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Synthesis of anisometric $KSr_2Nb_5O_{15}$ particles in the $SrNb_2O_6$–Nb_2O_5–KCl system

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Abstract Anisometric and agglomerate-free template particles are important for fabrication of grain-oriented ceramics. In the present work, preparation of acicular $KSr_2Nb_5O_{15}$ (KSN) particles was firstly explored in the $SrNb_2O_6$–Nb_2O_5–KCl system by molten salt synthesis (MSS) method. It was found that the molar ratio of $SrNb_2O_6$ to Nb_2O_5, the amount of KCl salt and synthesis time could significantly affect the phase structure and morphology of KSN particles. When calcined at 1,150 °C for 6 h with the molar ratio of $SrNb_2O_6$ to Nb_2O_5 was 1 and the weight ratio of salt to oxide source was 1.50, pure KSN particles with well-developed acicular morphology were successfully obtained in this system. They were agglomerate-free and with proper scale in the size range of 5–30 μm, which made them the ideal templates for fabricating textured ceramics. In addition, some new reaction and growth mechanisms were proposed in this work.

Introduction

Lead-free piezoelectric ceramics have received considerable attention due to the health and environmental protection in recent years. But the piezoelectric properties of present lead-free ceramics are much poorer than those of the conventional PZT piezoelectric ceramics, restricting their applications in many electric devices. It is well known that the control of crystallographic texture can improve the properties of ceramics to mimic the properties of single crystals with the same composition [1]. Recently, highly textured ceramics fabricated by templated grain growth (TGG) or by reactive templated grain growth (RTGG) technique have shown excellent anisotropic electrical properties [2–5], opening an effective way to fabricate high-performance functional ceramics. In both TGG and RTGG processes, large anisotropic template particles are oriented by external mechanical force in a fine-grained matrix in green body, and then a textured microstructure is developed by growth of aligned particles. So high-purity and anisotropic template particles are needed as growth templates to produce highly textured ceramics.

Molten salt synthesis (MSS) is a well-established and cost-effective technique to prepare particles with acicular-shaped or platelet-shaped morphology. Because of the easy anisotropic growth in molten salt liquid, MSS has often been used to synthesize anisotropic $Sr_2Nb_2O_7$, $Bi_4Ti_3O_{12}$, $Ba_2NaNb_5O_{15}$ materials, and so on [6–8]. Up to now, acicular $KSr_2Nb_5O_{15}$ (KSN) powders have been normally prepared using $SrNb_2O_6$–KCl system by MSS method [9]; however, the obtained powders are always contaminated by the impurity of blade-like $Sr_2Nb_2O_7$, making it difficult to control the composition of textured niobate ceramics. The $Sr_2Nb_2O_7$ impurity is formed by reaction between $SrNb_2O_6$ and $SrCl_2$ and its formation can not be avoided in the $SrNb_2O_6$–KCl system [9, 10]. Zhao et al. [10] employed the $SrCO_3$–Nb_2O_5–KCl system to prepare pure KSN with better morphology; unfortunately, larger amount of Nb_2O_5 was used. In order to synthesize high-purity and anisotropic KSN particles using relatively smaller amount of Nb_2O_5, a new

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$SrNb_2O_6$–Nb_2O_5–KCl system was explored in this work. By carefully controlling some processing parameters (i.e., the molar ratio of $SrNb_2O_6$ to Nb_2O_5, the amount of KCl salt and synthesis time), pure KSN particles with good anisotropic morphology were successfully obtained, which could be applied in fabricating textured ceramics by TGG or RTGG process. Some new reaction and growth mechanisms of this system were also proposed in this paper.

Experimental procedure

Sample preparation

Reagent-grade powders of $SrCO_3$ (99%) and Nb_2O_5 (99.5%) were used to prepare $SrNb_2O_6$ powder. After ball milling $SrCO_3$ and Nb_2O_5 for 12 h in ethanol using zirconia balls, the mixed powders were dried and calcined at 1,100 °C for 4 h. X-ray diffraction (XRD) result showed that the obtained $SrNb_2O_6$ was a single phase.

