**Variation of electrical properties with structural vacancies in
ferroelectric niobates ($\text{Sr}_{0.53}\text{Ba}_{0.47}$) $_{2.5-0.5x}\text{Na}_x\text{Nb}_5\text{O}_{15}$ ceramics**

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Abstract

$(\text{Sr}_{0.53}\text{Ba}_{0.47})_{2.5-0.5x}\text{Na}_x\text{Nb}_5\text{O}_{15}$ ceramics (SBNN, $0.0 \leq x \leq 2.5$) were prepared by the conventional solid-state reaction method. The Na^+ concentration varied from 0.0 to 2.5 so that the tetragonal tungsten bronze (TTB) crystal structure was designed to transform from ‘unfilled’ to ‘filled’ and then to ‘stuffed’ type. Apart from the change in the structural type, the effects of Na^+ concentration on the phase structure as well as microstructure, ferroelectric and dielectric properties were also investigated. X-ray diffraction analysis revealed that the crystallized SBNN ceramics with $x \leq 1.0$ had the tetragonal tungsten bronze structure with space group of $P4bm$. With further increasing x above 1.0, the broad asymmetrical diffraction peaks near 32° associated with EDX analyses indicated the existence of some amount of secondary NaNbO_3 -based phase due to the introduction of excessive Na^+ . It was also found that Na^+ concentration had a significant influence on the electrical properties of SBNN ceramics. Introducing Na^+ in A-sites to decrease the structural vacancies and increase the distortion degree of NbO_6 polar unit was beneficial for the electric properties, while excessive Na^+ content would deteriorate the electric properties owing to the presence of secondary NaNbO_3 -based phase.

Keywords: Structural modulation; NbO_6 distortion; Tungsten Bronze Niobates; Dielectric properties; Ferroelectric properties

1. Introduction

Ferroelectric crystals with tetragonal tungsten bronze structure (TTB) are important ferroelectric materials. Their interesting dielectric and ferroelectric properties have attracted extensive research activities studying on their structural and physical properties due to the compositional flexibility [1,2]. The TTB structure consists of a complex array of distorted BO_6 octahedron sharing corners in such a way, that three different types of interstices (pentagonal A2, square A1, and trigonal C sites) are available for cation-occupancy in unit cell of $(\text{A1})_2(\text{A2})_4(\text{C})_4(\text{B1})_2(\text{B2})_8\text{O}_{30}$. However, the presence of crystal nonequivalent A and B sites and an extra C site provide extra degrees of freedom for manipulation of the structure to offer huge compositional flexibility [3,4]. Generally, A1 with 12- fold coordinated sites in the crystal lattice structure and A2 (15- fold coordinated sites) sites can be filled by Sr^{2+} , Ba^{2+} , Ca^{2+} , Pb^{2+} , Na^+ and some rare earth cations, whereas B1 (9- fold coordinated sites) and B2 (6- fold coordinated sites) sites by either Nb^{5+} or Ta^{5+} , and the C sites by Li^+ and other small cations in the formula. The structure with A, B and C sites fully occupied represents the so-called ‘stuffed’ TB structure. The smallest interstice C sites are usually empty and then the formula $\text{A}_6\text{B}_{10}\text{O}_{30}$ is for the ‘filled’ tungsten bronze structure, in which all 6 A-sites are occupied. The structure with only 5 out of 6 A-sites occupied represents ‘unfilled’ structure [5]. It is found that the ion-occupying-situation and disorder-degree in A-sites, which are greatly dependent on the size and electronegativity of substituted ions, can significantly affect the distortion of NbO_6 octahedron polar unit, resulting in some characteristic dielectric and ferroelectric behaviors in TB materials [6-10].

$\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ (SBN) is a typical type of lead-free ferroelectric materials with ‘unfilled’ tetragonal tungsten bronze structure. In SBN crystal structure, it has been

generally accepted that Sr^{2+} ions with smaller ionic radii occupy both the A1 and A2 sites, while the bigger Ba^{2+} occupancy is restricted to the A2-sites. When the ratio of Sr/Ba varies, the distribution, ordering and the vacancy of A1 and A2 sites in the unit cell will change consequently, and these changes can greatly affect the physical and electrical properties of SBN compounds [11,12]. It is reported that SBN shows a wide range of solid solution compositions ($0.25 \leq x \leq 0.75$) [13-14], allowing us to adjust the Sr/Ba ratio to suit different needs with appropriate physical and electrical properties [15-17]. From the obtained findings [15,18], it was all found that the composition with $x = 0.53$ showed the better dielectric properties and had potential application prospects for lead free electronic components.

