which all 15- and 12-fold-coordinated sites are occupied by Ba and Na ions, respectively, with the exact Ba/Na ratio of 2:1 [1]. It has attracted much attention because it possesses a sequence of four or more phase transitions that involve ferroelectric, ferroelastic, excellent electro-optic, piezoelectric and non-linear optical properties, which allow technological applications as ferroelectric and optoelectronic materials [2–5]. But the high cost and the difficulty in production of high-quality BNN single crystal limit its application, while the random-oriented BNN ceramic has low electrical properties. In the last few years, textured alumina [6], mullite [7], $Bi_4Ti_3O_{12}$ [8,9], and $Sr_xBa_{1-x}Nb_2O_6$ $(0.25 \le x \le 0.75)$ [10,11] ceramics which possess improved electrical properties similar to single crystal have been successfully fabricated by templated grain growth (TGG). This opens up an approach to fabricate textured BNN ceramic with excellent electrical properties.

TGG technique relies on a certain amount of rod-like or plate-like seeds which are oriented in a fine powder matrix by extrusion or tape-casting [12–14]. During sintering, these larger anisotropic seeds grow at the expense of fine matrix grains, thus high-grain orientation will form. Therefore, it is very important to prepare high-purity and anisotropic single crystals as growth templates. Recently, high-purity acicular $Ba_2NaNb_5O_{15}$ seeds have been successfully synthesized via molten salt synthesis (MSS) by our group [15,16]. In this work, using these BNN single crystals as seeds and V_2O_5 as additive, the effect of sintering temperature on the densification behavior, grain orientation and textured microstructures of BNN ceramics was investigated.

2. Experimental procedures

$BaCO_3$ (>99.0%), Nb_2O_5 (>99.9%) and NaCl (>99.5%) were used as starting materials to prepare BNN seeds.

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$BaCO_3$ and Nb_2O_5 according to $BaNb_2O_6$ composition were first mixed together in ethanol for 24 h. Then the mixtures were again mixed with NaCl in ethanol for another 24 h with the weight ratio of NaCl to mixture of 2:1. The dried mixtures were calcined at 1200 °C for 4 h in covered alumina crucibles. Afterwards, the synthesized products were washed repeatedly with hot de-ionized water until no chloride ions were detected by silver nitrate.

The matrix powders of textured BNN ceramics, $BaNb_2O_6$ (BN) and $NaNbO_3$ (NN), were prepared by ball milling $BaCO_3$ or Na_2CO_3 (>99.8%) with Nb_2O_5 for 24 h in ethanol and then calcined at 950 and 750 °C for 3 h, respectively. Then appropriate amounts of calcined BN and NN powders were first mixed with 0.5 wt.% V_2O_5 additive, the solvent (60 vol.% toluene–40 vol% ethanol) and dispersant (triethanolamine) for 24 h. Afterwards, 10 wt.% BNN template seeds, poly(vinyl butyral) (binder) and diethyl-*o*-phthate (plasticizer) were added and mixed for another 24 h. The slurry was tape-casted to obtain some 0.1-mm thick sheets, which were cut and laminated at 150 MPa to form green compacts (12 mm × 7 mm × 6 mm). The green compacts were heated at 600 °C for 4 h to remove organic ingredients and then cold isostatically pressed at 200 MPa. Finally, the specimens were sintered between 1100 and 1300 °C in air for 3 h.

Random-oriented BNN ceramics without seeds and V_2O_5 were prepared by the reaction of calcined BN and NN powders. The mixed BN and NN powders were uniaxially pressed at 100 MPa and further isostatically pressed at 200 MPa. Then the compacts were sintered between 1100 and 1350 °C for 3 h.

The phase analysis of the synthesized powders was based on X-ray diffraction data from a Guinier–Hägg camera (Cu Kα radiation λ = 1.5405981 Å) using Si as the internal standard and the lattice parameters were precisely determined with the aid of PRIUM programs [17]. Scanning electron microscopy (SEM, Model HITACH S-270) was used to observe the morphology and size distribution.

