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Structure and dielectric properties of Cu and (K,Na) doped $SrBi_2Nb_2O_9$ ferroelectric ceramics

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Abstract Ferroelectric ceramics, $SrBi_2Nb_2O_9$ (SBN), $Sr_{0.8}Cu_{0.2}Bi_2Nb_2O_9$ (SCBN) and $Sr_{0.8}K_{0.1}Na_{0.1}Bi_2Nb_2O_9$ (SKNBN) were prepared by a solid state reaction process. X-ray diffraction analysis shows that the alkali and Cu almost diffuse into the SBN lattice to form a solid solution during sintering and some slight secondary phases was detected. The effect of alkali and Cu on dielectric properties of the SBN ceramics was discussed. The dielectric loss factor of (K,Na) doped SBN ceramics degraded considerably to 0.01 and their frequency and temperature stabilities were enhanced. The dielectric constant was enhanced by approximately 60% and the Curie temperature (*Tc*) was also improved for Cu doped $SrBi_2Nb_2O_9$ ceramics.

Keywords Ferroelectric ceramics · Bi-layer structure perovskite · Doped $SrBi_2Nb_2O_9$

1 Introduction

Recently bismuth layer-structured ferroelectrics (abbreviated to BLSF) have been extensively studied in the form of thin films because BLSF seems to be an excellent candidate material for nonvolatile FRAM (ferroelectric random access memory) in various commercial applications [1]. Symetrix Co. & Olympus Co reported the $SrBi_2Ta_2O_9$ thin films shows very high quality characteristics with fatigue-free property for FRAM [2, 3]. A family of BLSF is also attractive from applicational viewpoints for electronic materials such as dielectrics, piezoelectrics and pyroelectrics because BLSF are characterized by their low dielectric constant, high Curie temperature and large anisotropy in electromechanical coupling factors [4–6]. But these materials suffer from high dielectric loss due to the evaporation of bismuth oxide during sample preparation which limits its application. $SrBi_2Nb_2O_9$ (SBN), which is known to be n=2 member of the BLSF family, is a composition with less distorted octahedron stricture [7]. Much research has been reported in the open literature aimed at improving the dielectric and ferroelectric properties of SBN doped with various metal oxides [8, 9]. For example, Bi^{3+} doping results in an appreciable enhancement of dielectric properties [8]. Wu and Cao [10, 11] have substituted Nb^{5+} with V^{5+} and found a significant enhancement in dielectric and ferroelectric properties; meanwhile, the sintering temperature was significantly reduced by approximately 200 °C. M. J. Forbess et al. [12] and V. Shrivastava et al. [13–15] reported that the influence of La^{3+}, Ca^{2+} and Pb^{2+} substituted Sr^{2+} on structure and dielectric properties of SBN ferroelectric ceramics have been discussed and the insignificant changes are observed in the properties. Up to now, the influence of the alkali and copper on the structure, dielectric and ferroelectric properties of SBN has not been concerned.

The purpose of this paper is to investigate the effect of alkali and copper doping on the microstructure and dielectric properties of SBN ceramic.

2 Experimental

The $SrBi_2Nb_2O_9$, $Sr_{0.8}Cu_{0.2}Bi_2Nb_2O_9$ and $Sr_{0.8}K_{0.1}Na_{0.1}Bi_2Nb_2O_9$ ceramic samples were prepared by the standard solid-state reaction method. Reagent-grade oxide, carbonate and nitrate powders of Bi_2O_3, $SrCO_3$, K_2CO_3, Na_2CO_3, $Cu(NO_3)_2{\cdot}3H_2O$ and Nb_2O_5 were used as the starting materials. The powders of these raw materials were mixed and ball milled for 12 h using acetone as a medium,

