Transparency of $\text{K}_{0.5}\text{Nb}_{0.5}\text{O}_3\text{-Sr}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ lead-free ceramics modulated by relaxor behavior and grain size

Xiaoshuai Zhang,^a Dong Yang,^a Zhenyu Yang,^a Xumei Zhao,^a Qizhen Chai,^a Xiaolian Chao,^a Lingling Wei,^b and Zupei Yang^{a,†}

^a Key Laboratory for Macromolecular Science of Shaanxi Province, School of Materials Science and Engineering, Shaanxi Normal University, Xi'an, 710062, Shaanxi, P.R. China

^b School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an, 710062, Shaanxi, P.R. China

Corresponding authors at:

Key Laboratory for Macromolecular Science of Shaanxi Province

School of Materials Science and Engineering

Shaanxi Normal University, Xi'an, 710062, Shaanxi, P.R. China

Tel: +86-29-8153-0718; Fax: +86-29-8153-0702

E-mail address: yangzp@snnu.edu.cn

Abstract

High transparency was obtained in $(1-x)(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ - $x\text{Sr}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ($x = 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08$) lead-free ceramics by pressure-less sintering procedure. The effects of $\text{Sr}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ content on the microstructure, phase transition, optical properties and electrical properties were studied in detail. The X-ray diffraction results showed that the crystal structure of ceramics gradually transformed from orthorhombic phase into pseudo-cubic phase with doping of $\text{Sr}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$. The fine grain microstructure with clear grain boundary was observed in all compositions, while the grain size exhibited significant composition dependence. It was found that a more uniform distribution with smaller grain size was favorable to high optical transmittance, owing to the decreased scattering by grains and grain boundaries. In addition, a strong diffuse phase transformation in KNN-based ceramics induced by $\text{Sr}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ doping, causing the ceramics become more relaxor-like and transparent. The transmittance and electric properties results indicated that the $0.95(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ - $0.05\text{Sr}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ceramics exhibited higher transmittance (60% in the near-IR region) accompanied with better electrical properties ($\varepsilon_m = 2104$, $P_r = 5.0 \mu\text{C}/\text{cm}^2$, $d_{33} = 92 \text{ pC}/\text{N}$).

Keywords: Transparent ceramics; Grain size; Relaxor behavior; Electrical properties

1. Introduction

Nowadays, KNN-based ceramics have become one of the most extensively investigated lead-free piezoelectric system due to its large d_{33} and high T_c , which were considered as a good candidates to replace lead-based materials applied in many electronic devices such as sensors, actuators, ultrasound transducers, etc.¹⁻³ In 2004, a breakthrough of d_{33} value (~ 416 pC/N) was obtained in (K,Na,Li)(Nb,Ta,Sb)O₃-textured ceramics fabricated using reactive templated grain growth (RTGG) methods.⁴ Since then, a large number of efforts has been stimulated to focus on optimizing the piezoelectricity in KNN-based ceramics through constructing the multi-phase boundaries by doping additives, and studying the origin of high piezoelectricity in these materials.⁵⁻⁹

Besides the study on traditional electric properties, the optical properties has been explored and gradually studied in the KNN-based ceramics recently. After the discovery of transparency in 0.8(K_{0.5}Na_{0.5})NbO₃-0.2SrTiO₃ ceramics reported by Malic *et al.* in 2004,¹⁰ the transparent phenomenon also reported in 0.96(K_{0.5}Na_{0.5})NbO₃-0.04(Bi_{0.5}Na_{0.5})TiO₃ ceramics by Du *et al.*¹¹ However, the specific transparent performances were not discussed in these studies. In recent years, by employing sol-gel method and hot-pressing sintering procedure, Kwok *et al.* reported a series of KNN-based transparent ceramics with high transmittance of $\sim 60\%$ in the near-IR region by modification with Bi⁵⁺ or co-modification with Li⁺ and Bi⁵⁺, such as K_{0.48}Na_{0.52}Nb_{0.925}Bi_{0.075}O₃ and (K_{0.5}Na_{0.5})_{0.95}Li_{0.05}Nb_{0.95}Bi_{0.05}O₃ ceramics.¹²⁻¹⁴ Using the same hot-pressing sintering procedure, Geng *et al.* fabricated

$[(\text{K}_{0.5}\text{Na}_{0.5})_{1-2x}(\text{Sr}_{0.75}\text{Ba}_{0.25})_x]_{0.93}\text{Li}_{0.07}\text{Nb}_{0.93}\text{Bi}_{0.07}\text{O}_3$ transparent ceramics with transmittance up to 60 % in the UV–visible region.¹⁵ However, industrial applications are limited due to the high cost of hot-pressing sintering procedure.

