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Preparation and morphology of anisometric $KSr_2Nb_5O_{15}$ particles

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Abstract

Anisometric $KSr_2Nb_5O_{15}$ (KSN) particles were synthesized by conventional mixed-oxide (CMO) method and molten salt synthesis (MSS) method, respectively. In MSS method, preparation of KSN was carried out in both $SrCO_3$–Nb_2O_5–K_2CO_3–KCl system (system I) and $SrNb_2O_6$–Nb_2O_5–KCl system (system II). The results revealed that the single-phase KSN obtained by CMO method was clumped and without obvious acicular morphology, making it difficult to use in texturing processes. In system I, though acicular KSN particles were synthesized by controlling the amount of KCl salt, they were easily contaminated by the presence of blade-like $Sr_2Nb_2O_7$. In contrast, pure KSN particles with high aspect ratio and uniform size were successfully synthesized by controlling the ratio of $SrNb_2O_6/Nb_2O_5$ in the new system (system II). The obtained KSN particles which are 5–30 μm in length and 2–4 μm in diameter are ideal templates for fabricating textured ceramics with tungsten bronze structure. Growth mechanisms in MSS method were also proposed in this work.

Keywords: Grain growth; X-ray methods; Microstructure; Niobates; $KSr_2Nb_5O_{15}$

1. Introduction

Low crystal symmetry materials which exhibit useful anisotropic physical properties in the single-crystal form can be tailored to exhibit anisotropy in the polycrystalline form by texturing. Recently, highly textured ceramics fabricated by templated grain growth (TGG) or by reactive templated grain growth (RTGG) technique have shown excellent anisotropic electrical properties,[1–4] which opens an effective way to fabricate lead-free functional ceramics that mimic the properties of single crystals with the same composition. A target is to obtain textured niobate ceramics with tungsten bronze structure since improved performance can be achieved by texturing.

Both TGG and RTGG rely on the preferential growth of large oriented anisotropic template particles in a fine-grained matrix to produce high-density textured ceramics. It is reported that the platelet-shaped or acicular-shaped template particles in the size range of 5–50 μm, such as $Bi_4Ti_3O_{12}$,[5] Al_2O_3[6] and ZnO,[7] have been successfully used to fabricate textured ceramics. The purity, morphology and size of template particles not only determine the texture orientation but also affect the amount of final texture. $KSr_2Nb_5O_{15}$ (KSN) particles with acicular morphology are preferred templates for fabricating textured niobate ceramics with tetragonal tungsten bronze structure. Recently, though some works on KSN have been reported,[8] the synthesized particles always contain a certain amount of $Sr_2Nb_2O_7$ or $SrNb_2O_6$, making it difficult to control the composition of niobate ceramics. The requirements for the KSN templates can be summarized as: (1) high purity without the impurity of $Sr_2Nb_2O_7$ or $SrNb_2O_6$ (2) acicular, anisometric morphology with proper scale in the size range of 5–50 μm.

In this study, both conventional mixed-oxide (CMO) method and molten salt synthesis (MSS) method were applied to prepare KSN particles. Effects of processing parameters (i.e., the preparing method, the amount of KCl salt, reaction temperature and the ratio of $SrNb_2O_6/Nb_2O_5$) on the phase structure and morphology of the synthesized particles were investigated. Pure KSN particles with better morphology were firstly synthesized in the $SrNb_2O_6$–Nb_2O_5–KCl system by MSS method and some growth mechanisms were also proposed in detail.

2. Experimental procedure

2.1. Sample preparation

In CMO method, reagent-grade powders of $SrCO_3$ (99%), Nb_2O_5 (99.5%) and K_2CO_3 (99%) were used as oxide source.

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They were mixed by ball-milling in ethanol for 12 h using zirconia balls. The mixed powders were dried at 80 °C and then calcined at 1050, 1100, 1150 and 1200 °C for 6 h in air, respectively.