In addition to the SBN ceramics with ‘unfilled’ TB structure, increasing attentions have also been paid on the alkali metal ions-added SBN ceramics with formula of $(\text{Sr},\text{Ba})_2\text{ANb}_5\text{O}_{15}$ (A: K or Na), which are indexed to the ‘filled’ TB structure [19-23]. Owing to the difference of vacancies and chemical disorders in A1 and A2 sites, ‘filled’ TB SBN ceramics exhibit different electrical properties from ‘unfilled’ ones. For example, the increase of Sr/Ba ratio in ‘unfilled’ TB SBN can result in a transformation from ferroelectric to relaxor behavior [24,25]. While some unique low temperature dielectric relaxations are induced by the incommensurate structure changes for the ‘filled’ TB ceramics, such as $\text{Sr}_2\text{NaNb}_5\text{O}_{15}$ [26] and $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ [27]. Although many works have been devoted to the study of SBN ceramics, they are mainly focused on the two extreme structural types: ‘unfilled’ TB and ‘filled’ TB. As that the occupancy of A1 and A2 sites is the primary parameter governing the dielectric behaviors in TB structures, establishing the correlations of composition-structure-properties becomes urgent and important for the properties control by modulating the alkali metal ions amount in $(\text{Sr},\text{Ba})_2\text{ANb}_5\text{O}_{15}$.

In this work, the influences of structural modulation by Na⁺ concentration from ‘unfilled’ to ‘filled’ type on dielectric and ferroelectric properties of TB Sr_{0.53}Ba_{0.47}Nb₂O₆-based ceramics were studied in detail. More importantly, the Na⁺-rich compositions were also designed to form the ‘stuffed’ type to further study the electric behaviors related to the ion-occupying-situation in TB structures. The effects of introducing Na⁺ concentration on the phase structure, microstructure, dielectric and ferroelectric properties of (Sr_{0.53}Ba_{0.47})_{2.5-0.5x}Na_xNb₅O₁₅ (0.0 ≤ x ≤ 2.5) ceramics were studied experimentally and systematically. In addition, the underlying mechanisms for variations of the electric properties due to different Na⁺ concentrations were discussed in this work.

2. Experimental procedures

Conventional mixed-oxide method was used to prepare (Sr_{0.53}Ba_{0.47})_{2.5-0.5x}Na_xNb₅O₁₅ (0.0 ≤ x ≤ 2.5) with reagent grade BaCO₃, SrCO₃, Na₂CO₃ and Nb₂O₅. They were mixed by ball-milling in ethanol for 16 h using zirconia balls. The mixed powders were dried at 80 °C and calcined at 1200 °C for 6 h in air. Then, the synthesized particles were mixed with 5 wt% polyvinyl alcohol (PVA) solution and pressed into pellets with a diameter of 15 mm under 300 MPa pressure. After burning out PVA at 500 °C, the green samples were sintered at 1300-1360 °C for 4 h in air, respectively.

The phase structure of the prepared ceramics samples were characterized by X-ray diffraction (XRD, D/max-2200, Rigaku, Japan, Cu Kα) with scanning step of 0.02° in 2θ range of 20-60°. Raman scattering measurements were taken by the Raman spectrometer (Renishaw, invia) with a back scattering geometry. The laser source was 532 nm line obtained from an Ar ion laser. The surface morphologies and compositions of the ceramics were obtained using a field emission scanning electron

microscope (FESEM, Hitachi SU8000) equipped with an energy dispersive X-ray (EDX) analyzer. Silver electrodes were formed on both surfaces of each sintered disk by firing silver at 840 °C for 30 min. Temperature dependences of dielectric constant were measured on the LCR meter (Agilent E4980A) from ambient temperature to 500 °C at different frequencies. Dielectric dispersion were measured by Agilent 4294A (Palo Alto, CA) impedance analyzer in the frequency range of 100 Hz-1 MHz nearby the Curie temperature, respectively. The polarization versus electrical (*P-E*) hysteresis loops were observed by a Radiant Precision Workstation (Albuquerque, NM, USA).