In our previous work,¹⁶ a pressure-less procedure was successfully employed to fabricate $(1-x)(\text{K}_{0.37}\text{Na}_{0.63})\text{NbO}_3-x\text{Ca}(\text{Sc}_{0.5}\text{Nb}_{0.5})\text{O}_3$ lead-free ceramics with high transmittance of 60% in the near-IR region. Du *et al* also reported the transmittance of $0.8(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3-0.2\text{Sr}(\text{Sc}_{0.5}\text{Nb}_{0.5})\text{O}_3$ ceramics is over 60% (0.3 mm) in the near-IR region when studied the energy storage density of the ceramics.^{17,18} Subsequently, using the same pressure-less procedure, we also discovered the $0.975\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3-0.025\text{LaBiO}_3$ ceramics with excellent transmittance value over 74% in the visible spectrum, which was higher than that of PLZT transparent ceramics and other KNN-based ceramics reported before.¹⁹ But the electrical properties of $0.975\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3-0.025\text{LaBiO}_3$ ceramics were very poor, for which the dielectric constant was below 1000 and the P_r was only $0.5 \mu\text{C}/\text{cm}^2$. In order to obtain excellent transparent KNN-based ceramics simultaneously with good electrical properties, it is essential to systematically study the relationship among composition, structure and properties.

Thus in this work, our purpose is not only to explore a new KNN-based transparent ceramics with good electrical properties by pressure-less sintering, but also to further reveal the inner relationship among transmittance, grain size, phase structure and relaxor behavior. Through studying the relevant influence factors on transparent properties, it is found that the relaxor behavior induced by introducing a

second component in KNN-based ceramics is the key factor to obtain high transmittance.^{14,16,20} It is well known that $A(B_1B_2)O_3$ ($B_1 = Mg^{2+}, Zn^{2+}, \dots, B_2 = Nb^{5+}, Ta^{5+} \dots$) materials are ferroelectrics of perovskite type exhibiting a relaxor type diffuse phase transition, such as $Pb(Mg_{1/3}Nb_{2/3})O_3$ -based ceramics and $Pb(Zn_{1/3}Nb_{2/3})O_3$ -based ceramics.²¹⁻²² In this study, $Sr(Mg_{1/3}Nb_{2/3})O_3$ with similar structure as $Pb(Mg_{1/3}Nb_{2/3})O_3$ was selected and introduced into $(K_{0.5}Na_{0.5})NbO_3$ ceramics to induce the relaxor behavior. In addition, effects of $Sr(Mg_{1/3}Nb_{2/3})O_3$ content on the phase transition, microstructure, optical properties, and electrical properties of $(1-x)(K_{0.5}Na_{0.5})NbO_3-xSr(Mg_{1/3}Nb_{2/3})O_3$ ceramics were investigated systematically. Especially, the synergistic effect mechanism of grain size and relaxor behavior on transmittance and electrical properties were emphatically discussed.

2. Experimental procedures

$(1-x)(K_{0.5}Na_{0.5})NbO_3-xSr(Mg_{1/3}Nb_{2/3})O_3$ (KNN-SMN: $0.02 \leq x \leq 0.08$) powders were synthesized by solid state reaction using Na_2CO_3 , K_2CO_3 , $SrCO_3$, Nb_2O_5 and MgO as raw materials. The resultant powders were dried at 120 °C for 24 h and then were weighed for different KNN-SMN content according to stoichiometry. Then powders were ball-milled for 24 h with zirconia balls using ethanol as media. Then dried slurries were calcined at 900 °C for 5 h and re-milled for 12 h and the powders were mixed with 5 wt.% solution of polyvinyl alcohol (PVA) as a binder followed by uniaxially pressing into pellets with a diameter of 15 mm at 300 MPa. After burning off PVA, the pellets were sintered at 1220 °C for 6 h in a sealed alumina crucible containing the calcined powders as sintering atmosphere. The sintered pellets were

manually polished down to approximately 0.5 mm thickness manually using diamond slurry with a particle size of 0.1 μm for obtaining flatter surfaces.

