Preparation and characterization of $Sr_{0.5}Ba_{0.5}Nb_2O_6$ glass-ceramic on piezoelectric properties

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We studied the influence of heat treatment time on the optical, thermal, electrical, and mechanical properties of strontium barium niobate ($Sr_{1-x}Ba_xNb_2O_6$; hereafter SBN) piezoelectric glass-ceramics with tungsten bronze-type structure, which have good piezoelectric properties and are important lead-free piezoelectric materials. We found that the best heat treatment time is 4 h. The properties of the prepared materials are better than that of SBN ceramics and the glass-ceramic growth is faster than the SBN crystal when the heat treatment time of the SBN piezoelectric glass-ceramic is controlled, reducing the preparation costs greatly.

Keywords: strontium barium niobate, heat treatment time, piezoelectric coefficient, permittivity

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1. Introduction

Piezoelectric materials have been widely used in the transformation between mechanical energy and electric energy. Ceramic materials possess a high dielectric constant but a low dielectric strength. Polymer materials possess a high dielectric strength but a small dielectric constant (typically < 5). Glass-ceramics are a kind of special polymeric material which has the advantage of high dielectric constant and high dielectric strength. $Sr_{0.5}Ba_{0.5}Nb_2O_6$ piezoelectric glass-ceramic is generally prepared by sintering methods.[1,2] However, it is difficult to eliminate porosity via those methods, leading to low breakage strength. Niobate-based piezoelectric ceramic systems often contain lead which may cause environmental pollution,[3,4] so a variety of methods have been used to research piezoelectric ceramic glass,[5,6] which shows that lead-free piezoelectric ceramic glass has excellent development prospects.

Compared with other energy storage materials, the tungsten bronze-type structure and perovskite-type structure of glass-ceramics have attracted more attention. The perovskite-type structure of glass-ceramics has been studied in our previous work.[7] Hence, we focus on tungsten bronze-type structure of glass-ceramics in this paper. Glass-ceramics with tungsten bronze-type structure is a kind of most relevant material currently. The ion at each position leads to a strong spontaneous displacement polarization below the temperature of Curie point, which makes the crystals exhibit a high dielectric constant in the macro. At present, the study of glass-ceramics with tungsten bronze-type structure is mostly concentrated in the glass system whose main crystal phase is the niobium acid.

Du *et al.*[8] found that tungsten bronze-type structure $PbNb_2O_6$ appears in the heating temperature range of 850–900 °C in the Na_2O–PbO–Nb_2O_5–SiO_2 system, and the content of $PbNb_2O_6$ increases with the increase of the crystallization temperature. Reece *et al.*[9] found that (Sr, Ba, Pb) Nb_2O_6 glass-ceramics can be obtained in the PbO–BaO–SrO–Nb_2O_5–B_2O_3–Al_2O_3–SiO_2 system by sintering process, they also found that the content of Pb plays an important role in the dielectric constant of the sample and the dielectric constant increases with the increase of the content of Pb. Cheng *et al.*[10] found that in the PbO–BaO–SrO–Nb_2O_5–B_2O_3–SiO_2 system, only the (Pb, Sr, Ba) Nb_2O_6 (PSBN) crystal phase appears in the sample in the heating temperature range of 700–1000 °C and the content of PSBN phase increases with the increase of heating temperature in the crystallization temperature range.

However, all these materials used in the past contain Pb, which pollutes the environment, which is not conducive to long-term development. Therefore, niobate lead-free piezoelectric glass-ceramics was studied in this paper. The strontium barium niobate ($Sr_{1-x}Ba_xNb_2O_6$; hereafter SBN) with tungsten bronze-type structure was prepared by the high-temperature melting method. The effect of heat treatment time on the performance of the glass-ceramics was studied by experimental comparisons. We found that SBN lead-free piezoelectric glass-ceramics can also have a high dielectric constant and a high piezoelectric coefficient.

