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Preparation of $SrNb_2O_6$ and $KSr_2Nb_5O_{15}$ particles with anisometric morphology

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Abstract Particles with anisometric morphology were found to play an important role in the fabrication of textured ceramics. $SrNb_2O_6$ particles with tetragonal tungsten bronze (TTB) structure were synthesized by solid-state reaction (SSR) method and molten salt synthesis (MSS) technique respectively. Morphology and the growth mechanism of $SrNb_2O_6$ particles were investigated. It was found that the growth of $SrNb_2O_6$ particles is dominated by diffusion mechanism. $SrNb_2O_6$ particles synthesized by MSS method exhibited higher aspect ratio relative to those prepared by SSR method. Furthermore, anisometric $KSr_2Nb_5O_{15}$ particles, which exhibited higher aspect ratio than $SrNb_2O_6$ particles, were synthesized by MSS method. The length of $KSr_2Nb_5O_{15}$ particles was longer than that of $SrNb_2O_6$ particles.

Keywords Tetragonal tungsten bronze structure · Anisometric particle · Aspect ratio · Morphology

1 Introduction

A scientific breakthrough in the fabrication field of lead-free piezoelectric ceramics is recently reported. The piezoelectric coefficient (d_{33}) of some lead-free textured ceramics can exceed PZT-based ceramics [1], which stimulates the development of lead-free textured ceramics. The grains of textured ceramics grow in a prearranged direction, so the properties of textured ceramics exhibit anisotropic character [2]. For example, textured $Sr_{0.53}Ba_{0.47}Nb_2O_6$ ceramics display the largest d_{33} in <001> direction like a single crystal [3]. Reactive Templated Grain Growth (RTGG) technique and Templated Grain Growth (TGG) technique are proved to the two effective methods to fabricate textured ceramics [3–4]. The achievement of textured structure relies on the oriented grain growth of ceramics on template particles, which are firstly aligned well in the ceramic matrix in a certain direction. Only template particles with anisometric morphology can lead to the formation of highly textured ceramics although the thickness of slurry film in (R)TGG technique determines the proper length of template particles. Higher aspect ratio of template particles can assist to obtain the highly textured ceramics. Hence, the synthesis of template particles with high aspect ratio is a key procedure.

Both $SrNb_2O_6$ and $KSr_2Nb_5O_{15}$ are compounds with tetragonal tungsten bronze (TTB) structure, so as template particles, they can be used to texture ceramics with TTB structure. However, there is very little literature about these particles with anisometric morphology. In present work, anisometric $SrNb_2O_6$ and $KSr_2Nb_5O_{15}$ particles are synthesized by solid-state reaction (SSR) method or by molten salt synthesis (MSS) technique. The morphology and growth behavior of particles are investigated.

2 Experimental

The starting materials were analytical grade $SrCO_3$ (99.5%), Nb_2O_5 (99.6%), K_2CO_3 (99%) and KCl (99%).

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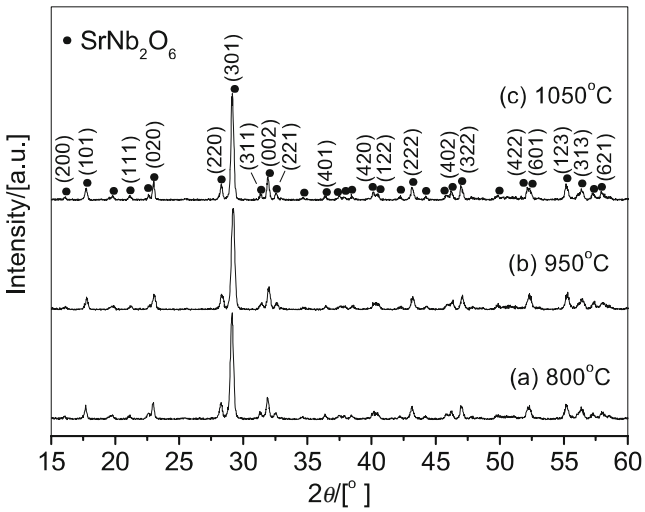

Fig. 1 $SrNb_2O_6$ powders calcined at different temperatures ((a) 800°C, (b) 950°C and (c) 1050°C)

For the synthesis of $SrNb_2O_6$, $SrCO_3$ and Nb_2O_5 were firstly mixed in a final stoichiometry by ball-milling. Ball-milling was carried out using zirconia grinding media in ethanol. Then the slurry was dried. In SSR processing, the dried mixture was calcined at 800–1050°C to prepare the aimed $SrNb_2O_6$ powders. While in MSS processing, the dried mixture was mixed with KCl and calcined at 800°C to get $SrNb_2O_6$ particle powders.