3. Results and discussion

The X-ray diffraction (XRD) patterns of $(\text{Sr}_{0.53}\text{Ba}_{0.47})_{2.5-0.5x}\text{NaNb}_5\text{O}_{15}$ (SBNN $0.0 \leq x \leq 2.5$) ceramics recorded at room temperature are shown in Fig. 1(a). When $x \leq 1.0$, all ceramics are of single tetragonal tungsten bronze (TTB) structure without any traces of impurity, indicating that Na^+ has diffused into the tungsten bronze structure lattice to form solid solutions. Further detailed XRD analyses in the 2θ range from 31° to 33° are shown in Fig. 1(b). It is found that all the diffraction peaks of SBNN ($0.0 \leq x \leq 2.5$) shift slowly to lower angle direction compared with pure SBN ceramics, suggesting that the unit cell is expanded during the ‘unfilled’ to ‘filled’ transformation by the increase of Na^+ in composition. For ‘stuffed’ structural ceramics with $x > 1.0$, the broad diffraction peaks observed around $31^\circ \sim 33^\circ$ in Figs. 1(a) and 1(b) can be attributed to the existence of some second phase. As a result, the rich Na^+ in composition can induce the coexistence of a tetragonal tungsten bronze structure $(\text{Sr}_{0.53}\text{Ba}_{0.47})_2\text{NaNb}_5\text{O}_{15}$ phase (SB₂N) and a perovskite structure NaNbO_3 -based phase (NN).

The broad diffraction peaks around $31^\circ \sim 33^\circ$ for the ceramics with $x > 1.0$ are

further separated by fitting the Gaussian-Lorentz line shape as shown in Fig. 2(a), and the positions of the reflections are fixed using the least square method. The diffraction peaks are characterized by the strongest (311)/(420) peak of tetragonal SB₂N phase and the strongest (110) peak of orthorhombic NN-based phase. The standard diffraction peaks are cited from JCPDS cards #39-1453 and #33-1270, respectively, which can specifically indicate the coexistence of tetragonal SB₂N phase and orthorhombic Sr, Ba-doped NN phase in Na⁺-rich compositions at room temperature. It can be clearly seen in Fig. 2(a) that with the increase of x above 1.0, the amount of perovskite structure NN-based phase increases gradually in the obtained compositions. We therefore can conclude that by modulating Na⁺ concentration in tungsten bronze (Sr_{0.53}Ba_{0.47})_{2.5-0.5x}Na _{x} Nb₅O₁₅ compositions, the structures change gradually from ‘unfilled’ to ‘filled’ type with increasing x from 0.0 to 1.0. Whereas when $x > 1.0$, the A1 and A2 sites in tungsten bronze crystal structure are fully occupied and the Na⁺ ions cannot enter into the extra smaller C sites, resulting in the coexistence of two different structural phases. The existence of perovskite structure NN-based phase will be further verified by the EDX and dielectric measurements in the following part.

Fig. 2(b) schematically shows the projection of TTB-type structure in the ab plane. The square, pentagonal, and triangular tunnels available for cation inclusion are labeled as A1, A2, and C, correspondingly. In tetragonal ‘unfilled’ SBN crystal, the bigger Ba²⁺ ions (1.61 Å) occupy only the 15-fold coordinated oxygen octahedral A2-sites, while the relatively smaller Sr²⁺ ions (1.44 Å) occupy initially the 12-fold coordinated oxygen octahedral A1-sites, and the residual Sr²⁺ ions will enter into the bigger A2-sites together with Ba²⁺ ions, leading to the disordered distribution in bigger A2-sites. Nb⁵⁺ ions (0.64 Å) occupy the B sites and form NbO₆ groups

associated with six oxygen atoms. When introducing Na^+ in SBN crystal, the structural vacancies gradually decrease, accompanied by the structural evolution from ‘unfilled’ to ‘filled’ type. Taking the radius of Na^+ ions (1.39 Å) into account, it is reasonable to consider that Na^+ ions have an preference to occupy the square tunnels A1-sites, Sr^{2+} occupy the residual A1-sites and then go into the bigger A2-sites. As a result, except for the disordered distribution in bigger A2-sites, the size similarity between Sr^{2+} and Na^+ ions also results in the disordered distribution in A1-sites with increasing x from 0.0 to 0.8. When x is increased to 1.0, the A1-sites are fully occupied by Na^+ ions, and Sr^{2+} is forced to occupy A2-sites together with Ba^{2+} ions, producing the ‘filled’ TB type. The ion-occupying-situation and disorder-degree in different tunnels of A1 and A2 sites can affect the distortion of NbO_6 octahedron polar unit both along c -axis and in ab plane, which can result in some characteristic dielectric and ferroelectric behaviors discussed subsequently.