The starting materials used to synthesize KSN particles were $SrNb_2O_6$, Nb_2O_5 and KCl (99.5%). They were first mixed by ball-milling in ethanol for 12 h using zirconia balls. After drying at 80 °C for 12 h, the mixtures were put into Al_2O_3 crucibles. Then they were heated at 1,150 °C for 3–6 h and cooled to room temperature at a cooling rate of 3 °C/min. The heating rate before 700 °C was 3 °C/min and then was increased to 6 °C/min in order to reduce the evaporation of KCl salt after its melting point (~770 °C). The synthesized particles were washed about ten times with hot distilled water until Cl^- could not be detected by Ag^+ reagent.

Characterization

Phase structure of synthesized particles was determined by X-ray diffraction (XRD, Model DMX-2550/PC, Rigaku, Japan). The analysis was performed at 40 kV and 50 mA with Ni-filtered Cu-Kα radiation, 2θ in the range of 10–70° with a step of 0.01°. The microstructure was observed by scanning electron microscopy (SEM, Model Quanta 200, FEI Company).

Results and discussion

Effect of the ratio of $SrNb_2O_6$ to Nb_2O_5 on the phase structure and morphology of KSN

Forty wt.% $SrNb_2O_6$ and Nb_2O_5 were mixed with 60 wt.% KCl and then calcined at 1,150 °C for 6 h. The molar ratio of $SrNb_2O_6$ to Nb_2O_5 is denoted as M, which is 4, 2 and 1, respectively. Figure 1 shows the phase structure of powders as a function of M. As shown in the figure, most of the products are KSN particles when M = 4. The impurity in the particles is $Sr_2Nb_2O_7$ and its amount rapidly decreases with increasing the amount of Nb_2O_5. When M = 1, a pure KSN compound is obtained with no detection of $Sr_2Nb_2O_7$ phase which can not be avoided in the $SrNb_2O_6$–KCl system [9, 10]. Nb_2O_5 is reported to be insoluble in alkaline chlorides [11]. Therefore, the possible reactions in the $SrNb_2O_6$–Nb_2O_5–KCl system are:

$$5SrNb_2O_6 + 2KCl \rightarrow 2KSr_2Nb_5O_{15} + SrCl_2, \quad (1)$$

$$SrCl_2 + SrNb_2O_6 + 1/2O_2 \rightarrow Sr_2Nb_2O_7 + Cl_2\uparrow, \quad (2)$$

$$SrCl_2 + Nb_2O_5 + 1/2O_2 \rightarrow SrNb_2O_6 + Cl_2\uparrow. \quad (3)$$

According to Brahmaroutu et al. [6], the reaction between $SrCl_2$ and Nb_2O_5 takes place at low temperature (about 550–750 °C). Further reaction of $SrNb_2O_6$ and $SrCl_2$ above the melting point of $SrCl_2$ results in the formation of $Sr_2Nb_2O_7$. Without Nb_2O_5, reaction (1) always takes place accompanied with reaction (2); therefore, it is impossible to obtain pure KSN in the $SrNb_2O_6$–KCl system. In our case, reactions (2) and (3) are competitive reactions. With increasing the amount of Nb_2O_5 in precursor mixture, $SrCl_2$ will preferably react with Nb_2O_5, which can decrease the amount of $Sr_2Nb_2O_7$ impurity formed by reaction (2). Then the existence of reaction (3) limits