For the synthesis of $KSr_2Nb_5O_{15}$ particle powders, only MSS method was used. $SrNb_2O_6$ powders prepared by SSR method at 1050°C were mixed with KCl in a desired ratio. Then, the KCl-mixed powders were calcined at different predefined temperatures.

After heat treatment, all of the aimed particle powders prepared by MSS technique were separated from the mass of solidified salt by repeated washing in deionized water to ensure complete removal of KCl salt.

The crystalline phases were identified by X-ray diffraction (XRD) (Model D/max-3c, Rigaku Co., Tokyo, Japan) using a Cu Kα radiation and a graphite monochromator. The micrographs of powders were obtained by scanning electron microscopy (SEM) (Model JSM-5800, JEOL, Japan & Model S-570, HITACHI, Japan).

3 Results and discussion

3.1 $SrNb_2O_6$ particle powders

3.1.1 Synthesis of $SrNb_2O_6$ in SSR method

Figure 1 shows XRD patterns of $SrNb_2O_6$ powders prepared at 800–1050°C by SSR method. All the samples are single phase of $SrNb_2O_6$. Figure 2(a–c) show the morphology of $SrNb_2O_6$ particle powders. It is evident that the average length (L) of $SrNb_2O_6$ particles increases with increasing calcining temperature (T). Some statistic data about L and T are shown in Fig. 3. In Fig. 3, ln$L$ is clearly linear dependence of $1/T$, which is the character of diffusion-controlled process. The growth of $SrNb_2O_6$ particles is derived from thermal diffusion. If supplied higher temperature, longer $SrNb_2O_6$ particles would be synthesized. However, the growth rate is so slow by only increasing temperature that the calculated temperature is *ca.* 2367°C for 5 μm $SrNb_2O_6$ particles in length. The aspect ratio of obtained $SrNb_2O_6$ particles by SSR method is too small for (R)TGG technique.

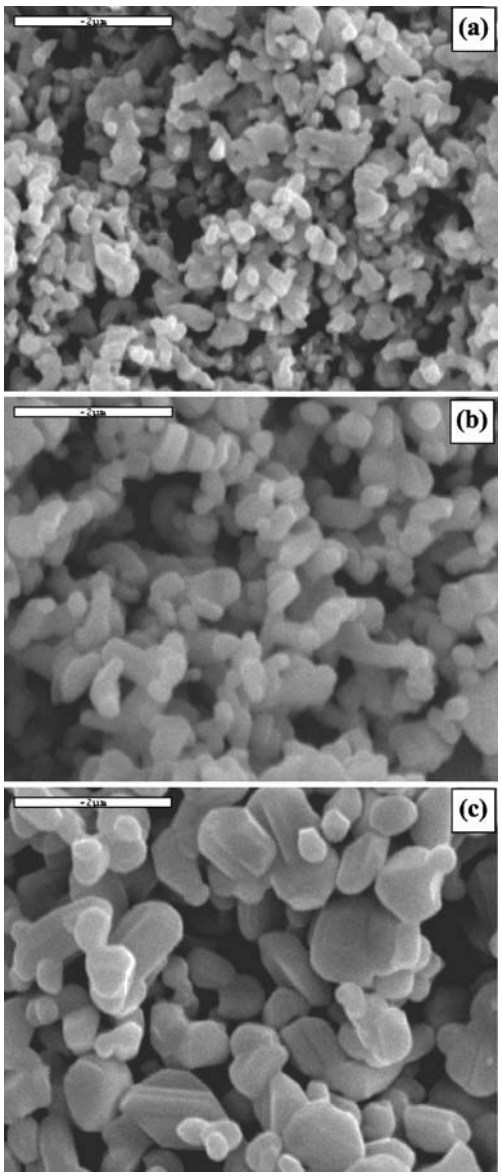

Fig. 2 SEM micrographs of $SrNb_2O_6$ powders calcined at (a) 800°C, (b) 950°C and (c) 1050°C (bar=2 μm)