Microstructural analyses by FESEM on the surface of SBNN ceramics ($0.0 \leq x \leq 2.5$) sintered at the appropriate temperature respectively are shown in Fig. 3. It can be clearly seen that all ceramics display considerably dense microstructure with high relative density values from 97.6% to 98.9%. The grain morphology exhibits obvious variation with x . All the samples obtain high. According to Figs. 3(a-c), the ceramics with homogenous equiaxed shape microstructure can be obtained in SBNN ceramics with ‘unfilled’ structural type when $x < 0.6$. With increasing x , the anisometric pillar-type grains increase, while the equiaxed shape grains decrease gradually with changing the structure from ‘unfilled’ to ‘filled’ type. Especially at $x = 1.0$ seen in Fig. 3(f), the ceramic surface is mainly of anisometric pillar-type grains, indicating that the ‘filled’ tungsten bronze structure prefers to the anisometric morphology. The occurrence of anisometric morphology may be attributed to the growth habit of TB

structure, for which the grain growth in (001) facet is faster due to the lower surface energy [20]. The increase in the size of pillar-type grains with higher x values may also be due to the existence of alkaline Na^+ ions to lower the sintering temperature for the ceramics, which will facilitate the grain growth and can result in the abnormal grain growth in tungsten bronze compositions [21,28-30]. For ceramics with $x > 1.0$, two different morphology type grains are observed in Figs. 3(g-i): the bigger pillar-type grains are surrounded by the smaller equiaxed shape grains. According to the phase structure results obtained from Figs. 1 and 2, it is reasonable to consider that the bigger pillar-type grains and the smaller equiaxed shape grains are tetragonal tungsten bronze SB_2N phase and perovskite NN phase (marked by red circle), respectively.

To further clarify the phase compositions for ceramics with $x > 1.0$, the SBNN samples with $x = 1.0$ and $x = 2.5$ are characterized by the EDX measurements in full area 1, selected area 2 and selected area 3, respectively. The derived results are shown in Fig. 4 and Fig. 5, respectively. As shown in Fig. 4, the measured $(\text{Sr} + \text{Ba})/\text{Na}$ ratios from three different areas (solid blue circles) are matched well with the theoretical value of 2.0 (red line) for the sample with $x = 1.0$, indicating that the chemical compositions are very average in the SBNN ceramics with ‘filled’ tungsten bronze structure. According to Fig. 5, it can be seen that the ratio of $(\text{Sr} + \text{Ba})/\text{Na}$ (solid purple circle) measured from full area 1 containing all grains and grain boundaries is very close to the theoretical values of 0.5 for the sample with $x = 2.5$. Meanwhile, it is also observed that the ratio of $(\text{Sr} + \text{Ba})/\text{Na}$ (solid blue circle) measured from selected area 2 with bigger pillar-type shape is close to the theoretical value of 2.0 as the ‘filled’ tungsten bronze structure, whereas the ratio of $(\text{Sr} + \text{Ba})/\text{Na}$ (solid yellow circle) in selected area 3 with smaller equiaxed shape is much lower than the theoretical value of 0.5 (red line), suggesting the coexistence of two

structural type phases: a tetragonal tungsten bronze structure SB₂N phase (selected area 2) and a perovskite structure NN-based phase (selected area 3). The EDX results further reveal that by modulating Na⁺ concentration in (Sr_{0.53}Ba_{0.47})_{2.5-0.5x}Na_xNb₅O₁₅ samples, the structure evolves from ‘unfilled’ to ‘filled’ type with increasing x from 0.0 to 1.0. However, the ‘stuffed’ tungsten bronze type cannot be obtained when $x > 1.0$, and the excessive Na⁺ will facilitate the appearance of second NN phase with perovskite structure as revealed by our previous XRD and SEM analyses.