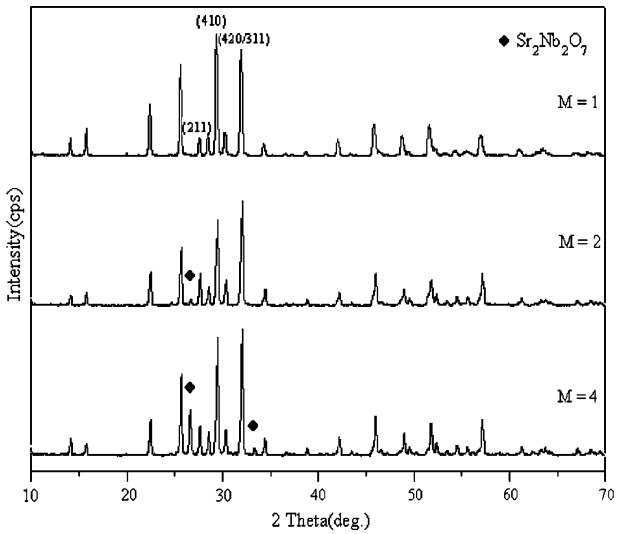

Fig. 1 The phase structure of powders as a function of the molar ratio of $SrNb_2O_6$ to Nb_2O_5

the synthesis of $Sr_2Nb_2O_7$ to some extent, so pure KSN particles can be obtained in this system when M = 1.

Figure 2 shows the microstructure of powders as a function of M. It can clearly be seen the blade-like $Sr_2Nb_2O_7$ particles decrease with the decreasing of M and then vanish. The results are consistent with the observation analyzed by XRD. The KSN needles in Fig. 2 appear to be thicker due to aggregation of several individual needles. This may indicate that $SrNb_2O_6$ has some but finite solubility in the molten KCl. In this system, we think the particle morphology is controlled initially by the formation process and later by the growth process. The formation process is related to the solubility of $SrNb_2O_6$ in molten KCl. If the $SrNb_2O_6$ amount in precursor mixture is more than its solubility in molten KCl, they will not be well diffused in the molten salt liquid, because some of them are insoluble and clumped together. Since $SrNb_2O_6$ powders behave as not only reaction sites but also seeds for forming KSN crystals, this will result in the multiple nucleation sites when KSN forms. The subsequent growth process is in accordance with the growth habits of KSN crystals, that is the (001) facet of tungsten bronze crystal grows faster due to its relatively lower interfacial energy [12].

Effect of the KCl amount on the phase structure and morphology of KSN

KCl plays an important role because it behaves as both the K^+ source for KSN and a molten salt liquid; therefore, the effects of KCl amount on the phase structure and morphology of the synthesized particles are also studied in this work. The oxide source of $SrNb_2O_6$ and Nb_2O_5 with a desired molar ratio (M = 1) were weighted and mixed with KCl salt at various weight ratios of salt to oxide source which is denoted as R (R = 0.67, 1.50 and 4.00, respectively). Then the mixtures were calcined at 1,150 °C for 6 h. Figure 3 shows the phase structure of synthesized powders as a function of R. Pure KSN can be obtained when R = 0.67 and 1.50 as shown in the figure. At R = 4.00, the products are mainly KSN particles, but some impurities of $Sr_2Nb_2O_7$ can also be detected. According to the reaction (1), the $SrCl_2$ amount will rapidly increase with increasing the amount of KCl salt, which can promote the reaction between $SrNb_2O_6$ and $SrCl_2$, thus leading to the formation of $Sr_2Nb_2O_7$.

Figure 4 shows the effect of KCl amount on the powders microstructure. According to Fig. 4, the obtained KSN particles all have acicular morphology and high aspect ratio.