The densities of sintered samples were measured by Archimedes method. The texture was characterized using X-ray diffractometry (XRD) with Cu Kα, and the degree of grain orientation was calculated by Lotgering method [18]. The microstructures of the polished surfaces parallel to tape-casting direction were observed by SEM.

3. Results and discussion

3.1. Synthesis of acicular BNN seeds

XRD pattern of the powders synthesized via MSS is shown in Fig. 1. It is in good agreement with $Ba_2NaNb_5O_{15}$ (JCPDF data card no. 40-1463). So the synthesized products are single-phase BNN (a = 17.605 Å and c = 7.983 Å). Fig. 2 shows SEM micrograph of the synthesized BNN powders. It can be seen that the synthesized powders are

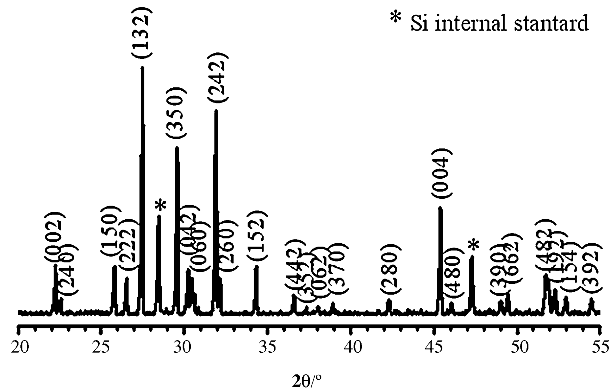

Fig. 1. XRD pattern of the powders synthesized by the reaction of $BaCO_3$ and Nb_2O_5 in molten NaCl at 1200 °C for 4 h.

acicular single crystals with a diameter of 4–7 μm and aspect ratio of 1.5–5.5.

3.2. Densification behaviour of BNN ceramics

Fig. 3 shows the effect of temperature on densification behaviour in sintered BNN ceramics with seeds and V_2O_5 as well as BNN ceramics without seeds and V_2O_5. The relative density was calculated based in the theoretical density of BNN (5.376 g cm^{-3}, JCPDF data card no. 34-0210). Compared with the ceramics without seeds and V_2O_5, BNN ceramics with seeds and V_2O_5 have relatively higher density at lower temperature. For example, sintered at 1200 °C the sample with seeds and V_2O_5 has a relative density of 93.9% while the sample without seeds and V_2O_5 only has 68.3%. The maximum relative density of 94.6% occurs at 1250 °C for the sample with seeds and V_2O_5, which is about 100 °C lower than the samples without seeds and V_2O_5. It has been reported that V^{5+} ions rarely are dissolved in the tungsten bronze structure; instead, they precipitate as separate islands at the triple junctions after sintering [10]. Thus, V_2O_5 exists as liquid phase above its

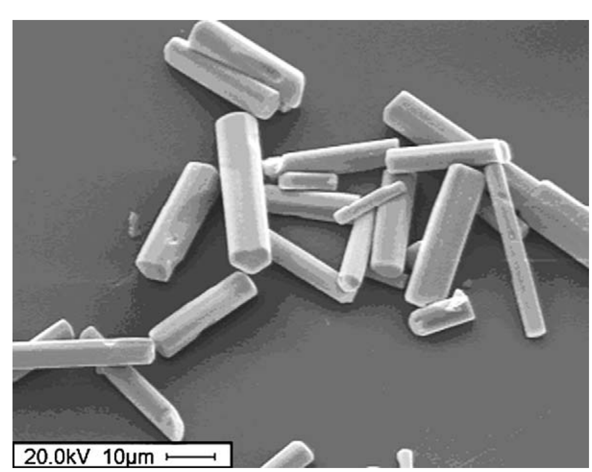

Fig. 2. SEM micrograph of the synthesized BNN powders by the reaction of $BaCO_3$ and Nb_2O_5 in molten NaCl at 1200 °C for 4 h.