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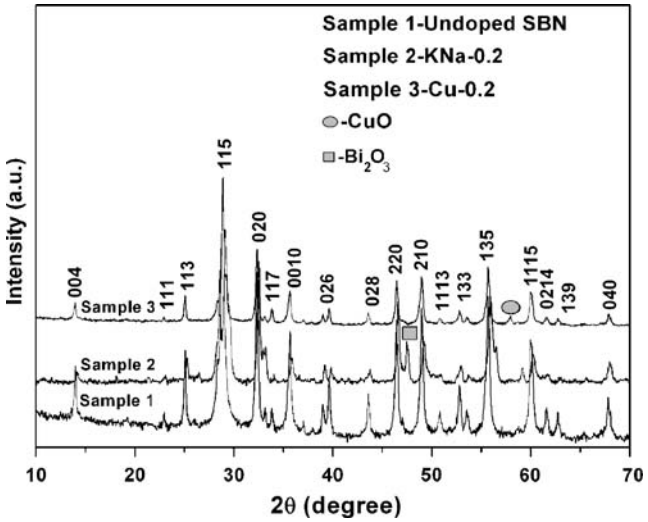

Fig. 1 XRD patterns of Cu and (K,Na) doped SBN ceramics with an applied voltage of 40 kV and current of 500 mA at room temperature

followed by calcining at 800 °C for 4 h, the calcined powder was milled again for 24 h. The obtained powder was pressed into pellets of 15 mm in diameter and ~1 mm in thickness by a cold isostatic pressing method (~100 MPa). The final sintering was performed at temperatures of 1020 °C for SCBN, 1080 °C for SKNBN and 1100 °C for SBN for 1 h covered by alumina crucible followed by furnace cooling. The densities of SBN, SKNBN and SCBN ceramics were measured by the Archimedes method. The crystal structure of each sample was characterized by an automated diffractometer (XRD; X'Pert PRO MPD, Philips, Eindhoven, Netherlands) with Cu $K\alpha_1$ radiation with an applied voltage of 40 kV and current of 500 mA. The morphology was observed by the scanning electron microscopy with an applied voltage of 20 kV (SEM, JSM-6360LV, Tokyo, Japan). The pellets were polished to the thickness of about 1 mm, and then silver paste was daubed on two sides and fired as electrodes at 850 °C for 30 min. Dielectric properties measurement was taken by Agilent 4294A impedance analyzer (Agilent, New Mexico, USA) with an applied voltage of 500 mV over the frequency range 100 Hz–100 MHz.

3 Results and discussion

The X-ray diffraction patterns of SBN doped (K,Na) and Cu ceramics are shown in Fig. 1. Both the peak positions and relative intensities of SCBN match closely that of SBN, but the peaks of SKNBN shift to the higher degree and the relative intensities weaken markedly, which mean that the size of the grain becomes smaller. The XRD patterns indicate that a solid solution with Bi-layered structure has been formed for all samples although the secondary phase Bi_2O_3 and some unknown phases appear in SKNBN sample. It is suggested that Cu and (K,Na) ions diffuse into the SBN lattice during sintering. For the SCBN sample, the secondary phase of CuO was confirmed according to the peak at 2θ ~58°. In a publish earlier, the set of (*hkl*) indices in 105

