Electrical and transparent properties induced by structural modulation in

$(\text{Sr}_{0.925}\text{Ca}_{0.075})_{2.5-0.5x}\text{Na}_x\text{Nb}_5\text{O}_{15}$ ceramics

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Abstract

The effects of Na^+ concentration on the microstructural, dielectric, ferroelectric and transparent properties of $(\text{Sr}_{0.925}\text{Ca}_{0.075})_{2.5-0.5x}\text{Na}_x\text{Nb}_5\text{O}_{15}$ (SCNN; $0.4 \leq x \leq 1.0$) ceramics prepared using a conventional solid-state reaction method were investigated. X-ray diffraction results showed that the phase structure transitioned from tetragonal to orthorhombic tungsten bronze along with the structural type changing from ‘unfilled’ to ‘filled’ state. The NbO_6 octahedron became more distorted and had higher interaction strength when introducing Na^+ in A-sites to decrease the structural vacancies, leading to the improvement of dielectric and ferroelectric properties. The dielectric spectra of all specimens showed two broad dielectric anomalies: a high-temperature anomaly (the ferroelectric phase transition) and a low-temperature anomaly caused by the subtle structural effects in ‘unfilled’ SCNN ceramics, which evolved into the ferroelastic phase transition in ‘filled’ SCNN ceramics.

Keywords: Structural modulation; NbO_6 distortion; Tungsten bronze niobates; Dielectric properties; Ferroelectric properties

1. Introduction

Lead-free piezoelectric ceramics showing perovskite and bismuth-layered structures have been extensively studied [1-2]. Besides these two families, increasing attention has also been paid to ferroelectric crystals with tungsten bronze (TB) structures, which have diverse properties (e.g., nonlinear optic, pyroelectric, and piezoelectric) as a result of their compositional flexibility [3-5]. The characteristic features of the TB structure are three types of open channels (square A1-sites, pentagonal A2-sites and trigonal C-sites) that develop within its corner-sharing BO_6 octahedron framework, as shown in Fig. S1. The TB crystal structure can be described using the general formula of $(\text{A1})_2(\text{A2})_4(\text{C})_4(\text{B1})_2(\text{B2})_8\text{O}_{30}$ [6-9]. The octahedron framework and open channels enable a wide range of substitutions within the TB structure. In these compounds, ferroelectricity arises from the interaction between Nb atoms and the oxygen framework in the polar BO_6 units.

Within the TB crystal structure, the smallest interstice C-sites are usually vacant. The formula $\text{A}_6\text{B}_{10}\text{O}_{30}$ represents the ‘filled’ TB structure, i.e., when all six A-sites are occupied. If the A-sites are not completely occupied, the structure is referred to as being ‘unfilled’. $\text{Sr}_{2-x}\text{Ca}_x\text{NaNb}_5\text{O}_{15}$ (SCNN, $0.05 < x < 0.35$) ceramics with a ‘filled’ TB structure have shown potential as lead-free piezoelectric materials [10-12]. SCNN single crystals with large piezoelectric constants at $x = 0.1$ have been reported [13-16]. However, applications of single crystals are limited because of the high-cost associated with fabrication of single crystals. Ceramics can be made into larger and more complex components at a lower cost than single crystals. Recently, Xie *et al.* successfully obtained fully-dense $\text{Sr}_{2-x}\text{Ca}_x\text{NaNb}_5\text{O}_{15}$ ceramics using spark plasma sintering technique and discussed the effects of Ca substitution of Sr on the crystal structure and electrical properties of ‘filled’ TB SCNN ceramics [13]. They reported

that the dielectric spectra of all specimens exhibited two broad dielectric anomalies: the high-temperature anomaly caused by the paraelectric ($4/mmm$)–ferroelectric ($4mm$) transition (ferroelectric phase transition), and a low-temperature anomaly caused by the ferroelectric ($4mm$)–ferroelastic ($mm2$) transition (ferroelastic phase transition) [14-16]. In addition, the peak of the low-temperature anomaly was reported to shift toward higher temperatures and the relaxor behavior weakened gradually with increasing Ca content in the ‘filled’ TB SCNN ceramics.