As mentioned in introduction, for the ferroelectrics with tungsten bronze structure, the ion-occupying-situation and disorder-degree in different tunnels of A1 and A2 sites can affect the off-center of B-site ions both along c -axis and in ab plane, which is further identified by Raman spectroscopy in the following section. Fig. 6(a) shows the room temperature Raman spectra results of all SBNN ceramics in the frequency range of 10-1000 cm⁻¹. Similar spectra are found for all samples. Three characteristic Raman peaks (ν_1 , ν_2 , ν_5) of NbO₆ octahedron in SBNN samples are determined around 840, 630 and 250 cm⁻¹, respectively. They have been identified as internal modes of NbO₆ octahedron, named as the Nb–O stretching (840, 630 cm⁻¹) and O–Nb–O bending (250 cm⁻¹) vibrations, which are consistent with the Raman spectrum vibrations recorded in other typical TTB niobate compounds [3,20,28,31]. The broadening of these peaks comes from the structural order-disorder caused by the modifications in the O–Nb–O and Nb–O–Nb bonds. The Raman spectra at low Raman shift part ($\nu < 200$ cm⁻¹) is considered as the external vibration modes involving cations motions relative to the NbO₆ octahedron framework [28]. The wavenumber of the external vibration modes does not change, while the wavenumbers of the internal vibration modes shift to higher values (blue shift) when the structure transforms from ‘unfilled’ to ‘filled’ type. In general, the Raman spectroscopy is very

sensitive to changes in the structure of oxides, especially in the region of metal-oxygen stretching and bending modes [32].

As shown in Fig. 6(a), slight blue shift can be observed for the two strong internal modes at 630 cm^{-1} and 250 cm^{-1} with increasing x from 0.0 to 1.0, while the vibration modes maintain the same Raman shift when $x > 1.0$. Usually, the blue shift for internal modes is due to the lattice contraction of NbO_6 octahedron [28], which can be induced by the extrusion of A-sites ions to the NbO_6 octahedron during the structural evolution from ‘unfilled’ to ‘filled’ type, showing that the interaction inside NbO_6 octahedron becomes more intense when reaching a ‘filled’ type structure. In addition, the full width at half maximum (FWHM) of the Raman lines in SBNN ceramics are extracted through fitting the profiles with individual Lorentz profiles. The fitting results are illustrated in Fig. 6(b). As the distortion degree of NbO_6 octahedron is sensitive to the nearby environment of A1 and A2 sites, the FWHM values of two internal modes increase slightly with increasing x from 0.0 to 1.0, suggesting more distortion degree of NbO_6 octahedron at higher Na^+ contents. However, the peak position doesn’t show obvious shift to higher values and the FWHM values keep almost unchanged when $x > 1.0$, which may be related to the existence of second perovskite NN phase as revealed by our previous XRD and EDX analyses. The results obtained from Raman spectra show that the structural evolution induced by the introducing Na^+ concentration in SBNN increases distortion degree and interaction strength inside NbO_6 octahedron, especially for the ‘filled’ tungsten bronze SBNN. The variation of NbO_6 octahedron can produce obvious effects on the dielectric and ferroelectric behaviors for SBNN ceramics, which will be discussed subsequently.

Fig. 7 shows the dielectric properties of SBNN ceramics as a function of

temperature (25-500 °C) measured at different frequencies (10, 100 and 1000 kHz) for all samples. With increasing the temperature, the tungsten bronzes undergo a ferroelectric tetragonal ($4mm$) phase to a noncentralsymmetric polar paraelectric ($4/mmm$) phase. The peaks of ϵ' are associated to the ferroelectric to paraelectric phase transition, which is corresponding to the Curie temperature (T_c). The variations of $\tan\delta$ with temperature for all SBNN ceramics show similar trend, that is, all samples show weak $\tan\delta$ peaks below T_c . This phenomenon is generally observed in ferroelectrics and arise from the improvement in interactions of the domain wall during the ferroelectric to paraelectric phase transition [18,33]. Above T_c , the monotonous increase in $\tan\delta$ can be attributed to the scattering of thermally activated charge carriers and some defects in the samples [33]. For the SBNN samples with $x > 1.0$, besides the dielectric peak nearby 275 °C for the tungsten bronze ferroelectrics, an extra abnormal dielectric peak is also found at about 150 °C, which may be due to the existence of perovskite NN-based phase. The dielectric results are consistent well with the previous XRD and EDS structural results. At $x = 0.0$, the ‘unfilled’ SBN exhibits relaxor dielectric behavior around T_c . While the relaxor behavior is restrained with tuning the structure from ‘unfilled’ to ‘filled’ type. At $x = 1.0$, the ‘filled’ SBNN exhibits normal ferroelectric behavior. It is suggested that both the vacancy and random cations distribution in A2-sites account for the relaxor behavior in ‘unfilled’ SBN.