Optical transmission spectrum from 200 to 2000 nm was measured by ultraviolet-visible-near infrared (UV-vis-NIR) spectroscopy (UV-3600; Shimadzu, Kyoto, Japan). Phase structure characterization was performed by X-ray diffraction (XRD, MiniFlex600, Rigaku, Tokyo, Japan, $\text{Cu K}\alpha$) technique on polished surfaces of sintered pellets. Raman scattering measurements were taken by a Raman spectrometer (Renishaw, invia) with a back scattering geometry. The laser source was 532 nm line obtained from an Ar ion laser. Density was measured by the Archimedes method with distilled water. The microstructures were observed by using a cold field emission scanning microscopes (FE-SEM, s-4800 Japan, Hitachi).

For electrical measurements, silver paste was coated on the top and bottom surfaces of the samples and heated at 840 $^{\circ}\text{C}$. The dielectric properties were measured at 1, 10, 100 kHz using an impedance analyzer (E4980A; Agilent technologies company, USA) from room temperature to 500 $^{\circ}\text{C}$. Room-temperature polarization-electric field (P - E) loops were measured at 1 Hz using a ferroelectric tester. The samples were poled in silicone oil at 3 kV/mm for 30 min at room temperature. Piezoelectric coefficient (d_{33}) was recorded from 1-day-aged samples using a quasistatic piezoelectric d_{33} meter (ZJ-3d, Institute of Acoustics Academic Sinica, Beijing, China).

3. Results and discussion

The photographs of KNN-SMN ceramics (0.5 mm thickness) are shown in Fig. 1,

and their optical transmittances (T) measured in the range of 200-2000 nm are shown in Fig. 2. As demonstrated in Fig. 1, all letters under samples can be seen clearly, suggesting that all designed compositions have good transparencies in the visible spectra. The transmittance spectra in Fig. 2 showed that the SMN content plays an important role in optical transparency, the transmittance initially increases with increasing x from 0.02 to 0.05 and then decreases at $x \geq 0.06$ in the measured wavelength region. The ceramic with $0.04 \leq x \leq 0.06$ exhibits stably high transmittance above 40% in the visible spectra, and about 60% in the red and infrared regions. It is anticipated that the transmittance in the visible region can be further improved by optical-grade polishing.^{13,19} Moreover, noting that the reflection loss occurs at the interface between air and ceramics, if proper antireflection coating is applied to eliminate the reflection loss, the transmittance of the KNN-SMN ceramics can be further enhanced.

Further study showed that the transmittance decreases gradually near zero at 400 nm and below. This absorption in the lower wavelengths of 200-400 nm should be attributed to the inter-band transition according to the results reported by Wang *et al.*²³ The optical band gap energy (E_g) can be calculated from the absorption spectra using Tauc equation.²⁴ For direct transition, the relationship between E_g and the absorption coefficient α is given as:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (1)$$

where ν is the photon frequency, h is Planck's constant and A is a constant. The absorption coefficient can be calculated from the transmittance (T) by

$$\alpha = \frac{1}{t} \ln\left(\frac{1}{T}\right) \quad (2)$$

where t is the thickness of the sample. Accordingly, E_g was determined for the KNN-SMN ceramics by plotting $(\alpha h\nu)^2$ versus $h\nu$ and extrapolating the linear portion of the curve to zero. Fig. 3 shows the calculated E_g of the ceramics with different x . According to Figs. 3(a-e), E_g changes slightly in the range of 3.00 eV to 3.10 eV, indicating that there is a mild effect of SMN doping on the band gap of the ceramics. With increasing x , E_g increases from initially 3.00 eV at $x = 0.02$, reaches the maximum value of 3.10 eV at $x = 0.05$, and then decreases slightly to 3.06 eV at $x = 0.08$. Moreover, the pretty transparent ceramics with $0.04 \leq x \leq 0.06$ exhibit higher E_g values (3.08 eV, 3.10 eV and 3.07 eV, respectively), which are close to the reported values of the KNN nanorods (3.09 eV)²³ and the $(\text{K}_{0.5}\text{Na}_{0.5})_{0.95}\text{Li}_{0.05}\text{Nb}_{0.95}\text{Bi}_{0.05}\text{O}_3$ transparent ceramics (3.09 eV).¹⁴ For KNN, the band gap is corresponding to the transition from the top of the valence bands occupied by O_{2p} electron state to the bottom of the conduction bands dominated by the empty Nb_{4d} states.