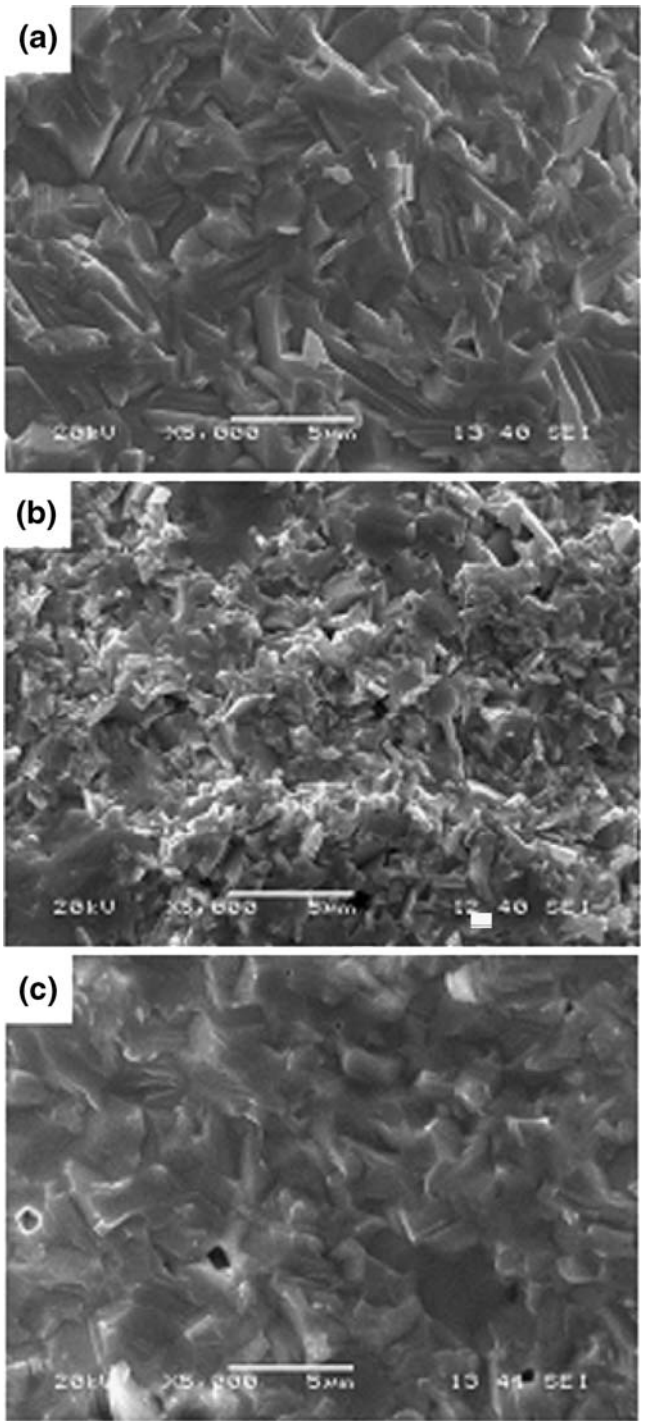

Fig. 2 SEM images of the cross-sectional surface Cu and (K,Na) doped SBN ceramics sintered at different temperature with an applied voltage of 20 kV: (**a**) SBN sintered at 1100 °C; (**b**) SKNBN sintered at 1080 °C; (**c**) SCBN sintered at 1020 °C

system ((*hkl*) indices of maximum intensity peak) is reported to be the set of pseudo tetragonal phase, but (*hkl*) indices set with 115 system is reported to be orthorhombic [16]. Moret et al. have reported that it was the coexistence of orthorhombic and tetragonal phases in these ceramics [17]. Based on the date of PDF card 49-0607, the XRD patterns of all samples could be indexed to an orthorhombic cell with A21am space group.

Figure 2 shows the SEM images of SBN and SBN doped Cu and (K,Na) sintered at different temperatures on the rupture surface. The micrograph of SBN is a typical Bi-layer structure and has clear grain boundaries. It is very clearly that doping (K,Na) makes the size of the grain of the SBN ceramic becoming smaller. Unclear grain boundaries are found in the micrograph of Cu doped SBN sample. At the same time, the densities of SBN, SKNBN and SCBN ceramics, measured by the Archimedes method, are 7.14935, 6.6116 and 7.1789 g/cm^3 respectively. It is indicated that the Cu doped SBN sample could improved the compact of SBN ceramics. The micrograph of Cu doped SBN sintered at relatively lower temperature 1020 °C [Fig. 2(c)] reveals a compact structure. It is indicated that the Cu ions enters into SBN lattice or promotes to form liquid phase at grain boundaries, which would increase effectively the diffusion velocity between the grains during sintering. However, this compact structure is not found in the micrograph of (K,Na) doped SBN [Fig. 2(b)] ceramics. The grain micrograph of (K,Na) doped SBN is not uniform and the abnormal grain growth are observed. Besides, some small voids or pores were found in the SKNBN ceramic. These phenomena indicates that (K,Na) into SBN may restrain the formation of layered perovskite phase, which is consistent with the results of Fig. 1.