$SrNb_2O_6$ powder was prepared by ball-milling $SrCO_3$ and Nb_2O_5 for 12 h in ethanol using zirconia balls. The mixed powders were dried and calcined at 1100 °C for 4 h. X-ray diffraction (XRD) pattern showed that the $SrNb_2O_6$ was a single phase.

In MSS method, the preparation of KSN was carried out in both $SrCO_3$–Nb_2O_5–K_2CO_3–KCl system and $SrNb_2O_6$–Nb_2O_5–KCl system, using KCl as molten salt. $SrCO_3$, Nb_2O_5, K_2CO_3 and KCl (99.5%) or $SrNb_2O_6$, Nb_2O_5 and KCl were used as raw materials to synthesize KSN particles, respectively. They were first mixed by ball-milling in ethanol for 12 h. After drying at 80 °C for 12 h, the mixtures were put into Al_2O_3 crucibles. Then they were heated at 1150 °C for 6 h in air 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 several times with hot distilled water until Cl^- could not be detected by Ag^+ reagent.

2.2. 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). Dimensional statistic of synthesized particles was collected by measuring SEM images of about 200 grains.

3. Results and discussion

3.1. Conventional mixed-oxide method

Fig. 1 shows the XRD patterns of synthesized particles calcined at different temperature by CMO method. The products calcined at 1050 °C are mainly $KSr_2Nb_5O_{15}$ particles, but some impurities of $SrNb_2O_6$ can also be detected. Further increasing temperature to 1100 °C results in the decrease of $Sr_2Nb_2O_6$ phase and pure KSN phase can be obtained at 1150 °C. SEM micrographs of single-phase KSN particles calcined at 1150 and 1200 °C are shown in Fig. 2. It can clearly be seen in Fig. 2a that the KSN particles are clumped and around 2 μm in length. Even at higher calcining temperature, morphology and size of KSN (Fig. 2b) cannot be improved further. Though the KSN synthesized by CMO method is a single phase, the clumped morphology and smaller size make it difficult to use in texturing processes.

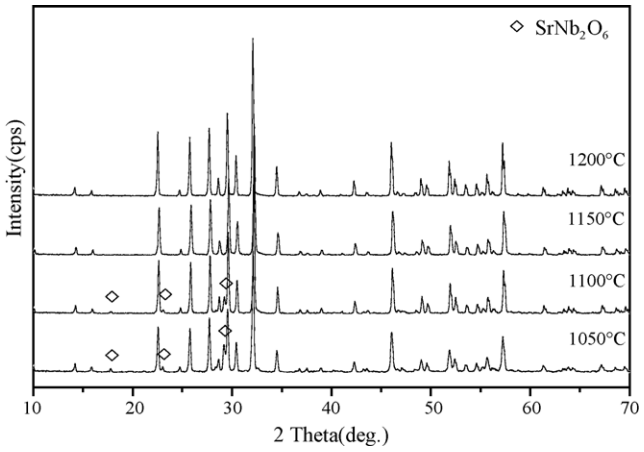

Fig. 1. XRD patterns of synthesized particles calcined at different temperature by CMO method.

3.2. Molten salt synthesis in $SrCO_3$–Nb_2O_5–K_2CO_3–KCl system (system I)

Molten salt synthesis is a well-established technique to prepare powders with platelet-shaped or acicular-shaped morphology. Because of the easy anisometric growth in molten salt liquid, MSS has often been used to synthesize anisotropic $Sr_2Nb_2O_7$, $Bi_4Ti_3O_{12}$ materials, and so on.[9–12] This method is used to synthesize KSN. The oxide source of $SrCO_3$, Nb_2O_5 and K_2CO_3 weighted in the stoichiometric ratio were mixed with KCl salt at various salt to oxide source ratios, which is denoted