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2. Experiments

Using analytically pure SiO_2, $SrCO_3$, $Ba(NO_3)_2$, Nb_2O_5, and H_3BO_3 as starting materials, we prepared glass-ceramics with different proportions. When the content of SiO_2 exceeded 60% (molar ratio), the melt temperature of the glass rose and the viscosity increased. It was difficult to remove small bubbles in the glass. When the content of the SiO_2 was less than 35%, the SBN glass crystallized easily. Therefore, the content of SiO_2 was maintained between 35% and 60%. The molar ratio of Sr^+ and Ba^+ was maintained at 1:1 and that of (Sr^{2+}+Ba^{2+}): Nb^{5+} between 1:2 and 1.5:2. To reduce the viscosity of the glass, we added an appropriate amount of boric acid. The starting materials were placed into a ball mill for mixing. The mixture was then transferred to a silicon carbide resistance furnace and melted for 20 min at the temperature of 1470 °C. It was then placed in a blender for 1.5 h. The SBN glass liquid was placed on a pre-heated iron to mold in order to obtain SBN glass samples. The glass was annealed in a muffle furnace at 550 °C for 10 h to obtain the SBN glass. Finally, the SBN glass was placed in a muffle furnace at 680 °C and fired for 2 h, 4 h, 6 h, 8 h, and 10 h to produce five SBN glass-ceramic samples. In this way, the prepared glass has a short production cycle and the glass-ceramic grain growth may be easily controlled, which is an advantage for large-scale industrial production.

3. Results and discussion

3.1. Thermal properties of the SBN glass

The SBN glass was placed in the thermal expansion coefficient tester. The transition temperature of the SBN glass was about 655 °C and the softening temperature of the SBN glass was about 701 °C as shown in Fig. 1. Thus, the appropriate heat treatment temperature is about 680 °C. When the temperature is above 700 °C, which exceeds the softening temperature of the SBN glass, the SBN glass-ceramics will deform. This is not good for the next stages of processing and testing. According to the measured data, it can be calculated that the thermal expansion coefficient of the SBN glass-ceramics is 70×10^{-7}°C^{-1} in the temperature range of 200 °C–300 °C.

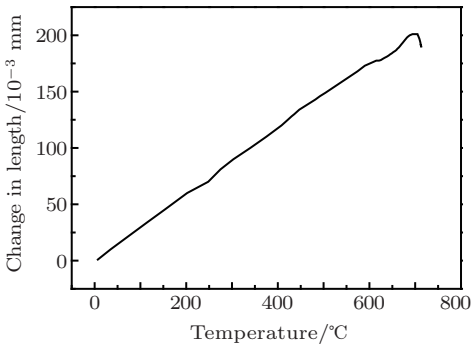


Fig. 1. The curve of thermal expansion coefficient of SBN glass.

3.2. Microstructure of SBN glass-ceramics

Figures 2(a)–2(e) show SEM micrographs of the SBN glass-ceramics by heat treatment for 2 h, 4 h, 6 h, 8 h, and 10 h, magnified 10000 times, respectively. Figure 2(a) shows an SEM micrograph of the irregular section. It is clear that microcrystalline particles have been generated and encircled by glass. Figure 2(b) shows that there are a large number of