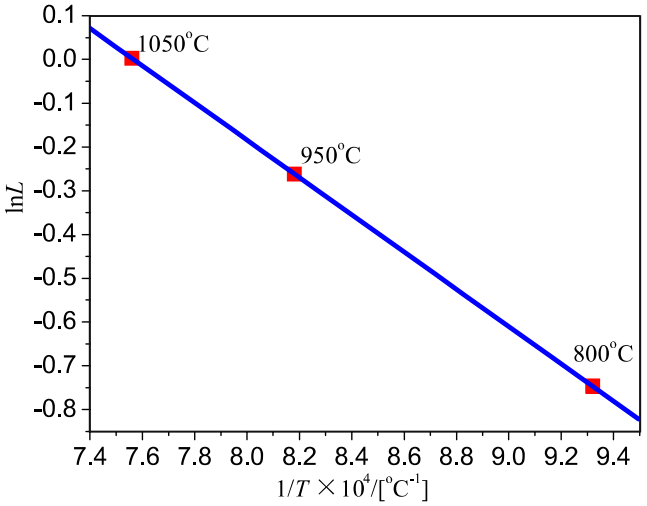

Fig. 3 A curve of ln$L$ versus $1/T$

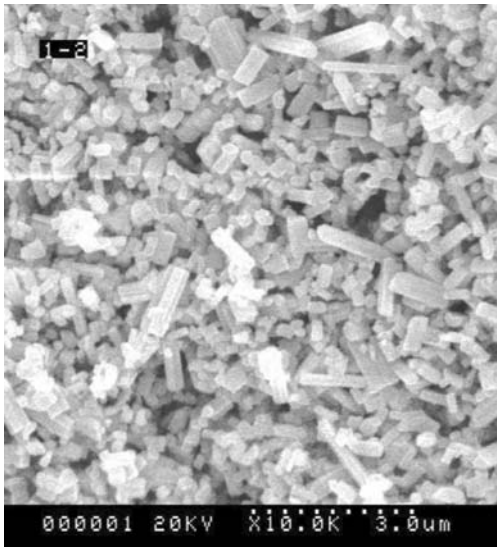

Fig. 5 A SEM micrograph of $SrNb_2O_6$ powders prepared by MSS method at 950°C

3.1.2 Synthesis of $SrNb_2O_6$ in MSS method

Particle powders of $SrNb_2O_6$ were also synthesized by MSS method. Figure 4 depicts XRD patterns of $SrNb_2O_6$ particle powders. XRD patterns show that $SrNb_2O_6$ is a main product in the range of 850–950°C. Above 950°C, $KSr_2Nb_5O_{15}$ is a dominant phase. Morphology of $SrNb_2O_6$ particles synthesized at 950°C for 6h is now shown in Fig. 5. From Fig. 5, we can see $SrNb_2O_6$ particles synthesized by MSS are 0.3–1.5 μm in length and ~0.3 μm in diameter. Compared to Fig. 2, it is distinct that $SrNb_2O_6$ particles synthesized by MSS had higher aspect ratio. Moreover, by this method, the growth rate of $SrNb_2O_6$ particles was also more rapid than that by SSR method. So $SrNb_2O_6$ particles made by MSS technique is more suitable to be as template particles in (R)TGG technique. In liquid molten salt surroundings, the grown particles involve dissolution and precipitation processes, which accelerate the growth rate of $SrNb_2O_6$. At the same time, due to a free circumstance in liquid, particles are apt to grow according their growth habitus. For TTB structure, many particles usually grow in [001] direction. Therefore, particles synthesized by MSS method usually exhibit higher aspect ratio than those synthesized by SSR method. The following synthesis of $KSr_2Nb_5O_{15}$ also supports this argument.