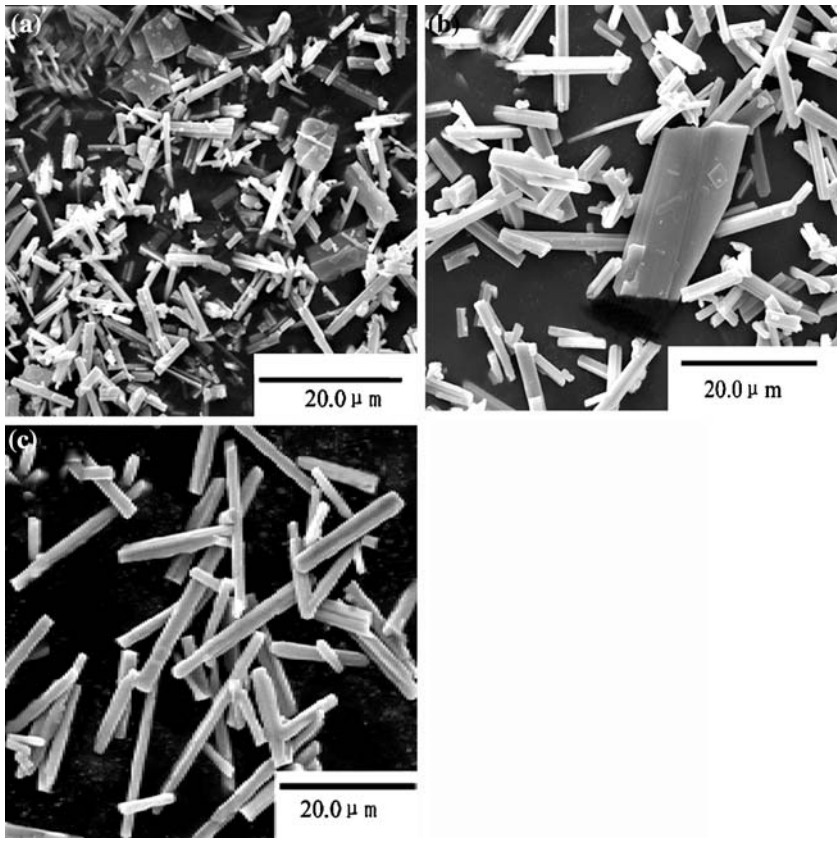

Fig. 2 The microstructure of powders as a function of the molar ratio of $SrNb_2O_6$ to Nb_2O_5: (**a**) M = 4 (2,000×); (b) M = 2 (2,000×); (c) M = 1 (2,000×)

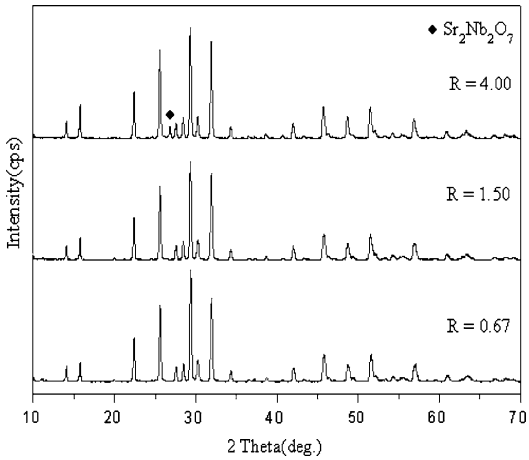

Fig. 3 Effect of KCl amount on the compositions of powders

The diameter of KSN needles in Fig. 4a is thicker than that in Fig. 4b and 4c, which is related to the formation process of KSN. Since $SrNb_2O_6$ has some but finite solubility in molten KCl, it will be well diffused in the molten salt liquid with increasing the amount of KCl salt. In addition, because the particles are more isolated from each other with higher KCl concentration, the necking of the particles in contact which can also cause agglomeration does not occur. Then the KSN particles without stepwise surface morphology in Fig. 4c can be obtained. Though the synthesized KSN particles in Fig. 4c have better morphology, they are easily contaminated by the impurity of $Sr_2Nb_2O_7$. Pure KSN particles can be obtained when R = 0.67, but in order to avoid some changes in purity and morphology of the obtained KSN caused by the evaporation of KCl salt, the better weight ratio of salt to oxide source is 1.50.

Effect of the synthesis time on the phase structure and morphology of KSN

Figure 5 shows the XRD pattern and SEM micrograph of KSN particles synthesized at 1,150 °C for 3 h with M = 1 and R = 1.50. The XRD pattern in Fig. 5a shows that the obtained KSN is pure. But some small particles with around 5 μm size and lower aspect ratio shown in Fig. 5b are difficult to be employed in TGG or RTGG process. In the $SrNb_2O_6$–Nb_2O_5–KCl system, the formation of KSN particles is through a solution-precipitation process. Above the melting point of KCl, the oxides may start to dissolve and form a liquid containing cations and anions. The KSN precipitates with increasing concentration of ions, and then the subsequent growth process is performed. The