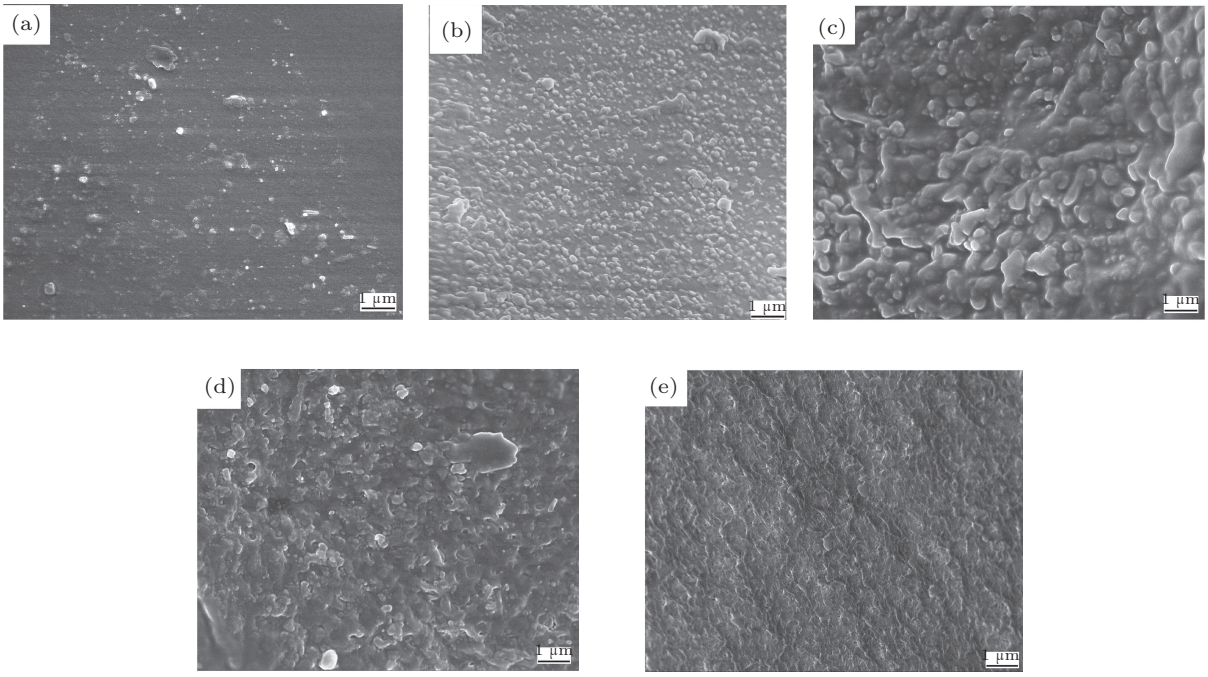


Fig. 2. SEM micrographs of SBN glass by heat treatment for 2 h (a), 4 h (b), 6 h (c), 8 h (d), 10 h (e) magnified 10000 times respectively.

microcrystalline particles with unequal sizes on the irregular glass surface. Thus, for heat treating, the best heat treatment time is 4 h. In Fig. 2(c), the microcrystalline particles grow extremely large and there is little glass. The abnormal grain growth may be due to the high obstruction caused by the particles or impurities in the second phase during the normal grain growth. A few grains may grow into coarse grains by consuming fine grains nearby. However, it should be avoided because the coarse grain structure would lead to poor mechanical properties of materials.[11] In Figs. 2(d) and 2(e), we can see that the microcrystalline particles become small and dense. It is probable that the crystallization time was too long and had a detrimental effect on the glass-ceramic properties.

Figure 3(a) shows that the size of the crystallite is moderate. However, in Fig. 3(b), the crystallites exhibit a non-uniform distribution. The size of crystallite is about 107 nm. Hence, the best heat treatment time for the SBN glass-ceramic appears to be 4 h.

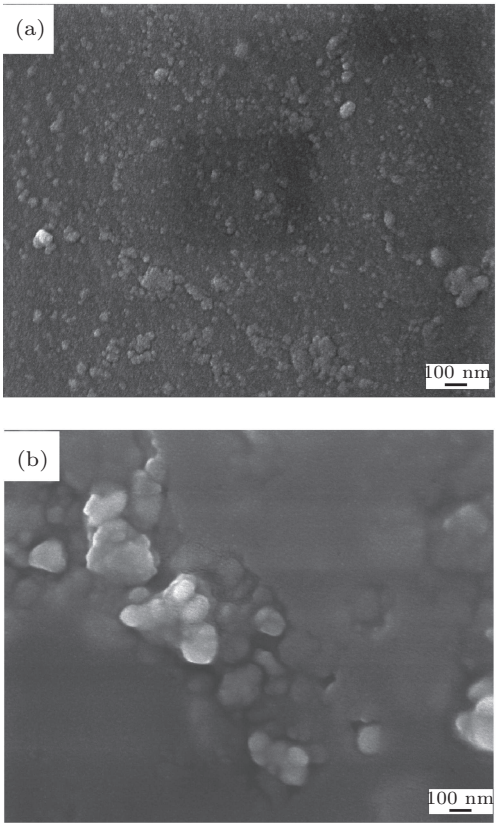


Fig. 3. SEM micrographs of SBN glass by heat treatment for 4 h (a) and 6 h (b) magnified 50000 times, respectively.

3.3. Structure of the SBN glass-ceramics

Figure 4 shows the XRD curve of the SBN glass by heat treatment for 4 h. The SBN glass-ceramics clearly display a tetragonal tungsten bronze-type structure. There is no other miscellaneous peak and the main phase of glass-ceramics is $Sr_{0.5}Ba_{0.5}Nb_2O_6$. Using the Scherrer formula

$$D = \frac{0.89\lambda}{\beta \cos\theta}, \tag{1}$$

where λ is the wavelength of x-rays (Å), β is the half height of the diffraction peak width (°), and θ is the angle of diffraction (°), we obtain that the particle size is about 50 nm, which is consistent with the SEM test data.

