Structural and Piezoelectric Properties of Sr$_{0.6}$Ba$_{0.4}$Nb$_2$O$_6$ Micro-rods Synthesized by Molten-Salt Method

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Abstract: Sr$_{0.6}$Ba$_{0.4}$Nb$_2$O$_6$ micro-rods are prepared by the molten-salt method with K$_2$SO$_4$, KCl, K$_2$SO$_4$, and KCl as fluxes. It reveals that the Sr$_{0.6}$Ba$_{0.4}$Nb$_2$O$_6$ synthesized with KCl as a flux exhibits a single phase with tetragonal tungsten bronze structure. The measurement of X-ray diffraction indicates that the Sr$_{0.6}$Ba$_{0.4}$Nb$_2$O$_6$ micro-rods synthesized at 1300 °C are anisotropic. The morphology of the powders is examined by transmission electron microscope. It reveals that the length-diameter ratio of Sr$_{0.6}$Ba$_{0.4}$Nb$_2$O$_6$ micro-rods increases with increasing annealing temperature from 900 °C to 1300 °C. At 1300 °C, the rod possesses a large length-diameter ratio of 8:1. Moreover, the analysis of the piezoelectric properties of single micro-rods using a piezo-response force microscope indicates that the domains of the material are arranged along its radial direction.

Key words: Sr$_{0.6}$Ba$_{0.4}$Nb$_2$O$_6$ micro-rods; molten salt method; X-ray diffraction patterns; transmission electron microscope (TEM) imaging; piezoresponse force microscope (PFM) detection

0 Introduction

Piezoelectric materials have been extensively applied in informatics, lasers, navigation, biology, etc.$^{[1-4]}$. Nowadays, the lead zirconate titanate (PZT) family is worldwide used$^{[1-4]}$. However, PZT materials contain a large amount of Pb which is an environmental pollutant. Therefore, this study on the Pb-free preparation of piezoelectric materials and the development of the preparation technologies is expected to shape a more promising future for the application of piezoelectric materials$^{[4,5]}$.

With tetragonal tungsten bronze structure, strontium barium niobate (SBN) Sr$_x$Ba$_{1-x}$Nb$_2$O$_6$ (0.25 $\leq x \leq$ 0.75), is a solid solution crystal made of SrNb$_2$O$_6$ and BaNb$_2$O$_6$$^6$. This type of material has been widely recognized and presents excellent pyroelectric, electro-optic, piezoelectric, and photorefractive properties in industry.

Traditionally, SBN ceramics are prepared by means of a solid state reaction method. However, the sintering temperature of SBN is generally high, i.e. $1100-1480$ °C$^{[7,8]}$. Compared with the solid state reaction method, the powders prepared by molten salt method are uniform without agglomeration or with weak agglomeration. Moreover, the reaction process and the subsequent cleaning process of the molten salt synthesis (MSS) method are beneficial for obtaining one-dimensional crystals with high purity as the salts can be easily removed. What’s more, it is a large scale, facile and environmentally friendly synthesis method. There are several reports on MSS of preparing large quantities of SBN or other textured crystals at low temperatures$^{[9-12]}$.

Recently, the piezoelectric properties of one-dimensional materials were studied using piezo-response force microscope (PFM)$^{[12,15]}$. Hence, 

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the PFM study on Sr$_{0.6}$Ba$_{0.4}$Nb$_2$O$_6$ would be desired. In the present work, Sr$_{0.6}$Ba$_{0.4}$Nb$_2$O$_6$ micro-rods are prepared by the molten salt method with K$_2$SO$_4$, KCl-K$_2$SO$_4$, and KCl as fluxes. The result indicates that the monophase Sr$_{0.6}$Ba$_{0.4}$Nb$_2$O$_6$ with tetragonal tungsten bronze structure can be prepared using KCl as a flux. Upon increasing the annealing temperature from 900 °C to 1 300 °C, the length-diameter ratio gradually increases and rods with a length-diameter ratio of 8 : 1 can be obtained at 1 300 °C. The PFM results reveal that the domain structure of the rod is radially arranged, which makes Sr$_{0.6}$Ba$_{0.4}$Nb$_2$O$_6$ micro-rods a favourable piezoelectric material.