The frequency dependence of dielectric constant and dielectric loss factor of (K,Na) and Cu doped SBN at room temperature is shown in Fig. 3. It is seen that dielectric constant changes hardly and dielectric loss factor degrades to 0.01 with the increase of frequency in the (K,Na) doped SBN ceramics. Furthermore, the dielectric constant and dielectric loss factor of (K,Na) doped ceramics become more plane with the frequency increasing. This indicates that the frequency stability is obviously improved. The oxygen vacancies are a dominant defect in the layer-Bi structure material due to volatilization of Bi_2O_3 [18]. One Na^+ or K^+ ion evaporation from the lattice will induce 1/2 O^{2-} vacancy, but one Bi^{3+} ions evaporation from the lattice will induce 3/2 O^{2-} vacancy. For the same amount of cation vacancy, the (K,Na) occupying A site (Sr^{2+} and Bi^{3+}) can reduce remarkable oxygen vacancies. So the frequency stability of this composition is enhanced.

In contrast, the dielectric constant and dielectric loss factor of Cu doped ceramics are significantly dependent on frequency. The dielectric constant of Cu doped SBN

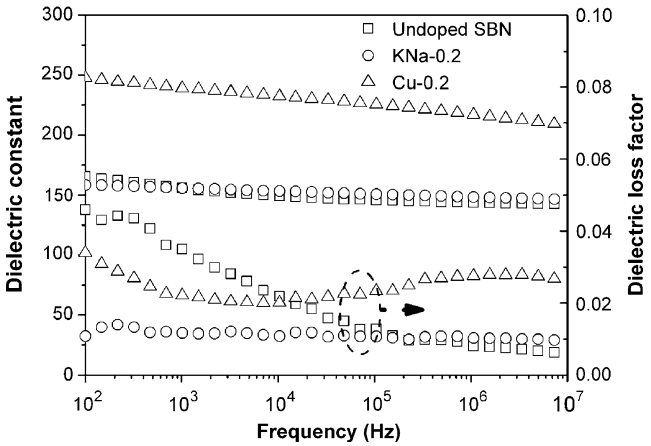

Fig. 3 Dielectric constant and loss factor of Cu and (K,Na) doped SBN ceramics as a function of frequency with a driving voltage of 500 mV