The temperature dependence of ϵ and $\tan\delta$ for SBNN ceramics measured at 10 kHz with different Na^+ contents are shown in Fig. 8(a). The dielectric constant ϵ_r and dielectric loss $\tan\delta$ of SBNN ceramics measured around room temperature at 10 kHz as a function of x are presented in Fig. 8(b). The dielectric results measured at room temperature show that the better dielectric properties are obtained at $x = 1.0$ with a

higher ϵ_r value of 690 and a relatively lower $\tan\delta$ value of 0.03. The dielectric constant ϵ_m is the maximum value of dielectric constant obtained at T_c . Curie temperature (T_c) and dielectric constant (ϵ_m) with respect to Na^+ content at 10 kHz are plotted in Fig. 8(c). T_c shifts sharply to higher temperatures from 80 °C to 280 °C with increasing x from 0.0 to 1.0, showing that Na^+ introduction is beneficial to improve T_c in SBNN ceramics by modulating the structure from ‘unfilled’ to ‘filled’ type. The value of T_c depends on the octahedron distortion [7]: introducing Na^+ in A-sites can lead the stronger crystal structural distortion and the restricted rattling space for the ions inside the oxygen octahedron, which will increase the ionic displacements and thus the Curie temperature goes up. With further increasing x above 1.0, T_c is held constant. As verified by the EDX results in Fig. 5, excessive Na^+ will facilitate the formation of second NN phase with perovskite structure. But the tungsten bronze composition in the obtained ceramics with $x > 1.0$ is always the ‘filled’ type $(\text{Sr}_{0.53}\text{Ba}_{0.47})_2\text{NaNb}_5\text{O}_{15}$ (SB_2N), which show constant T_c as high as 280 °C. ϵ_m increases initially, reaches the maximum value at $x = 1.0$, and then decreases with further increasing x above 1.0. It can be concluded that for SBNN ceramics, introducing Na^+ in A-sites to decrease the structural vacancies and increase the distortion degree of NbO_6 polar unit is beneficial for the dielectric properties, while the dielectric properties will be deteriorated at excessive Na^+ content due to the existence of second NN-based phase.

The low temperature dependence of dielectric constant ϵ for SBNN ceramics with different x ($x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.5, 2.0$ and 2.5) measured at different frequencies are shown in Fig. 9. The obvious dielectric dispersion extending over a broad temperature range from -193 to 100 °C is observed. With increasing temperature, a steep increase of ϵ and a notable frequency diffuse are observed for

compositions with $x = 0.0$ and 0.4 , indicating the relaxor behavior in unfilled SBNN.

In contrast, the low temperature anomaly peak around $-90\text{ }^{\circ}\text{C}$ occurs obviously at $x = 1.0$. Two factors can account for the low temperature anomaly. One factor might be related with the polarization perturbation [34]. The polar direction is along (001) (out-of-plane) for tetragonal TB structure and along (110) (in-plane) for orthorhombic TB structure. Indeed, the orthorhombic TB structure has been confirmed in $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ and $\text{Sr}_{1.9}\text{Ca}_{0.1}\text{NaNb}_5\text{O}_{15}$ ceramics with ‘filled’ type, and the orthorhombic distortion of the TB structure exists in a wide range of temperature [23]. Therefore, local nano-regions in the current samples (tetragonal at room temperature) might change to orthorhombic symmetry at a lower temperatures (This process can be driven by the concerted rotation of the octahedral NbO_6) and these nano-polar regions will lead to an increase of local disorder which is responsible for the diffused transition at low temperatures. Another factor is associated with the local structural fluctuation rather than the phase transition of macro-structure [20]. These effects of local structural fluctuation may include the concerted rotation of oxygen octahedron in the ab plane and the delocalization of small cations in A-sites with the tungsten bronze structure. At $x = 1.0$, the SBNN ceramics show ‘filled’ tungsten bronze structural type so that the A1-sites are occupied fully by Na^+ ions, while the bigger A2-sites are occupied simultaneously by Sr^{2+} and Ba^{2+} ions. Size difference between Sr^{2+} and Ba^{2+} ions in same A2-sites result in the stronger crystal structural distortion and more intense interaction between A-sites ions and NbO_6 octahedron, which has been verified by the Raman spectra results. The complex structural distortions make SBNN still remain in ferroelectric phase and may be responsible for the local structural fluctuation at lower temperatures.