2 Results and Discussion

In order to examine the ideal flux, the XRD was used to observe the Sr$_{0.6}$Ba$_{0.4}$Nb$_2$O$_6$ powders synthesized with K$_2$SO$_4$, KCl-K$_2$SO$_4$, and KCl as fluxes at different temperatures. Fig. 1 presents XRD patterns of the Sr$_{0.6}$Ba$_{0.4}$Nb$_2$O$_6$ powders synthesized with K$_2$SO$_4$ as the flux at 1 300 °C and synthesized with KCl-K$_2$SO$_4$ as the flux at 900 °C, 1 100 °C and 1 300 °C. As is shown in Fig. 1, apart from the diffraction spectrum of the Sr$_{0.6}$Ba$_{0.4}$Nb$_2$O$_6$ powders, the samples synthesized with K$_2$SO$_4$ have peaks from other components in their XRD patterns at 1 300 °C. This implied that the samples synthesized with K$_2$SO$_4$ contained other impurities including BaSO$_4$, which is consistent with the previous reports. Although these BaSO$_4$ can be eliminated by conventional sedimentation treatment, it involves a complicated procedure, indicating a non-ideal synthetic effect. Meanwhile, we can find that the intensities of peaks (330) and (550) are much higher than those of the standard spectrum [Powder Diffraction Standards (JCPDS) Card No. 39-0265], indicating that Sr$_{0.6}$Ba$_{0.4}$Nb$_2$O$_6$ crystals have a preferential growth direction. When the flux was replaced by 50 at. % KCl, the impurities disappeared at 1 100 °C. The diffraction intensities of the (320) and (410) peaks for the obtained powders were enhanced, accompanied by a decrease in those of the (211) and (311) peaks. As a result, the (410) became the strongest peak, which indicates that the growth direction differs...
with the different flux between K₂SO₄ and mixed KCl and K₂SO₄. Nevertheless, the obtained powders were anisotropic, suggesting that 1 300 °C is an ideal synthesis temperature, at which a one-dimensional structure with ideal length-diameter ratio can be generated.

The obtained Srₓ₀.₆Baₓ₀.₄Nb₂O₆ powders in KCl flux exhibit single phase at low temperature of 900 °C. This temperature is much lower than 1 200—1 480 °C in traditional solid state method, indicating that the molten synthesis method is an effective way to obtain single phase Srₓ₀.₆Baₓ₀.₄Nb₂O₆ powders in the flux of KCl at low temperature. The peaks of (311) is the strongest at 900 °C and 1 100 °C, while the (410) peak becomes the strongest for the powders at 1 300 °C, suggesting the growth direction is changing when the temperature is higher.

Considering the impurities in the samples synthesized with K₂SO₄, only those samples prepared in KCl were analysed by TEM. Fig. 3 show the typical TEM images of the samples obtained at different temperatures. Similar to the inferences based on the XRD spectra, all the samples synthesized at 1 300 °C presented favourable one-dimensional characteristics including good length-diameter ratio, ease of dispersion, and non-agglomeration. As can be seen from Fig. 3(c), the length-diameter ratio of this rod is high up to 8 : 1, which is smaller than the previous report[8]. In contrast, the samples acquired at

Fig. 1 XRD patterns of Srₓ₀.₆Baₓ₀.₄Nb₂O₆ powders synthesized with K₂SO₄ as the flux at 1 300 °C and synthesized with KCl-K₂SO₄ as the flux at 900 °C, 1 100 °C and 1 300 °C.

Fig. 2 shows XRD patterns of Srₓ₀.₆Baₓ₀.₄Nb₂O₆ powders synthesized with KCl as the flux at different temperatures from 900—1 300 °C. These patterns are almost the same with the powders synthesized with the flux of 50 at. % KCl and 50 at. % K₂SO₄ but quite different with K₂SO₄.