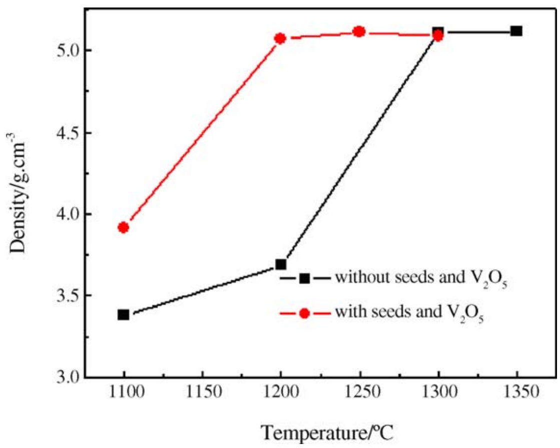

Fig. 3. Densities of sintered BNN ceramics as a function of temperature.

melting point (690 °C), and promotes the densification of BNN ceramics due to faster growth of the high-surface-energy planes (e.g., {0 0 *l*} in BNN), while the template seeds will grow via solution-reprecipitation in which small particles dissolve in the liquid phase and then reprecipitate on the larger template particles. With increasing temperature, the viscosity of molten V_2O_5 decreases, which helps V_2O_5 to spread out across the seeds and consequently density increases. However, too high sintering temperature will result in the decrease of density owing to the evaporation of V_2O_5.

3.3. Degree of grain orientation and microstructure of BNN ceramics

XRD patterns of BNN ceramics with and without seeds sintered at 1300 °C for 3 h are shown in Fig. 4. It can be seen that single-phase $Ba_2NaNb_5O_{15}$ form in all samples. Compared with the seed-free sample, the intensity of {0 0 *l*} peaks samples with seeds enhances in the direction perpendicular to tape-casting while the intensity of other peaks weakens. In contrast, the {*h k* 0} peaks enhance and the {*h k l*} peaks weaken in the direction parallel to tape-casting,

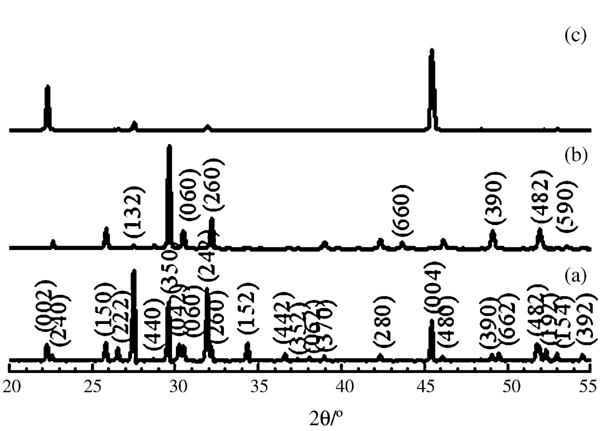

Fig. 4. XRD patterns of (a) random-oriented and BNN ceramics with seeds (b) parallel and (c) perpendicular to the tape-casting direction sintered at 1300 °C.