With the possibility of modulated crystal structures, the TB structure offers significant compositional flexibility [17-19], which can directly affect the dielectric properties. In addition to the A-site-ion effects, the A-sites-occupancy is another key parameter governing the dielectric behaviors in TB compounds. Correlations among the composition, structure and properties can be studied by modulating the alkali metal ion content in the A-sites of the TB $(A1)_2(A2)_4Nb_{10}O_{30}$ composition to tune the structure (i.e., changing the structure from ‘unfilled’ to ‘filled’ type). Previously, we have formed the $(Sr_{0.53}Ba_{0.47})_{2.5-0.5x}Na_xNb_5O_{15}$ ($0.0 \leq x \leq 1.0$) compounds by introducing the alkali metal Na^+ into the ‘unfilled’ $Sr_{0.53}Ba_{0.47}Nb_2O_6$ ceramics [20]. It was found that the low-temperature dielectric anomalies were not observed in ‘unfilled’ $Sr_{0.53}Ba_{0.47}Nb_2O_6$ ceramics. However, when the Na^+ content increased to decrease the structural vacancies in the A-sites, peaks corresponding to the low-temperature anomaly appeared; the dielectric anomaly was gradually enhanced as the degree of structural filling increased. The dielectric anomaly observed in $(Sr_{0.53}Ba_{0.47})_{2.5x-0.5x}Na_xNb_5O_{15}$ ceramics was as slight as that observed in $Sr_2NaNb_5O_{15}$ ceramics at approximately $-33\text{ }^{\circ}C$, which was associated to the smeared-out phase transition state and correlated to the subtle structure effects [21].

To understand the evolution of ferroelectric and dielectric behaviors in TB

SCNN compounds, the relation between structural type and electrical properties has been studied by modulating the Na^+ concentration to tune the A-sites-occupancy. Studies involving the effects of Sr/Ca ratio on electrical properties of SCNN ceramics have shown that the ceramics with $x = 0.15$ showed better electrical properties and had application prospects in lead-free electronic components [15, 22]. In this work, $(\text{Sr}_{0.925}\text{Ca}_{0.075})_{2.5-0.5x}\text{Na}_x\text{Nb}_5\text{O}_{15}$ (SCNN, $0.4 \leq x \leq 1.0$) ceramics were designed and synthesized using a conventional mixed-oxide method. The influences of structural modulation, which is caused by the Na^+ concentration to tune the structure changing from the ‘unfilled’ to ‘filled’ state, on dielectric and ferroelectric properties of TB SCNN ceramics were studied in detail. All of the SCNN ceramics studied showed optical transmittance. The underlying mechanisms causing variations of the electric and transparent properties were discussed.

2. Experimental procedures

A conventional mixed-oxide method was used to prepare $(\text{Sr}_{0.925}\text{Ca}_{0.075})_{2.5-0.5x}\text{Na}_x\text{Nb}_5\text{O}_{15}$ ($0.4 \leq x \leq 1.0$) from reagent grade CaCO_3 , SrCO_3 , Na_2CO_3 and Nb_2O_5 powders. The starting powders were weighed according to the molecular formula $(\text{Sr}_{0.925}\text{Ca}_{0.075})_{2.5-0.5x}\text{Na}_x\text{Nb}_5\text{O}_{15}$ ($x = 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0$) and then subsequently ball milled in ethanol for 16 h using zirconia balls. The mixed powders were calcined in air at 1200 °C for 4 h and then pressed into pellets with diameters of 15 mm under 300 MPa pressure. The pellets were sintered in air at 500 °C for 2 h and then at 1330–1360 °C for 4 h.

The phase structure of the prepared ceramics samples was characterized using X-ray diffraction (XRD; D/max-2200, Rigaku, Japan, $\text{Cu K}\alpha$) with a scanning step of 0.02° over a 2θ range of $20\text{--}60^\circ$. Raman scattering data were collected using a Raman spectrometer (Renishaw, inVia) with a back-scattering geometry using a 532-nm laser-line from an Ar-ion laser. The relative densities were also measured and

calculated based on the theoretical density for each composition, which is calculated from the unit cell volumes according to XRD results. High-dense values from 98.0% to 98.8% were obtained for all the sintered SCNN ceramics. Microstructures of the polished surface of the ceramics were obtained using a field-emission scanning electron microscope (FESEM; Hitachi SU8000). Temperature dependence of the dielectric constant was measured on a LCR meter (Agilent E4980A) over a temperature range from ambient temperature to 500 °C at different frequencies. The ferroelectric hysteresis loops (i.e., polarization versus applied electrical field loops or P – E loops) and the leakage current density hysteresis loops (i.e., leakage current intensity versus applied electrical field loops or J – E loops) were observed using a Radiant Precision Workstation (Albuquerque, NM, USA). Optical transmittance of the SCNN ceramics was measured in the range of 200–2000 nm using an UV/VIS/NIR Spectrometer (UV-Lambda 950, PerkinElmer, USA).