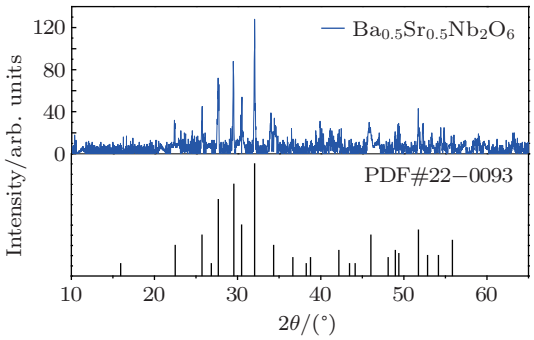


Fig. 4. (color online) XRD curve of SBN glass by heat treatment for 4 h.

3.4. Mechanical properties of the SBN glass-ceramics

A hardness tester was used to investigate the hardness of the SBN glass-ceramics. The hardness was calculated using the following equation:

$$\mathrm{HV} = \frac{2P\sin(136^\circ/2)}{d^2} = 1.8544\frac{P}{d^2}, \tag{2}$$

where d is the indentation length (mm) and P is the load (kilogram-force) of the SBN glass-ceramics.

The hardness of the same samples was measured 5 times and the mean value was calculated. Figure 5 shows the Vickers hardness of the SBN glass-ceramics. In Fig. 5, the Vickers hardness of the SBN glass-ceramics first increases and then decreases with the heat treatment time. As the heat treatment time increases, tiny microscopic particles appear in the original glass, which changes the internal structure of the glass and reduces its hardness. When the heat treatment time is prolonged, a large amount of dense microscopic particles appear in the glass and its hardness changes again, achieving its maximum hardness. When the heat treatment time is 6 h, the hardness of the SBN glass-ceramics is the lowest, 634 kg/mm^2. When the heat treatment time is 8 h, the hardness of the SBN glass-ceramics is the highest, 728 kg/mm^2.

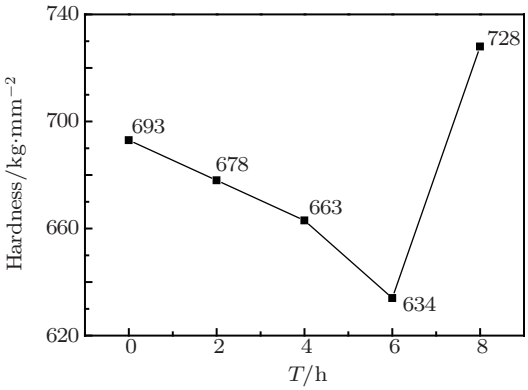


Fig. 5. The Vickers hardness of SBN piezoelectric glass-ceramics with different heat treatment time.

3.5. Transmittance of the SBN glass-ceramics

Transmittance is a mainly-used quantity to describe the transparency of substance. When the transmittance of a substance is greater than 10%, the substance is defined as a transparent body, but when it is less than 10%, the substance is defined as a non-transparent body.[12] We measured the transmittance of the SBN glass-ceramics after 0 h, 2 h, 4 h, 6 h, and 8 h heat treatment time using a spectrophotometer and the results are shown in Fig. 6, where the thickness of samples is 0.4 mm and the measurement range is 0–1500 nm.

Figure 6 shows that the SBN glass-ceramics permit visible light (wavelength range of 390–780 nm) and infrared (wavelengths greater than 780 nm) through, but block ultraviolet light (wavelength range 390 nm). With the increase of the heat treatment time, the transmission of the SBN glass-ceramics decreases steadily. This indicates that with the increase of heat treatment time, the size of the small grains in the glass increases, reducing the light transmission through the glass, and thus transmissivity. After a heat treatment time of 8 h, small grains are arranged densely and uniformly in the glass, forming a completely opaque glass-ceramic.

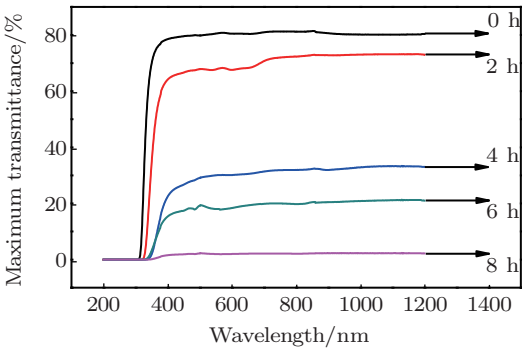


Fig. 6. (color online) The transmittance of the SBN glass-ceramics changing with wavelength under different heat treatment time.