Fig. 10 displays the frequency dependence of dielectric properties for SBNN ceramics ($x = 0.0, 1.0, 1.5, 2.5$) measured around T_c in the frequency range from 100 Hz to 1 MHz. It is clearly seen in Figs. 10(a) and 10(b) for SBNN ceramics with $x \leq 1.0$, the dielectric constant changes a little and shows a relative plateaus over the range of measured frequencies, suggesting that these compositions exhibit little frequency dispersion around T_c . But for the SBNN ceramics with $x > 1.0$, the value of ε decreases obviously in the low-frequency region whereas decreases slowly in the high-frequency region. The obvious decrease of ε with increase of frequency is also observed in other TTB compounds, such as $(\text{Ca}_{0.28}\text{Ba}_{0.72})_{2.5-0.5x}\text{Na}_x\text{Nb}_5\text{O}_{15}$ [31] and $\text{Li}_2\text{Pb}_2\text{Pr}_2\text{W}_2\text{Ti}_4\text{Ta}_4\text{O}_{30}$ [33]. This type of dielectric behavior is not usually intrinsic but is rather associated with the presence of space charges in ceramics, and then is ascribed to extrinsic behavior [31].

Fig. 11 shows the polarization levels versus applied electrical field (P - E) hysteresis loops of SBNN ceramics with different x measured at room temperature. All samples display well-saturated P - E loops, demonstrating that all SBNN ceramics possess good ferroelectric properties. The values of the remnant polarization (P_r) and coercive field (E_c) as a function of alkali-dopant concentration are illustrated in Fig. 12. Both P_r and E_c increase initially with increasing x , and reach the maximum values at $x = 1.0$. After reaching a maximum value at $x = 1.0$, E_c keeps almost constant with further increasing x above 1.0, whereas P_r declines gradually when $x > 1.0$. The ferroelectricity in TB compounds [20,28] is believed to come from the off-center displacements of B-site ions both along c -axis and in ab plane (i.e. the distortion of NbO_6 octahedron polar unit in TTB niobates). As the Raman spectra confirmed, the vibrations of Nb–O stretching and O–Nb–O bending become stronger when increasing Na^+ concentration to decrease the ‘unfilled’ degree. As a result, the

ferroelectrics with ‘filled’ structure showed larger P_r compared with those with ‘unfilled’ structure.

The electric field induced relaxor-ferroelectric phase transition is not only driving electric field-dependent but also temperature-dependent. Fig. 13 provides the temperature dependent polarization hysteresis loops of SBNN ceramics ($x = 0.0, 1.0, 2.5$) in the range of room temperature to 140 °C under the same electric field. As increasing the measuring temperature, the hysteresis loop exhibits a typical relaxation ferroelectric characteristics with slim and almost linear response above T_c for $x = 0.0$. For the samples with $x = 1.0$ and 2.5, well-saturated P - E loops can be obtained at different measuring temperatures. The hysteresis loops become slim with increasing temperature. The remnant polarization (P_r) and coercive field (E_c) decrease monotonically, suggesting decreasing stability of the field-induced long-range ferroelectric order and increasing of the energy barrier for the formation of ferroelectric domains out of the PNRs for all samples. Combining Figs. 8, 12 and 13, it is therefore concluded that the ‘filled’ SBNN ceramics with $x = 1.0$ show better comprehensive dielectric and ferroelectric properties. Both the stronger structural distortion of NbO_6 polar unit and the homogeneous microstructure with high densification account for the improved electric properties. Whereas the existence of second NN-based phase caused by excessive Na^+ content will deteriorate the electric properties when $x > 1.0$.