3. Results and discussion

XRD patterns recorded at room temperature in the 2θ range of 20°–60° are shown in Fig. 1(a). When $x < 0.9$, all of the patterns agreed with the Joint Committee on Powder Diffraction Standards Card (JCPDS card #34-0429), revealing a phase of pure ‘unfilled’ tetragonal TB structure; no secondary phases were detected. This indicated that Na^+ ions diffused into the TB lattice to form a new homogeneous solid solution. However, for the designed ‘nearly-filled’ and ‘filled’ structural ceramics with $x = 0.9$ and $x = 1.0$, a few cubic phase $\text{Na}_{0.5}\text{Sr}_{0.25}\text{NbO}_3$ (NSN, JCPDS cards #27-0788) was observed in the XRD patterns. The perovskite-type NSN phase was also detected using powder X-ray and neutron diffraction in ‘filled’ TB $\text{Sr}_2\text{NaNb}_5\text{O}_{15}$ ceramics [21]. Torres-Pardo *et al.* showed that the ‘filled’ TB SCNN compounds were easily contaminated by the perovskite-type $\text{Na}_{0.5}\text{Sr}_{0.25}\text{NbO}_3$ phase due to the solid

solution limit [21, 22]. According to Fig. 1(a), the XRD spectra measured from the SCNN ceramics with $x = 0.4$ showed that the peak at approximately 46.7° split into two peaks: a relatively lower (620) peak and a higher (002) peak, showing that the ceramics had a tetragonal TB structure. As x increased from 0.4 to 0.8, the two peaks merged together, suggesting that the SCNN ceramics changed into an orthorhombic TB phase at room temperature. The peak merging phenomenon became apparent in the ‘nearly-filled’ and ‘filled’ SCNN ceramics with higher x values.

Figure 1. (a) XRD spectra from the SCNN ceramics with different x ; (b) enlarged view of the XRD spectra in the range from 31.7° to 33.6° .

To further study the structure distortion caused by Na^+ substitution, the lattice parameters of SCNN ceramics with different Na contents were calculated from the Rietveld refinements on X-ray diffraction data and shown in Tables S1. According to the obtained cell parameters, at $x = 0.4$, the difference between a (12.3501 Å) and b (12.3575 Å) was so negligible that the ceramics with $x = 0.4$ could be considered to be tetragonal phase. With x increases, the value of $\Delta(b-a)$ gradually increased from 0.0074 (at $x = 0.4$) to 0.0434 (at $x = 1.0$), indicating that the crystal structure slightly distorted from the tetragonal phase and became the orthorhombic phase at room

temperature. In addition, the lattice parameter c increased slightly and the lattice unit volume V increased obviously with increasing the Na^+ content. Detailed analyses of the XRD spectra in the 2θ range from 31° to 33° are shown in Fig. 1(b). All of the diffraction peaks shifted toward lower angles as the Na^+ content increased, further suggesting that the unit cell expansion was accompanied by the structural change from ‘unfilled’ to ‘filled’ state.

Figure 2. FESEM polished surface micrographs of SCNN ceramics with different Na^+ contents (a) $x = 0.4$, (b) $x = 0.6$, (c) $x = 0.7$, (d) $x = 0.8$, (e) $x = 0.9$ and (f) $x = 1.0$.