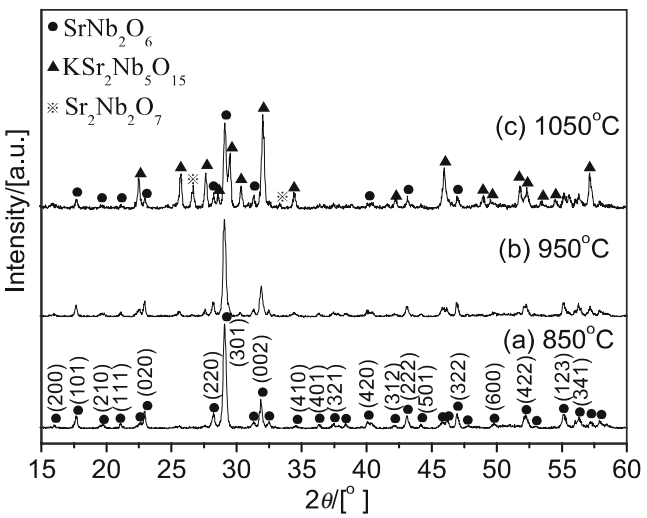

Fig. 4 XRD patterns of $SrNb_2O_6$ powders prepared by MSS method

3.2 $KSr_2Nb_5O_{15}$ particle powders

Although anisometric $SrNb_2O_6$ particles can be synthesized by MSS technique, the size of particles is limited by calcined temperature. Sometimes, we need longer template particles with TTB structure for a thick slurry film.

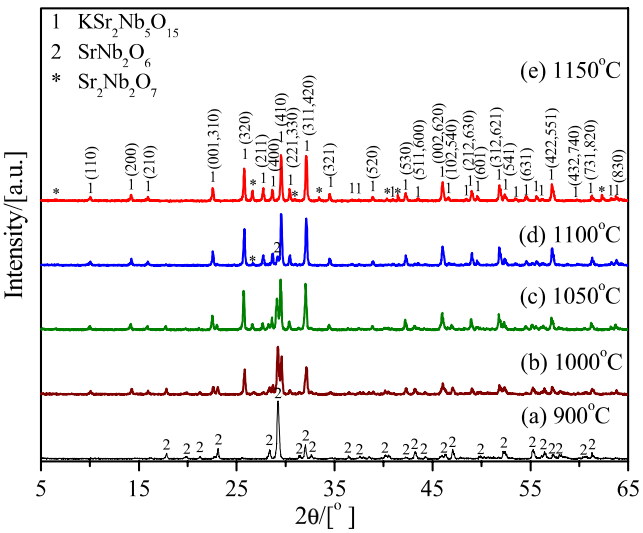

Fig. 6 XRD patterns of $KSr_2Nb_5O_{15}$ particle powders synthesized at different temperatures

Fig. 7 A SEM micrograph of $KSr_2Nb_5O_{15}$ particle powders synthesized at 1150°C

Consequently, the synthesis of anisometric $KSr_2Nb_5O_{15}$ particles was investigated.

Using $SrNb_2O_6$ and KCl as raw materials, $KSr_2Nb_5O_{15}$ particles were synthesized by MSS method. XRD patterns of the powders synthesized at different temperatures are shown in Fig. 6. Above 1000°C, the dominant phase was $KSr_2Nb_5O_{15}$. Impurities in powders were $SrNb_2O_6$ and small amount of $Sr_2Nb_2O_7$. The impurity of $SrNb_2O_6$ phase diminishes as sintering temperature increases. At 1150°C, no $SrNb_2O_6$ phase was detected. Accordingly, the formation mechanism of $KSr_2Nb_5O_{15}$ phase can be described by the following equation:

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

A little $Sr_2Nb_2O_7$ impurity in powders is resulted from the following reaction.

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

Figure 7 shows a typical morphology of $KSr_2Nb_5O_{15}$ particles. It is evident from Fig. 7 that $KSr_2Nb_5O_{15}$ particles had high aspect ratio. The length of $KSr_2Nb_5O_{15}$ particles was in the range of 5–40 μm, which was longer than that of $SrNb_2O_6$ particles. They are very suitable for thick film fabrication in (R)TGG technique. In addition, these $KSr_2Nb_5O_{15}$ particles have a prominent character. That is, the outside surfaces of particles are always stepwise. We have already confirmed this phenomenon is derived from the big starting size of $SrNb_2O_6$ particles [5].

4 Conclusions

Both $SrNb_2O_6$ particles and $KSr_2Nb_5O_{15}$ particles were synthesized by SSR method or MSS technique. Particles growth mechanism, powders phases and particles morphology were discussed. In SSR processing, the growth mechanism of $SrNb_2O_6$ particle is determined by thermal-diffusion process. The particle growth rate in MSS is faster than that in SSR processing because the dissolution and precipitation processes accelerate the growth of particles in molten liquid salt. In addition, molten liquid salt provides a free circumstance, which makes the particle grows along its habitual direction. $KSr_2Nb_5O_{15}$ particles synthesized by MSS technique exhibited higher aspect ratio and longer size than $SrNb_2O_6$ particles.

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