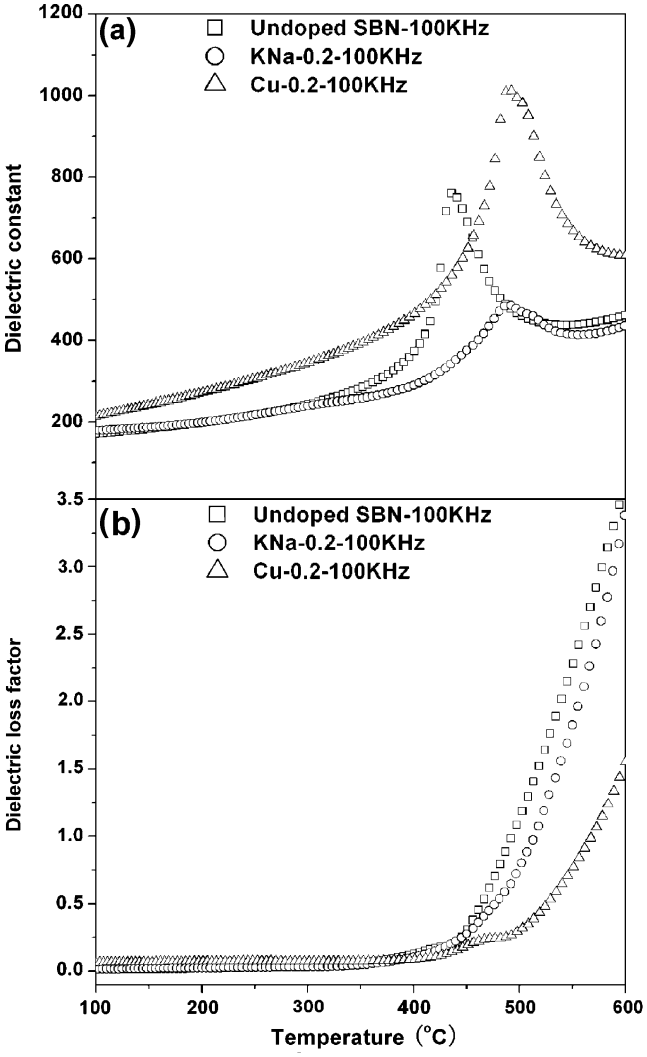

Fig. 4 Dielectric constant and dielectric loss factor as function of temperature for Cu and (K,Na) doped SBN ceramics at 100 kHz

ceramics decreases by approximately 20% with the driving frequency increasing. The existence of secondary phases results in abnormal dielectric loss factor at room temperature. The dielectric loss factor firstly decreases and then increases with frequency increasing, which indicates that two different dielectric loss mechanisms predominate respectively in different frequency ranges. The leakage current produced by the slight electron conductance is predominant in the dielectric loss below ~10^5 Hz, but the dielectric response is predominant in the dielectric loss above ~10^5 Hz.

The temperature dependence of dielectric constant of (K, Na) and Cu doped SBN at 100 kHz between 100 °C and 600 °C was shown in Fig. 4(a). Only one peak, corresponding to a phase transition from ferroelectric to paraelectric phase [19, 20], is observed during the heating process. The *Tc* of pure SBN is about 445 °C which is consistent with the previous result [21]. It can be seen from this figure, the *Tc* of Cu and (K,Na) doped SBN ceramics are much higher than that of pure SBN ceramics. Moreover, the temperature stability of (K,Na) doping SBN ceramics is improved obviously. In addition, the dielectric peak of (K,Na) doping SBN ceramics is broadened and form a relaxor type phase transition where formation of micro polar regions occurs and each of regions has its own transition temperature [22]. Jona and Shirane reported that the change of dielectric constant at *Tc* is attributed to the change in tetragonal lattice strain [23]. The ionic radius of Cu^{2+} ions is 0.72 Å are substituting Sr^{2+} ions (1.12 Å), so it would bring much larger lattice distortion and this could lead improvement in dielectric constant response. The highest dielectric constant (~1,025) could be observed at *Tc* (~490 °C). The effect of (K,Na) substituting Sr on the *Tc* of SBN ceramics is the same as Cu.

The temperature dependence of dielectric loss factor of (K,Na) and Cu doped SBN at 100 kHz between 100 °C and 600 °C are shown in Fig. 4(b). The dielectric loss factors of all samples do not changed significantly below 450 °C, but which remarkable changes are observed beyond 450 °C. The dielectric loss factors continue to increase with the increase of temperature which might be attributed to the higher conductivity at high temperature. The oxygen vacancy is a dominant defect in the layered structure perovskites materials, so the higher concentration of charge carrier of oxygen vacancies and other defects all might enhance the conductivity [24].

4 Conclusions

Ferroelectric ceramics SBN, SKNBN and SCBN were prepared by a solid state reaction process. X-ray diffraction analysis shows that the (K,Na) and Cu diffuse into the SBN to form a solid solution during sintering although some slight secondary phases were detected. The SEM image of SCBN ceramics reveals a compact structure. The dielectric loss factor of (K,Na) doped SBN ceramics degraded considerably to 0.01 and its frequency and temperature stability were improved. The dielectric constant was enhanced by approximately 60% and the *Tc* was also increased for Cu doping SBN ceramics. Additionally, Cu doping SBN offers highest dielectric constant (~1,025) at *Tc* (~490 °C) and does not show remarkable decay up to 1 MHz.

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