FESEM polished surface micrographs of SCNN ceramics in Fig. 2 showed that no cracks were observed and all ceramics displayed dense microstructure. The grain morphology varied obviously with composition x . According to Fig. 2(a), the grains with homogenous equiaxed shape can be obtained in SCNN ceramics with ‘unfilled’ structural type at $x = 0.4$. Most of the grains in SCNN ceramics with ‘filled’ structural type at $x = 1.0$ showed anisometric pillar-type shape with preferred grain growth along the c -axis direction [23-25]. As the Na^+ concentration increased, the grains grew bigger and the anisometric growth behavior became more apparent. Elongation along the c -axis was due to a higher growth rate of along the c -plane caused by larger

attachment energy on the *c*-plane [26]. These results indicated that the ‘filled’ TB structure preferred to the grain growth with anisometric morphology.

Fig. 3(a) shows the room-temperature Raman spectra measured for the SCNN ceramics over the frequency range from 10 cm^{-1} to 1000 cm^{-1} . Three characteristic Raman peaks (ν_1 , ν_2 , ν_5) corresponding to the NbO_6 octahedron were observed. These peaks were identified as the internal modes of NbO_6 octahedron, which were referred to the Nb–O stretching (840 cm^{-1} and 630 cm^{-1}) and O–Nb–O bending (250 cm^{-1}) vibrations [19, 22, 26, and 27]. The Raman spectra at low Raman shifts ($\nu < 200 \text{ cm}^{-1}$) was dominated by external vibration modes involving cation motions relative to the NbO_6 octahedron framework [27, 28]. As the structure changed from ‘unfilled’ to ‘filled’ state, the wavenumbers of the external vibration modes (99.5 cm^{-1} , 135.6 cm^{-1} and 175.3 cm^{-1}) did not change, while the wavenumbers of the internal vibration modes shifted to higher values (blue shift). As shown in Figs. 3(b) and 3(c), a slight blue shift was observed for the internal modes at 250 cm^{-1} (O–Nb–O bending) and 630 cm^{-1} (Nb–O stretching) as x increased from 0.4 to 1.0. In general, lattice contraction of NbO_6 octahedron can result in blue shifting internal modes [28]. This suggests that the interaction of Nb and O atoms inside NbO_6 octahedron became more intense because of the extrusion of A-site ions onto the NbO_6 octahedron when the structural evolution approached the ‘filled’ state. The full width at half maximum (FWHM) of the Raman lines in the SCNN ceramics was extracted by fitting the profiles with individual Lorentz profiles. As shown in Fig. 3(d), the FWHM values of the two internal modes increased as x increased from 0.4 to 1.0, which suggests that the NbO_6 octahedron became more distorted as x increased. The Raman spectra showed that the structural evolution induced by increasing the Na^+ concentration in SCNN ceramics to decrease the structural vacancy could enhance the degree of

distortion and increased the interaction strength inside the NbO_6 octahedron, which should have obvious impact on the dielectric and ferroelectric behaviors of the SCNN ceramics.

Figure 3. (a) Raman spectra of SCNN ceramics as a function of x ; (b) enlarged view of Raman shift around 250 cm^{-1} ; (c) enlarged view of Raman shift around 630 cm^{-1} ; (d) FWHMs of 250 cm^{-1} and 630 cm^{-1} modes.

Fig. 4(a) presents the temperature dependence of relative permittivity (ε) for the SCNN ceramics with different Na^+ concentrations measured at 10 kHz. The ε peaks were associated with the ferroelectric-to-paraelectric phase transition, which occurred at the Curie temperature (T_c). The maximum relative permittivity (ε_m) was obtained at T_c . Fig. 4(b) presents T_c and ε_m as a function of x . T_c shifted toward higher temperatures from 260°C to 306°C as x increased from 0.4 to 1.0, which indicated that introducing Na^+ could improve T_c in SCNN ceramics by modulating the structure to change from ‘unfilled’ to ‘filled’ type. Introducing Na^+ into A-sites could increase

the distortion in crystal structure and restricted the rattling space available for the ions inside the oxygen octahedron, which could increase ionic displacements and then cause T_c to increase [29, 30]. ε_m increased as x increased from 0.4 to 0.8, reached a maximum value of 1320 at $x = 0.8$, and then decreased as the Na^+ content increased further. The relative permittivity (ε_r) and dielectric loss ($\tan\delta$) near room temperature at 10 kHz are presented in Fig. 4(c). As x increased from 0.4 to 0.7, $\tan\delta$ showed almost no change, reached a minimum value at $x = 0.8$, and then increased when $x > 0.8$. ε_r increased gradually from 997 at $x = 0.4$ to 1530 at $x = 0.9$, and then decreased at $x = 1.0$. The dielectric results indicated that the best overall dielectric performance was achieved at $x = 0.8$, when the ceramics showed relatively high relative permittivity values ($\varepsilon_m = 1320$, $\varepsilon_r = 1394$) and a low value of $\tan\delta$ (0.006). This result could be attributed to the presence of a pure TB phase at $x = 0.8$ and the enhanced distortion degree of NbO_6 octahedron caused by increasing the Na^+ content in A-sites to decrease the structural vacancy.