3.6. Electrical properties of the SBN glass-ceramics

3.6.1. Permittivity of the SBN glass-ceramics

An Agilent-16451B was used to measure the dielectric constant of the SBN piezoelectric ceramic glass following the equation:

$$\varepsilon = \frac{4\pi KdC}{S}, \tag{3}$$

where K is the electrostatic constant, $K = 8.988 \times 10^9$ N·m^2·C^{-2}, d is the plate spacing (mm), C is the measuring capacitance (pF), and S is the acreage (cm^3).

3.6.2. Piezoelectric coefficient of the SBN glass-ceramics

The sample was heated for 20 min and then placed in a ZJ-3AN quasi-static d_{33} meter to obtain piezoelectric coefficient d_{33} (pC·N^{-1}).

Table 1 shows the permittivity and piezoelectric coefficient of the SBN ceramic-glass for heat treatment time of 2 h, 4 h, 6 h, and 8 h. We can find that the SBN piezoelectric glass-ceramic has a high permittivity which is very close to the permittivity of PZT and higher than that of SBN-based piezoelectric ceramics. Thus, the SBN piezoelectric glass-ceramic is a potential alternative to leaded piezoelectric materials.

Table 1. Permittivity and piezoelectric coefficient of the glass.

Sample	2 h	4 h	6 h	8 h
ε_r	1588	1653	723	231
d_{33}/pC·N^{-1}	152	194	136	83

4. Conclusions

A novel glass-ceramic has been successfully prepared by heat treating SBN glass at 680 °C with various durations (2 h, 4 h, 6 h, 8 h, or 10 h). The analysis of the resulting samples leads to the following conclusions.

1) The transition temperature of SBN glass is about 655 °C and the softening temperature of the SBN glass is about 701 °C. The best heat treatment temperature for the SBN glass-ceramics was determined to be 680 °C. The thermal expansion coefficient of the SBN glass-ceramics was found to be 7×10^{-6} °C^{-1} from 20 °C to 300 °C.

2) The optimum heat-treatment time for an SBN glass-ceramic was determined to be 4 h, at which the crystallite size in the glass-ceramics is approximately 50 nm, which is consistent with the results obtained by SEM and XRD.

3) As the heat treatment temperature increases, the hardness of the SBN glass-ceramics first increases, and then decreases, the transmittance of the glass decreases.

4) The highest dielectric constant ($\varepsilon_r = 1653$) and piezoelectric coefficient ($d_{33} = 194$ pC·N^{-1}) were obtained for the SBN glass-ceramics heat treated for 4 h.

References

[1] Shyu J J and Chen C H 2003 *J. Ceramics Int. Soc.* **29** 447
[2] Ding J, Yu J C, Zheng X H, Ni W Q and Chen B 2006 *J. Electronic. Components and Materials. Soc.* **25** 20
[3] Luo J, Du J, Tang Q and Mao C H 2008 *J. Electron Devices Soc.* **55** 3549
[4] Cheng C T, Lanagan M, Jones B, Lin J T and Pan M J 2009 *J. Am. Ceramic. Soc.* **31** 411
[5] Michale J R, Clive A W, Graham J H and Roger M 1996 *J. Am. Ceramic. Soc.* **79** 17
[6] Yao K, Zhang L Y, Yao X and Zhu W G 1997 *J. Am. Ceramic. Soc.* **32** 3659
[7] Jiang S, Wang X M, Li J Y, Zhang Y, Zheng T and Lv J W 2015 *J. Chin. Phys. Soc.* **24** 067701
[8] Du J, Jones B and Lanagan M 2005 *J. Mater. Lett. Soc.* **59** 2821
[9] Reece M J, Worrell C A, Hill G J, *et al.* 1996 *J. Am. Ceram. Soc.* **79** 17
[10] Cheng C T, Lanagan M, Jones B, *et al.* 2005 *J. Am. Ceram. Soc.* **88** 3037
[11] Ding J, Yu J C, Zheng X H, *et al.* 2006 *Electronic Components and Materials* **25** 20
[12] Shi J L and Feng T 2008 *Inorganic Optical Transparent Ceramics* (1st edn.) (Shanghai: Shanghai Popular Science Press) p. 12 (in Chinese)