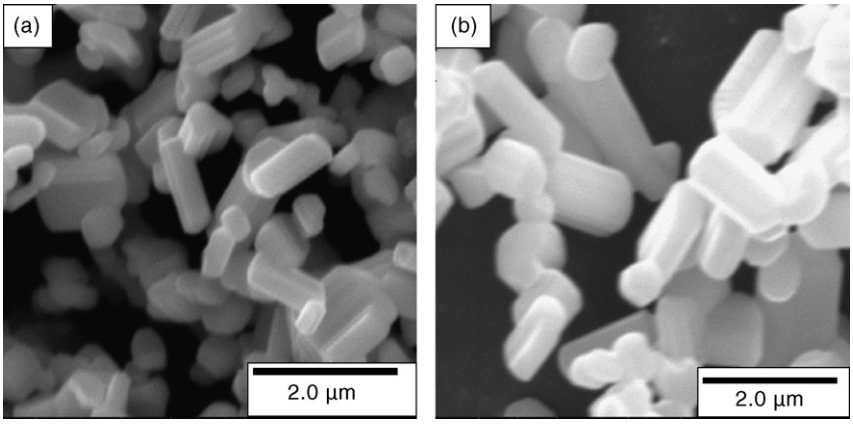

Fig. 2. SEM micrographs of single-phase KSN particles calcined at different temperature: (a) 1150 °C (×20,000); (b) 1200 °C (×20,000).

as R ($R = 0.11$, 0.25, 0.67 and 1.50, respectively). Then the mixtures were calcined at 1150 °C for 6 h. Fig. 3 shows the phase structure of synthesized powders as a function of KCl amount. At $R = 0.11$, single-phase KSN is obtained. When R is above 0.25, the impurity of $Sr_2Nb_2O_7$ can be detected and its amount increases with increasing the amount of KCl. This may indicate that $SrNb_2O_6$ has some solubility in the molten KCl. Neiman et al.[13] reported that in the $SrCO_3$–Nb_2O_5 solid-state system $SrCO_3$ decomposes at low temperature (550–650 °C), which leads to the formation of SrO (reaction 1). Then $SrNb_2O_6$ is formed by reaction between SrO and Nb_2O_5 (reaction 2). Nb_2O_5 is insoluble in alkaline chlorides.[14] SrO has a solubility of about 0.2/100 g KCl at 800 °C and about 1/100 g KCl at 1100 °C.[15] When temperature is above the melting point of KCl (~770 °C), the SrO solubility in molten KCl promotes the $SrNb_2O_6$ solubil-

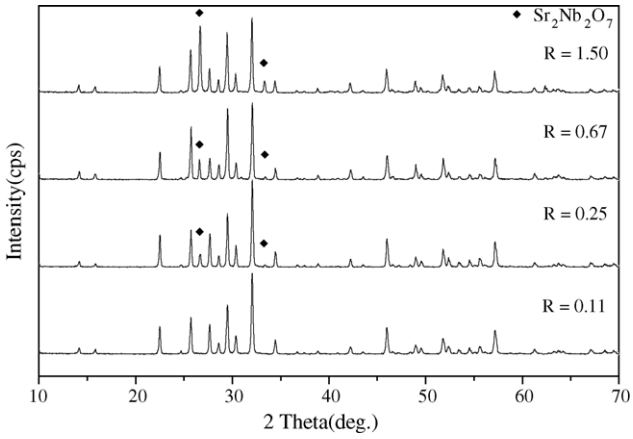

Fig. 3. Effect of KCl amount on the powders compositions.