Figure 4. (a) ε for SCNN ceramics measured at 10 kHz as a function of x ; (b) T_c and ε_m for SCNN

ceramics measured at 10 kHz as a function of x ; (c) ε_r and $\tan\delta$ of SCNN ceramics measured at 10 kHz as a function of x .

Fig. 5 shows the temperature dependence of ε at low temperatures measured at selected frequencies. In addition to the high-temperature dielectric anomaly associated with the ferroelectric ($4mm$)-to-paraelectric ($4/mmm$) phase transition shown in Fig. 4(a), a low-temperature dielectric anomaly (T_s) was observed for all of the SCNN ceramics. At $x = 0.4$, the broad peak associated with the low-temperature dielectric anomaly in the ‘unfilled’ SCNN ceramics showed obvious relaxor behavior: the position of maximum relative permittivity shifted toward higher temperatures as the frequency increases. The relaxor behavior of the low-temperature dielectric anomaly is similar to that observed in $(\text{Sr}_{0.53}\text{Ba}_{0.47})_{2.5-0.5x}\text{Na}_x\text{Nb}_5\text{O}_{15}$ and $\text{Sr}_2\text{NaNb}_5\text{O}_{15}$ ceramics [20, 21]. In those materials, the relaxor behavior can be attributed to the smeared-out phase-transition state, combined with subtle structure effects [20, 21]. As x increased from 0.6 and 0.8, the height of the low-temperature dielectric anomaly peak was more intense than that of SCNN ceramics with $x = 0.4$. At $x = 1.0$, the low-temperature dielectric anomaly peak was the most notable, while the relaxor behavior was inhibited. The low-temperature dielectric anomaly in the ‘nearly-filled’ and ‘filled’ SCNN ceramics is similar to that observed in ‘filled’ $\text{Sr}_{2-x}\text{Ca}_x\text{NaNb}_5\text{O}_{15}$ ceramics [31]. The enhanced low-temperature dielectric anomaly peak in the ‘nearly-filled’ and ‘filled’ SCNN ceramics with higher x values could be considered as a ferroelastic phase transition, i.e., the ferroelectric ($4mm$)-ferroelastic ($mm2$) transition. These results demonstrated that as x increased to tune the structure of SCNN ceramics to change from an ‘unfilled’ to a ‘filled’ state, introducing Na^+ into the A-sites could cause the distortion in tetragonal crystal structure, along with the enhanced distortion degree of NbO_6 octahedron and the increased interaction strength inside NbO_6

octahedron, which acted together to induce the subtle structure effects existed in ‘unfilled’ SCNN ceramics evolve into the structural phase transition from ferroelectric ($4mm$)-to-ferroelastic ($mm2$) (ferroelastic phase transition) in ‘nearly-filled’ and ‘filled’ SCNN ceramics with higher x values.

Figure 5. Low temperature dependence of ε' and $\tan\delta$ for SCNN ceramics with different x ($x = 0.4$, 0.6, 0.8 and 1.0) measured at selected frequencies.

At the ferroelastic phase transition temperature (T_s), ε' reached its maximum value (denoted as ε_s). As shown in Fig. S2, with increasing x from 0.4 to 1.0, T_s shifted toward higher temperatures from -67°C to 51°C and ε_s increased gradually from 1196 to 1748, demonstrating that modulating the structure of the SCNN ceramics from ‘unfilled’ to ‘filled’ type could improve both T_s and ε_r . T_s was -67°C for the ‘unfilled’ SCNN ceramics with $x = 0.4$, which was lower than room temperature, indicating that the obtained ceramics show tetragonal TB phase. As x increased to 0.9, T_s shifted to higher temperature near to room temperature, indicating that the orthorhombic TB and the tetragonal TB phases were all present in the

obtained ceramics. At $x = 1.0$, T_s was 50 °C, which was higher than room temperature, suggesting the ‘filled’ SCNN ceramics were with an orthorhombic TB phase at room temperature. The phase structure results obtained from the dielectric properties measured at low temperatures are consistent well with the structural results observed using XRD.