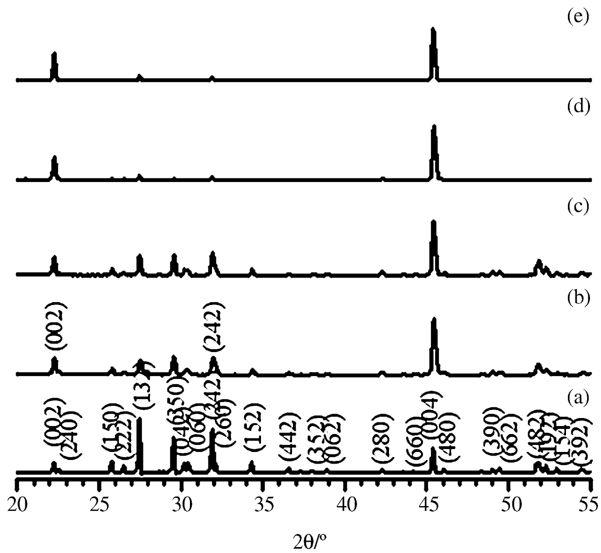

Fig. 5. XRD patterns of (a) random-oriented BNN ceramics and textured BNN ceramics perpendicular to the tape-casting direction sintered for 3 h at (b) 1100, (c) 1200, (d) 1250 and (e) 1300 °C.

while the {0 0 *l*} peaks disappear basically. The results indicate that the ceramics with seeds and V_2O_5 have obvious textured characteristics.

Fig. 5 shows XRD patterns of BNN samples perpendicular to the tape-casting direction sintered at different temperatures as well as random-oriented BNN ceramics sintered at 1300 °C. It can be seen that the relative intensity of {0 0 *l*} peaks increases gradually with temperature. The degree of grain orientation increases quickly from 38.1 to 79.5% when the temperature increases from 1100 to 1250 °C. However, it increases slightly above 1250 °C and reaches 80.1% at 1300 °C (see Fig. 6). It is well known that the seeds grow up at the expense of fine-grained matrix particles during TGG and higher temperature is beneficial for seed growth. But once fine-grained matrix particles are used up, the seeds will grow slowly despite the further increase of temperature, and thus there is a slight increase in

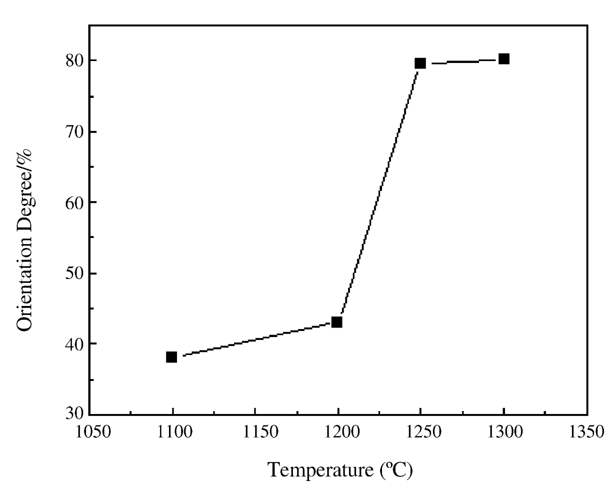

Fig. 6. Degree of grain orientation for samples with seeds and V_2O_5 as a function of temperature.