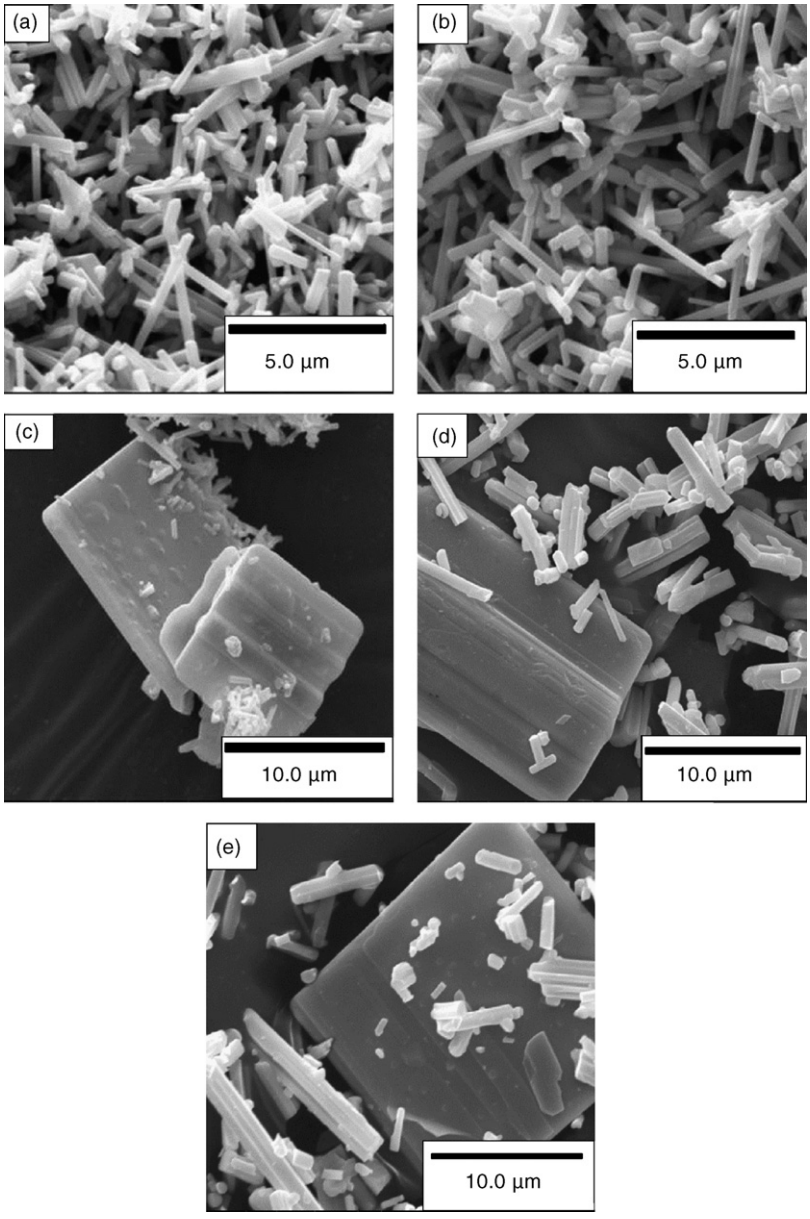

Fig. 4. Effect of KCl amount on the powders microstructure: (a) $R = 0.11$ (×10,000); (b) $R = 0.25$ (×10,000); (c) $R = 0.25$ (×5000); (d) $R = 0.67$ (×5000); (e) $R = 1.50$ (×5000).

ity, releasing Sr^{2+}, O^{2-} and Nb_2O_5. And the $SrNb_2O_6$ solubility is small because it is limited by the SrO solubility. So $Sr_2Nb_2O_7$ is formed by diffusion of Sr^{2+} and O^{2-} in the vicinity and surface of undissolved $SrNb_2O_6$ particles (reaction 3). The possible reactions of $Sr_2Nb_2O_7$ formation are

$$SrCO_3 \rightarrow SrO + CO_2\uparrow, \quad (1)$$

$$SrO + Nb_2O_5 \rightarrow SrNb_2O_6, \quad (2)$$

$$SrNb_2O_6 + SrO \rightarrow Sr_2Nb_2O_7. \quad (3)$$

Fig. 4 shows the effect of KCl amount on the powder microstructure. According to Fig. 4a and b, most of the KSN particles have acicular morphology, but they are clumped. According to Fig. 3, the blade-like product in Fig. 4c is $Sr_2Nb_2O_7$, which also exists in Fig. 4d and e, respectively. And its morphology is similar to that obtained by Zhao et al.[16] in the $SrCO_3$–Nb_2O_5–KCl system. Though the morphology of KSN in Fig. 4d is better than that in Fig. 4b, some of the particles are clumped and the length of them is not uniform. Even when increasing the amount of KCl from $R = 0.67$–1.50, there is little change in the size and morphology of KSN. In system I, the acicular morphology of KSN is related to the solubility of $SrNb_2O_6$ in the molten KCl, which promotes the migration of the ions and accelerates the crystal growth of KSN needles especially in the (0 0 1) facet of tungsten bronze crystal.