The measured P – E loops (red lines) and J – E loops (blue lines) are shown in Fig. S3. All of the samples showed well-saturated P – E loops, indicating that they possessed good ferroelectric properties. However, an insulation leakage exists in actual ferroelectrics, which causes the measured P – E loops to deviate from the actual P – E loops [32, 33]. For J – E curves, the leakage current density from dielectric with no ferroelectric property is almost a constant value, while for the contribution from the ferroelectric domain switching [33], the current density peak appears at the coercive fields [32]. These features confirmed the domain structure and long-range ferroelectric order for all of the SCNN ceramics at room temperature. The P – E hysteresis loops of SCNN ceramics with different x are shown in Fig. 6(a). The values of remnant polarization (P_r) and coercive field (E_c) as a function of x are shown in Fig. 6(b). P_r increased initially, reached a maximum value of 5.5 $\mu\text{C}/\text{cm}^2$ at $x = 0.8$, and then decreased with further increasing x above 0.8. Meanwhile, the corresponding value of E_c was 19.0 kV/cm at $x = 0.8$. Reports have suggested that ferroelectricity in TB compounds can be affected by off-center displacements of the B-site ions [27], oxygen octahedral tiling, A- and B-sites cation occupation [34] and the microstructure of the ceramics [26]. Combining the results of structure, dielectric and ferroelectric properties, the best electrical performance was obtained at $x = 0.8$. The degree of occupancy increased with increasing Na^+ content, which could result in more crystal structural distortion and more intense interaction between A-site ions and NbO_6

octahedron (verified by Raman spectroscopy). This suggested that the SCNN ceramics with ‘nearly-filled’ or ‘filled’ structural types possessed superior electrical properties. However, in this study, the electrical properties were observed to deteriorate with higher Na^+ content at $x = 1.0$ due to the presence of the second cubic phase of NSN.

Figure 6. (a) Ferroelectric properties of SCNN ceramics with different Na^+ contents measured at room temperature; (b) P_r and E_c of SCNN ceramics measured at room temperature as a function of x .

To obtain more information for SCNN ceramics with $x = 0.8$, P - E loops and J - E loops were measured at different temperatures. Fig. 7(a) shows the temperature-dependent P - E loops measured from SCNN ceramics with $x = 0.8$ in the temperature range from 20 °C to 120 °C under the same electric field. As the temperature

increased, well-saturated P - E loops were obtained, while P_r and E_c decreased monotonically. As shown in Fig. 7(b), the depolarization current peaks appeared and shifted toward lower fields as the temperature increased from 40 °C to 120 °C. This phenomenon agreed with the results shown in Fig. 7(a). A similar trend was also observed in lead-based ceramics and lead-free ceramics [32, 35]. This phenomenon suggested the decreasing stability of the field-induced long-range ferroelectric order and an increasing energy barrier for the formation of ferroelectric domains out of the Polar Nano-Regions for all samples.

Figure 7. Polarization-electric field (P - E) hysteresis loops (a) and polarization current intensity-electric field (J - E) loops (b) of SCNN ceramics with $x = 0.8$ measured at different temperatures.

Fig. 8 shows the UV-visible spectra corresponding to SCNN ceramics with different x . Optical transmittance (T) of the SCNN ceramics was measured in the wavelength range of 200–2000 nm at room temperature. For all of the SCNN ceramics, T increased gradually with wavelength and was nearly saturated in the near-IR region. Photographs of the 0.5-mm-thick ceramics are shown as an inset of Fig. 8. A relatively high T (35% to 40%) was obtained for all the SCNN ceramics in the wavelength range from 600 nm to 1600 nm. Although the measured T values are much lower than those of KNN-based ceramics ($\approx 72\%$) [36], the optical phenomena in SCNN ceramics were worth studying because the SCNN materials have a low degree of crystal symmetry, while the transparent KNN-based ceramics exhibit a high degree of crystal symmetry (cubic phase). For the SCNN ceramics, T increased as x increased from 0.4, reached its maximum value at $x = 0.5$, and then decreased when $x > 0.5$. Lower T at higher Na^+ content may be caused by the increased presence of anisometric, pillar-shaped grains, which were harmful to the T because of the weakness of light scattering. The second phase, which was presented when $x = 0.9$ and 1.0, can also cause T to deteriorate.