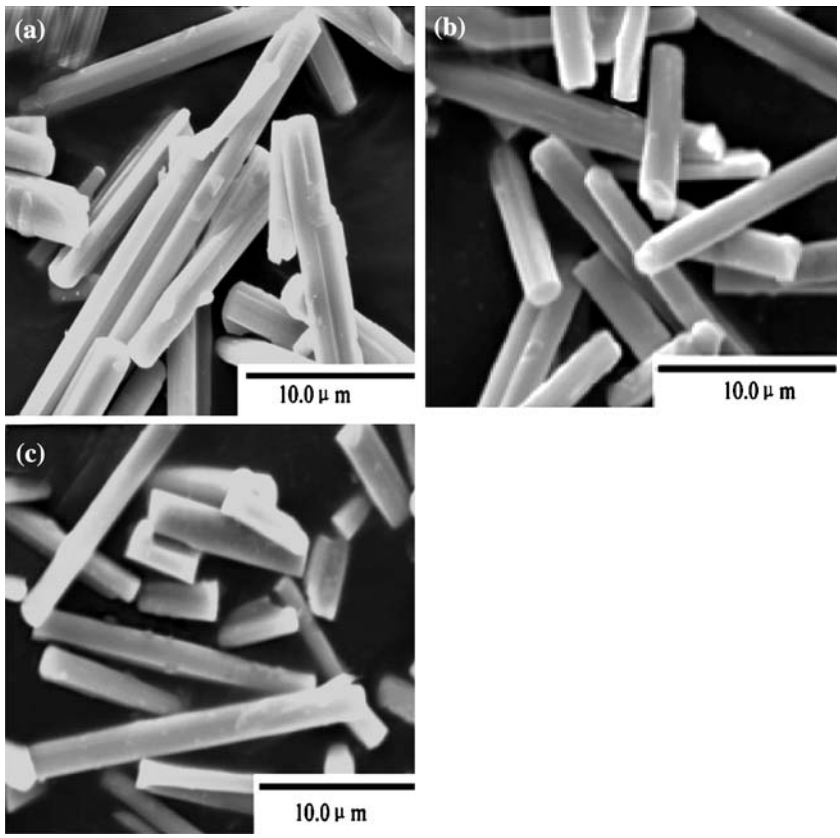

Fig. 4 Effect of KCl amount on the powders microstructure: (**a**) R = 0.67 (5,000×); (**b**) R = 1.50 (5,000×); (**c**) R = 4.00 (5,000×)

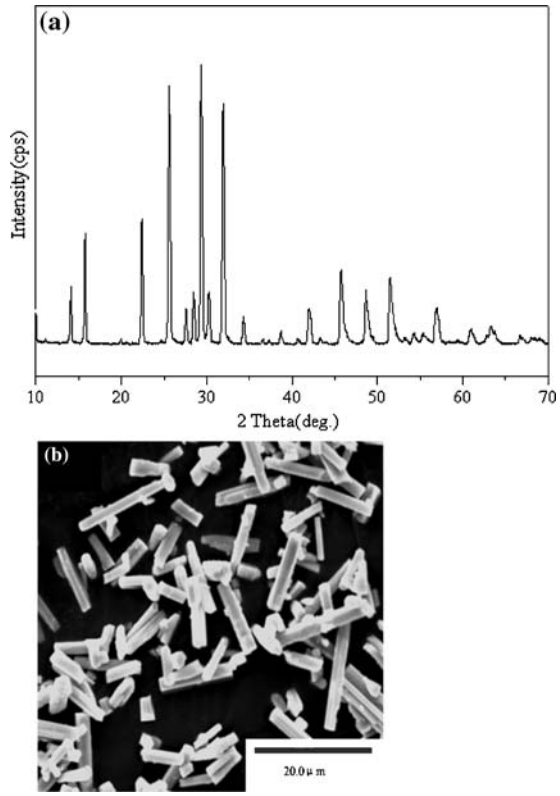

Fig. 5 XRD pattern (**a**) and SEM micrograph (**b**, 2,000×) of KSN particles synthesized at 1,150 °C for 3 h

longer processing time allows further growth of acicular particles, resulting in more uniform size and higher aspect ratio for KSN synthesized at 1,150 °C for 6 h in Fig. 2b than those in Fig. 5b.