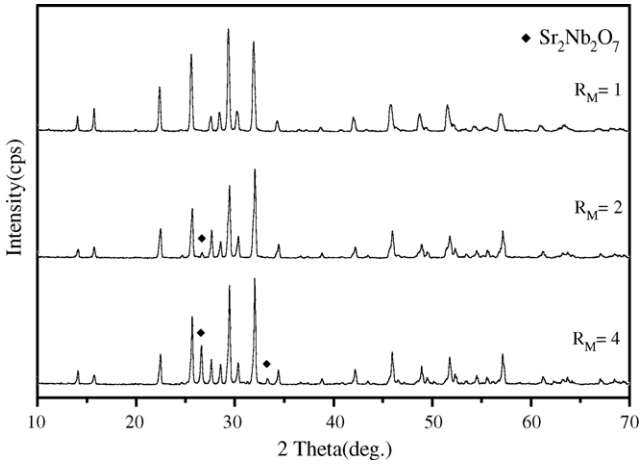

Fig. 5. Effect of the ratio of $SrNb_2O_6/Nb_2O_5$ on the powders compositions.

In this system, synthesized KSN particles are easily contaminated by the impurity of blade-like $Sr_2Nb_2O_7$ and the formation of $Sr_2Nb_2O_7$ cannot be avoided, which make it difficult to control the composition of niobates. In addition, the morphology and size of synthesized particles are not suitable for the texturing requirements. In order to obtain ideal templates, it is necessary to explore a new system.

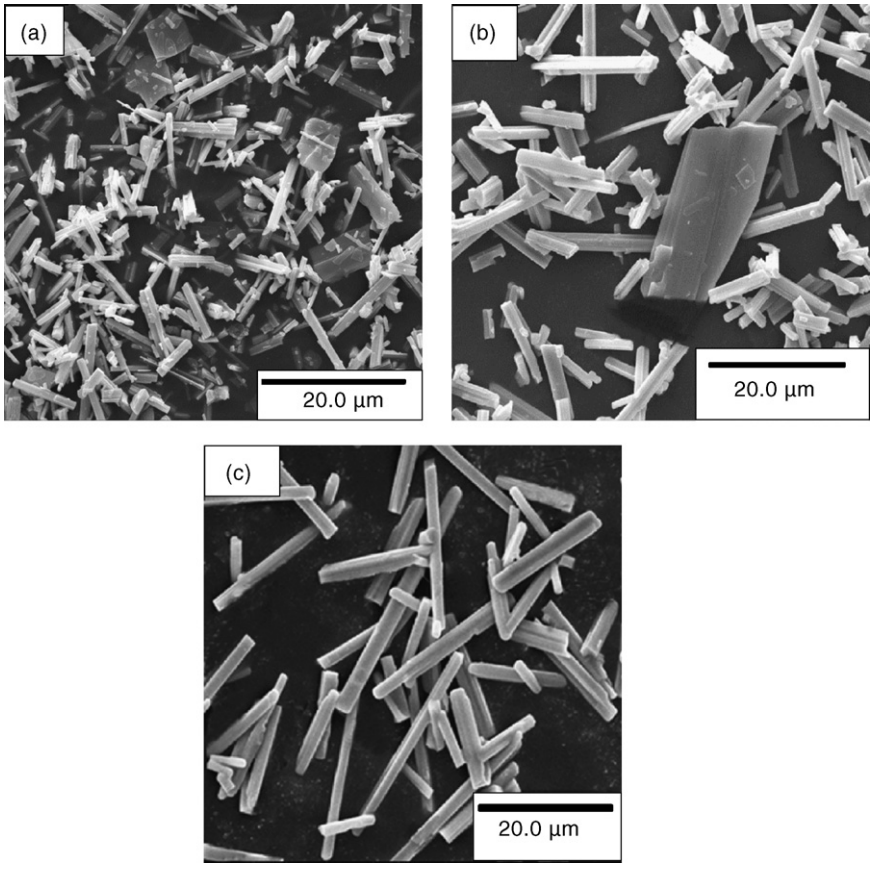

Fig. 6. Effect of the ratio of $SrNb_2O_6/Nb_2O_5$ on the powders microstructure: (a) $R_M = 4$ (×2000); (b) $R_M = 2$ (×2000); (c) $R_M = 1$ (×2000).