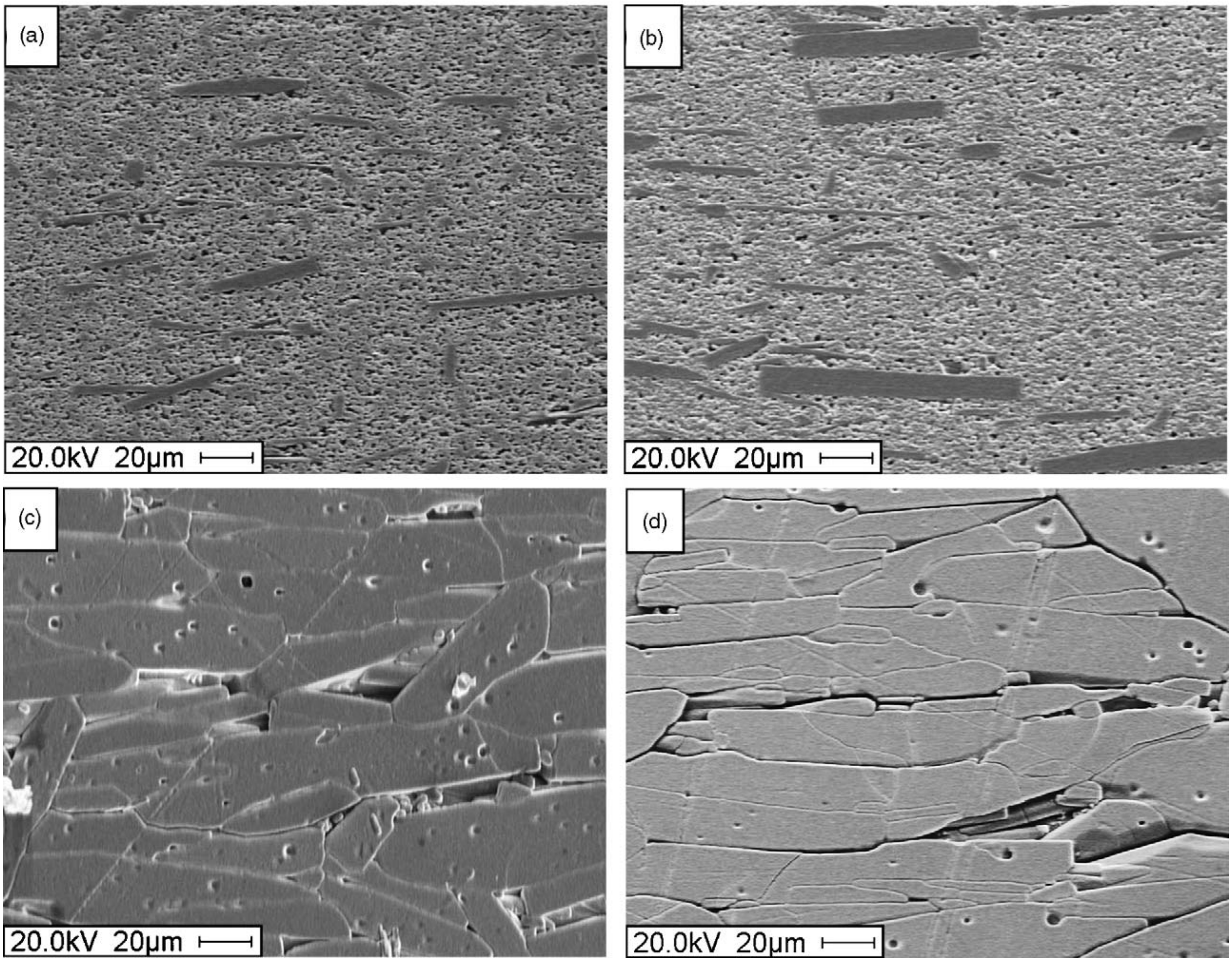

Fig. 7. SEM micrographs of surfaces parallel to the tape-casting direction sintered for 3 h at (a) 1100, (b) 1200, (c) 1250 and (d) 1300 °C.

the degree of grain orientation. A similar result can also be proved by SEM observation. Fig. 7 shows SEM micrographs of textured BNN ceramics. In the sample at 1100 °C there are a lot of fine-grained matrix particles around some big seeds. A few fine-grained matrix particles remain at 1250 °C. At 1300 °C, all the fine-grained matrix particles disappear and most of rod-like particles arrange along the tape-casting direction, and finally the textured microstructure forms.

4. Conclusions

The acicular $Ba_2NaNb_5O_{15}$ (BNN) single crystals with a diameter of 4–7 μm and aspect ratio of 1.5–5.5 were prepared by the reaction of $BaCO_3$ and Nb_2O_5 in molten NaCl at 1200 °C for 4 h. Using these single crystals as seeds and V_2O_5 as additive, textured BNN ceramics were successfully prepared via templated grain growth (TGG). The degree of grain orientation increases with temperature and reaches 80.1% at 1300 °C. Most of the rod-like grains arrange along the tape-casting direction at higher temperature since the seeds grow at the expense of fine-grained matrix grains.

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