Fig. 2 XRD patterns of Srₓ₀.₆Baₓ₀.₄Nb₂O₆ powders synthesized with KCl as the flux at different temperatures

Fig. 3 TEM images of Srₓ₀.₆Baₓ₀.₄Nb₂O₆ powders
100 °C also showed good one-dimensional characteristics, but their length-diameter ratio was slightly inferior to that of the samples synthesized at 1300 °C. These samples were not easily dispersed with a tendency to agglomerate. And the samples synthesized at 900 °C exhibited poor one-dimensional characteristics, as there was serious agglomeration causing difficulties with their dispersal. Moreover, no obvious one-dimensional structures could be observed.

The piezoelectric property in local regions of Sr$_{0.6}$Ba$_{0.4}$Nb$_2$O$_6$ powders synthesized in KCl at 1300 °C using PFM. A small amount of the synthesized Sr$_{0.6}$Ba$_{0.4}$Nb$_2$O$_6$ powders was dispersed in an acetone solution by ultrasonic machine. Some floating droplets were deposited on the Pt/Ti/SiO$_2$/Si base and then dried. In the testing process, to avoid the influence of some uncontrollable factors on the Sr$_{0.6}$Ba$_{0.4}$Nb$_2$O$_6$ powders, the base was heat-treated at 500 °C for 2 h so that the Sr$_{0.6}$Ba$_{0.4}$Nb$_2$O$_6$ powders could be fully adsorbed on. Among a rod of Ø 500 nm × 4 μm, the smoothest and cleanest part with a diameter of about 500 nm and a length of about 800 nm was selected for analysis. A rough estimation shows that the maximum applied filed is about 24 kV/cm. Fig. 4(a, b) show the morphologies and radial piezoelectric responses of the Sr$_{0.6}$Ba$_{0.4}$Nb$_2$O$_6$ powders observed by AFM and PFM, respectively. As shown in Fig. 4(a), the rod surface can be clearly observed. While the alternate bright/dark regions in Fig. 4(b) present that domain structures are radially arranged. The typical “butterfly shaped” amplitude-voltage hysteresis loop and a square phase-voltage hysteresis loop are shown in Fig. 4(c, d), which verified the piezoelectric effect in the Sr$_{0.6}$Ba$_{0.4}$Nb$_2$O$_6$ powders. Asymmetry behaviors were observed in these two hysteresis loops. Similar behaviors were also reported in PFM study in copolymer of vinylidene fluoride and trifluoroethylene P (VDF-TrFE) nanorods$^{[15]}$. The shift of the loop along the voltage axis might be ascribed to the asymmetry of the tip/sample/bottom electrode configuration or space charges of the interfaces between sample/electrode and the sample/tip$^{[16]}$.

![Image](image.png)

Fig. 4 Piezoelectric properties in local regions of Sr$_{0.6}$Ba$_{0.4}$Nb$_2$O$_6$ rod studied by a scanning probe microscope
3 Conclusions

With K$_2$SO$_4$, KCl-K$_2$SO$_4$, and KCl as fluxes, Sr$_{0.5}$Ba$_{0.5}$Nb$_2$O$_6$ micro-rods were prepared by a molten salt method. Then, the obtained samples were detected by XRD and their morphologies were observed using TEM. In addition, PEM was applied to detect the piezoelectric properties of the samples. The results showed that the Sr$_{0.5}$Ba$_{0.5}$Nb$_2$O$_6$ micro-rods synthesized with KC1 as the flux at 1 300 °C were anisotropic with a favourable length-diameter ratio and radially arranged domain structures. What’s more, the highly grain-oriented ceramics may be economically prepared with these one-dimensional Sr$_{0.5}$Ba$_{0.5}$Nb$_2$O$_6$ rods by the previous reported method$^{[17,18]}$, which needs further investigation.

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