3.3. Molten salt synthesis in $SrNb_2O_6$–Nb_2O_5–KCl system (system II)

In system II, KCl plays an important role because it behaves as both a molten salt liquid and the K^+ source for KSN. Forty weight percent $SrNb_2O_6$ and Nb_2O_5 were mixed with 60 wt.% KCl and calcined at 1150 °C for 6 h. The mole ratio of $SrNb_2O_6$ and Nb_2O_5 is denoted as R_M, which is 4, 2 and 1, respectively. Fig. 5 shows the phase structure of powders as a function of R_M. The $Sr_2Nb_2O_7$ amount rapidly decreases with increasing the amount of Nb_2O_5 as observed in Fig. 5. In addition, a pure KSN compound can be synthesized when $R_M = 1$. Nb_2O_5 is reported to be insoluble in alkaline chlorides. Therefore, the possible reactions in the $SrNb_2O_6$–Nb_2O_5–KCl system are:

$$5SrNb_2O_6 + 2KCl \rightarrow 2KSr_2Nb_5O_{15} + SrCl_2, \quad (4)$$

$$SrCl_2 + SrNb_2O_6 + 1/2O_2 \rightarrow Sr_2Nb_2O_7 + Cl_2\uparrow, \quad (5)$$

$$SrCl_2 + Nb_2O_5 + 1/2O_2 \rightarrow SrNb_2O_6 + Cl_2\uparrow . \quad (6)$$

Brahmaroutu et al.[9] determined by using thermogravimetry and XRD that the reaction between $SrCl_2$ and Nb_2O_5 is easier to take place than that between $SrCl_2$ and $SrNb_2O_6$. The existence of reaction (6) limits the synthesis of $Sr_2Nb_2O_7$ to some extent. Therefore, pure KSN particles can be obtained in this system due to the moderate Nb_2O_5 amount.

Fig. 6 shows the powder microstructure as a function of the mole ratio of $SrNb_2O_6$ and Nb_2O_5. The blade-like $Sr_2Nb_2O_7$ particles decreases with the decreasing of R_M and then vanishes as shown in Fig. 6. The results are consistent with the observation analyzed by XRD. Note that the KSN needles in Fig. 6 appear to be thicker due to aggregation of several individual needles, indicating that $Sr_2Nb_2O_6$ has some but finite solubility in the molten KCl. In system II, 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 is in accordance with the growth habits of KSN crystals with tungsten bronze structure which grow faster along c direction than along any other axis direction.

Fig. 7 shows the XRD pattern, SEM micrograph and aspect ratio of KSN particles synthesized at 1150 °C for 6 h with $R_M = 1$. The XRD pattern (Fig. 7a) is indexed to the KSN composition (JCPDS Card # 34-0108), indicating the obtained KSN is pure. The most intense peak is (4 1 0), instead of (3 1 1, 4 2 0),