In the $SrNb_2O_6$–Nb_2O_5–KCl system, the phase structure and morphology of KSN particles are dependent on the molar ratio of $SrNb_2O_6$ to Nb_2O_5, the amount of KCl salt and synthesis time. When synthesized in molten KCl salt at 1,150 °C for 6 h with M = 1 and R = 1.50, a pure KSN compound can be obtained. According to the XRD patterns in Fig. 1, the most intense peak is (410) instead of (420,311), and the intensity of (211) decreases by more than half. This indicates that the fiber axis is along the (001) orientation [9, 13]. The morphology of pure KSN particles is shown in Figs. 2(c) and 4(b). The acicular particles have better morphology and higher aspect ratio, whose size is 5–30 μm in length and 2–4 μm in diameter. According to our study, the acicular KSN particles obtained in the $SrNb_2O_6$–Nb_2O_5–KCl system are easier to reproduce not only in purity but also in size. In addition, the amount of Nb_2O_5 used to obtain pure KSN in this system is lower than that used in the $SrCO_3$–Nb_2O_5–KCl system reported by Zhao et al. [10]. All of the above results show that they are ideal template particles for the fabrication of textured ceramics.

Conclusions

In the $SrNb_2O_6$–Nb_2O_5–KCl system, the reaction between Nb_2O_5 and $SrCl_2$ can limit the formation of $Sr_2Nb_2O_7$ impurity, making it possible to obtain high-purity KSN particles. With increasing the amount of KCl, $SrNb_2O_6$ may be well diffused in the molten salt liquid, resulting in the KSN particles without stepwise surface morphology. Unfortunately, the impurity of $Sr_2Nb_2O_7$ can also be detected simultaneously due to the higher amount of KCl. In addition, the longer processing time makes the obtained KSN have more uniform size and higher aspect ratio as a result of further growth of acicular particles.

When synthesized in molten KCl salt at 1,150 °C for 6 h with M = 1 and R = 1.50, pure KSN particles with higher aspect ratio and anisotropic morphology can be obtained, whose size is 5–30 μm in length and 2–4 μm in diameter. The most intense peak of the obtained KSN is (410) instead of (420,311), indicating that they are ideal template particles for fabrication of textured ceramics.

References

1. Kimura T, Sakuma Y, Murata M (2005) J Eur Ceram Soc 25:2227
2. Seabaugh MM, Kerscht IH, Messing GL (1997) J Am Ceram Soc 80:1181
3. Duran C, Trolier-McKinstry S, Messing GL (2000) J Am Ceram Soc 83:2203
4. Saito Y, Takao H, Tani T, Nonoyama T, Takatori K, Homma T, Nagaya T, Nakamura M (2004) Nature 432:84
5. Sakuma K, Kimura T (2005) J Mater Sci 40:4811
6. Brahmaroutu B, Messing GL, Trolier-McKinstry S (1999) J Am Ceram Soc 82:1565
7. Kan YM, Jin XH, Wang PL, Li YX, Cheng YB, Yan DS (2003) Mater Res Bull 38:567
8. Xu J, Zhu LH, Huang QW, Gu H (2004) J Mater Sci 39:3445
9. Duran C, Messing GL, Trolier-McKinstry S (2004) Mater Res Bull 39:1679
10. Zhao LL, Gao F, Zhang CS, Zhao M, Tian CS (2005) J Cryst Growth 276:446
11. Picard G, Bocage P (1991) Mater Sci Forum 73:505
12. Huang QW, Xu J, Zhu LH, Wang PL (2005) J Am Ceram Soc 88:447
13. Yang ZP, Wei LL, Chang YF (2007) J Eur Ceram Soc 27:267