4. Conclusions

$(\text{Sr}_{0.53}\text{Ba}_{0.47})_{2.5-0.5x}\text{Na}_x\text{Nb}_5\text{O}_{15}$ ceramics (SBNN, $0.0 \leq x \leq 2.5$) were prepared by using the conventional solid-state reaction method. The structural modulation controlled by Na^+ concentration had great influences on the phase structure, microstructure, dielectric and ferroelectric properties for SBNN ceramics. XRD and

EDS analyses revealed that by modulating Na⁺ concentration in (Sr_{0.53}Ba_{0.47})_{2.5-0.5x}Na_xNb₅O₁₅ samples, the structure evolved from ‘unfilled’ to ‘filled’ type with increasing x from the 0.0 to 1.0. However, the ‘stuffed’ tungsten bronze type was not obtained when $x > 1.0$ as that the excessive Na⁺ would promote the formation of second NN-based phase with perovskite structure. Na⁺-introduction could lower the sintering temperature and induce the growth of anisometric pillar-type grains. Three dielectric anomalies were observed in SBNN ceramics: (i) the ferroelectric phase transition associated with T_c of tetragonal tungsten bronze structure phase at temperatures between 80 and 280 °C, (ii) the ferroelectric phase transition associated with T_c of perovskite structure NN-based phase at about 150 °C, (iii) the low temperature dielectric anomaly occurred in the temperature range of -200 ~ -50 °C especially for the ‘filled’ SBNN ceramics with $x = 1.0$. Introducing Na⁺ in A-sites to decrease the structural vacancies was beneficial for the dielectric and ferroelectric properties. The better comprehensive dielectric and ferroelectric properties were obtained at $x = 1.0$ due to the bigger distortion degree of NbO₆ polar unit and homogeneous microstructure with high densification, whereas the electric properties would be deteriorated at excessive Na⁺ content due to the existence of second NN-based phase.

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Figure Captions

Fig. 1. XRD patterns of SBNN ceramics as a function of Na^+ content. (a) SBNN ceramics with different x sintered at the appropriate sintering temperature, respectively; (b) the magnification of Fig. 1(a) in the range from 31° to 33° .

Fig. 2. (a) peak-differentiating and fitting for SBNN ceramics with $x = 1.5, 2.0, 2.5$; (b) the schematic representation of the TTB-type structure projected on the ab plane, the A1-, A2-, and C-sites are labeled.

Fig. 3. FESEM surface-view micrographs of SBNN ceramics with different Na^+ contents (a) $x = 0.0$, (b) $x = 0.2$, (c) $x = 0.4$, (d) $x = 0.6$, (e) $x = 0.8$, (f) $x = 1.0$, (g) $x = 1.5$, (h) $x = 2.0$ and (i) $x = 2.5$.

Fig. 4. Composition analysis of $x = 1.0$ by EDX in full area 1, selected area 2 and selected area 3, respectively.

Fig. 5. Composition analysis of $x = 2.5$ by EDX in full area 1, selected area 2 and selected area 3, respectively.

Fig. 6(a). Raman spectra of SBNN ceramics as a function of x ; (b) FWHMs of 250 cm^{-1} and 630 cm^{-1} modes.

Fig. 7. Temperature dependence of dielectric constant and dielectric loss for SBNN ceramics with different x .

Fig. 8. Dielectric properties of SBNN ceramics with different Na^+ contents: (a) the temperature dependence on ε and $\tan\delta$ for SBNN ceramics measured at 10 kHz as a function of x ; (b) ε_r and $\tan\delta$ of SBNN ceramics measured at 10 kHz as a function of x ; (c) T_c and ε_m for SBNN ceramics measured at 10 kHz as a function of x .

Fig. 9. Low temperature dependence of dielectric constant and dielectric loss of SBNN ceramics.

Fig. 10. Frequency dependence of dielectric properties ranges from 300 Hz to 1 MHz of SBNN ceramics with different Na⁺ contents ($x = 0.0, 1.0, 2.0, 2.5$).

Fig. 11. Ferroelectric properties of SBNN ceramics with different Na⁺ contents.

Fig. 12. P_r and E_c of SBNN ceramics measured at room temperature as a function of x .

Fig. 13. Polarization-electric field (P - E) hysteresis loops of SBNN ceramics with $x = 0.0, 1.0, 2.5$ measured at different temperatures.

Figure(s)

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