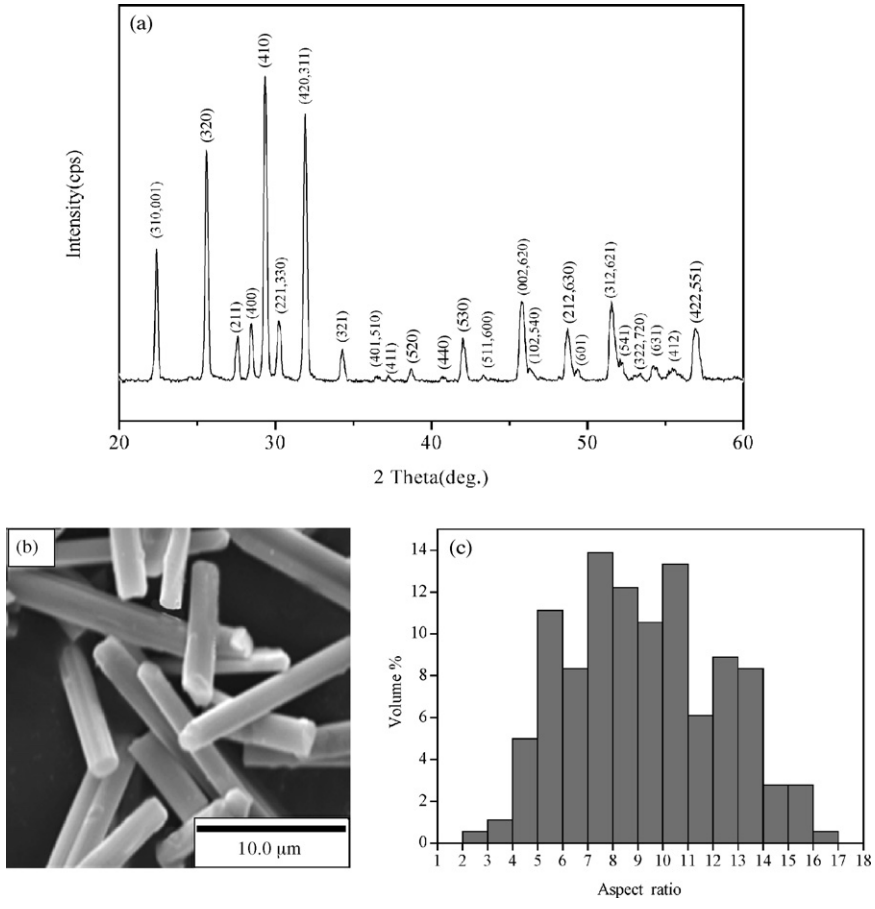

Fig. 7. XRD pattern (a), SEM micrograph (b) and aspect ratio (c) of pure KSN particles synthesized at 1150 °C for 6 h in system II.

and the intensity of (2 1 1) decreases by more than half, which indicates that the fiber axis is along the (0 0 1) orientation. This agrees with the results of Duran et al.[8] Apparently it can be seen in Figs. 6c and 7b that the pure KSN needles are not clumped and with better morphology, whose size is 5–30 μm in length and 2–4 μm in diameter. The thicker diameter of KSN needles ensures that they are not easy to break off during tape casting process. According to Fig. 7c, the aspect ratio of KSN particles is from 2 to 17. In addition, acicular KSN particles synthesized at 1150 °C for 6 h in system II are more uniform and easier to reproduce in size relative to those formed in system I, which is ideal template particles for fabrication of textured ceramics.

4. Conclusions

The anisometric KSN particles were synthesized by using both CMO method and MSS method. The results are summarized as follows:

1. Though pure KSN particles could be obtained by CMO method, the particles without obvious acicular anisotropic morphology are not well suitable for texturing processes.
2. In the $SrCO_3$–Nb_2O_5–K_2CO_3–KCl system, some but finite solubility of $SrNb_2O_6$ in molten KCl can result in the acicular morphology of KSN particles. However, the synthesized KSN particles are always contaminated by the impurity of blade-like $Sr_2Nb_2O_7$, which we think is formed by the reaction between SrO and $SrNb_2O_6$.
3. Pure KSN particles with uniform size can be synthesized in the $SrNb_2O_6$–Nb_2O_5–KCl system due to the reaction between Nb_2O_5 and $SrCl_2$. The obtained anisometric KSN particles have better morphology and higher aspect ratio, whose size is 5–30 μm in length and 2–4 μm in diameter. The thicker diameter which is caused by multiple nucleation sites when KSN forms make them hard to break off during tape casting process. The particles are ideal templates for fabrication of textured ceramics.

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