Figure 8. The transmittance curves of the SCNN ceramics with different Na^+ contents.

4. Conclusions

$(\text{Sr}_{0.925}\text{Ca}_{0.075})_{2.5-0.5x}\text{Na}_x\text{Nb}_5\text{O}_{15}$ ($0.4 \leq x \leq 1.0$) ceramics were prepared using the conventional solid-state reaction method. Structural modulations controlled by the Na^+ concentration had a strong influence on the phase structure, microstructure, transparent properties, dielectric properties, and ferroelectric properties of the SCNN ceramics. XRD results showed that the phase structure changed from tetragonal to orthorhombic TB as x increased, along with the changing of the structural type from ‘unfilled’ to ‘filled’ state. The ‘filled’ TB structure was easily contaminated by a small amount of cubic phase NSN. FESEM images showed that introducing Na^+ into the crystal structure induced the growth of anisometric, pillar-type grains. Introduction of Na^+ decreased the structural vacancies on the A-sites, which was beneficial for the dielectric and ferroelectric properties of the SCNN ceramics because it enhanced the distortion degree of the NbO_6 octahedron in the unit cell and increased the interaction strength inside NbO_6 octahedron. Overall, the best dielectric and ferroelectric properties were obtained at $x = 0.8$. For $x > 0.8$, the electric properties deteriorated with increasing Na^+ content because of the presence of a second cubic NSN phase. The dielectric spectra measured for all of the specimens had two broad dielectric anomalies over the temperature range of interest. The high-temperature anomaly was associated with the paraelectric ($4/mmm$)–ferroelectric ($4mm$) transition (ferroelectric phase transition). The low-temperature anomaly was observed in the temperature range from $-100\text{ }^\circ\text{C}$ to $120\text{ }^\circ\text{C}$; this feature was the result of subtle structural effects for the ‘unfilled’ SCNN ceramics and the ferroelastic phase transition for the ‘filled’ SCNN ceramics. All of the SCNN ceramics exhibited some transmittance in the visible spectra, even though they had a low degree of crystal symmetry.

Acknowledgements

This work was supported by National Science Foundation of China (NSFC) (Grant No. 21401123).

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Figure Captions

Figure 1(a). XRD spectra from the SCNN ceramics with different x ; (b) enlarged view of the XRD spectra in the range from 31.7° to 33.6° .

Figure 2. FESEM **polished surface** micrographs of SCNN ceramics with different Na^+ contents (a) $x = 0.4$, (b) $x = 0.6$, (c) $x = 0.7$, (d) $x = 0.8$, (e) $x = 0.9$ and (f) $x = 1.0$.

Figure 3. (a) Raman spectra of SCNN ceramics as a function of x ; (b) enlarged view of Raman shift around 250 cm^{-1} ; (c) enlarged view of Raman shift around 630 cm^{-1} ; (d) FWHMs of 250 cm^{-1} and 630 cm^{-1} modes.

Figure 4. (a) ε for SCNN ceramics measured at 10 kHz as a function of x ; (b) T_c and ε_m for SCNN ceramics measured at 10 kHz as a function of x ; (c) ε_r and $\tan\delta$ of SCNN ceramics measured at 10 kHz as a function of x .

Figure 5. Low temperature dependence of ε and $\tan\delta$ for SCNN ceramics with different x ($x = 0.4, 0.6, 0.8$ and 1.0) measured at selected frequencies.

Figure 6. (a) Ferroelectric properties of SCNN ceramics with different Na^+ contents **measured at room temperature**; (b) P_r and E_c of SCNN ceramics measured at room temperature as a function of x .

Figure 7. Polarization-electric field (P - E) hysteresis loops **(a)** and polarization current intensity–electric field (J - E) **loops (b)** of SCNN ceramics with $x = 0.8$ measured at different temperatures.

Figure 8. The transmittance curves of the SCNN ceramics with different Na^+ contents.

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