Figs. 4(a-d) show the SEM images for the fracture surface of KNN-SMN ceramics. When x increases from 0.02 to 0.05, the fracture surface tends to be more densification. Further increasing x to 0.08 can result in less densification for the obtained ceramics, indicating that higher SMN content is harmful to the densification behavior. The dependence of composition x on relative density for the KNN-SMN ceramics is presented in Fig. 4(e). The highest relative density reaches 98.6% at $x = 0.05$. In brief, the 0.95KNN-0.05SMN ceramics obtain the best densification, the highest relative density and the highest transmittance, whereas the ceramics with x

above 0.06 show lower relative density and weakened transmittance. Then it is suggested that the densification plays an important role in high transmittance because the light scattering increases when pores exist. The difference of refractive index between pores and polycrystalline causes intense scattering of incident light, therefore, the ceramic exhibits a lower transmittance.

Figs. 5(a-f) show SEM micrographs of surface for the KNN-SMN samples. It can be seen that all the samples show cubic-like grain, which is the typical shape of KNN-based ceramics, and the grain growth is obviously restrained by adding SMN. For the KNN-SMN ceramics $x \leq 0.03$, the grain size is non-uniform from approximately 2 μm to below 500 nm. The similar grain size difference phenomena can also be found in KNN-SMN ceramics with higher SMN content at $x = 0.08$, which have some smaller grain size below 500 nm along with a few bigger grains above 1 μm . For the compositions with $0.04 \leq x \leq 0.06$, the grains become more uniform, and the average grain size shows great dependence on x . The average grain size of 0.95KNN-0.05SMN ceramics with highest transmittance is about 400 nm, which is smaller than that of 0.96KNN-0.04SMN ceramics (700 nm). Combined the grain size results with the transmittance trend of KNN-SMN ceramics, it is found that in addition to the porosity, the grain size also has vital important effect on the transmittance. The smaller grain size along with uniform size distribution is beneficial to obtain high transmittance for transparent ceramics. Thus, the ceramic of 0.95KNN-0.05SMN ceramic exhibits the highest value of transmittance over 60% in the IR-region due to the fine-grained structure. The relationship result can be

verified by the previous references reported by Rolf Apetz *et al.*²⁵ and Lu *et al.*²⁶

Crystal structure, is another important factor, determines the optical transmittance of obtained ceramics. The ceramics with a cubic perovskite structure generally have high optical transmittance due to the single refractive index, thus the scattering of light is small at the grain boundaries with isotropic lattice structure when the light travels from one grain to another. Fig. 6(a) shows the XRD patterns of KNN-SMN ceramics with different x . A series of continuous solid solutions between KNN and SMN are formed since no trace of secondary phases can be detected by XRD. It is shown that the crystal structure of KNN-SMN ceramics changed as adding a small amount of SMN from the characteristic peak at 45° . To clarify the effect of SMN content on the phase structure more clearly, the fine scanning XRD patterns in the 2θ range from 44° to 47° of the sample were fitted by Gaussian function as plotted in Fig. 6(b). The KNN-SMN ceramics with $x = 0.02$ and 0.03 display the reflection feature of $(202)_O/(020)_O$, showing that the ceramics possess a similar orthorhombic phase to pure KNN ceramic at room temperature. Further increasing x , however, the two diffraction peaks merge into one peak, suggesting that the structure of KNN-SMN ceramics at room temperature have a tendency to transform into another phase with similar lattice constants, e.g., pseudo-cubic. Then the only one sharp (200) diffraction peak at 45° shown in Fig. 6(b) demonstrates that the KNN-SMN ceramics with $x \geq 0.04$ have pseudo-cubic phase.

In addition, the (110) peak at 31.5° moves to smaller angle with increasing x in

Fig. 6(c), which can be explained by the increase of lattice parameters. The cell lattice expansion can be attributed to the bigger Mg^{2+} ($0.89\text{\AA}$) ions occupying the B site in ABO_3 perovskite structure of KNN. To further confirm the effect of SMN content on phase structure, the calculated lattice parameters of a , b , c , and ratio a/c of KNN-SMN ceramics using the least square method from XRD data are listed in Table 1. As expected, the lattice parameters of the KNN-SMN ceramics gradually increase with increasing x . After x above 0.04, a is very close to b and the value of a/c almost equals to 1, indicating that the KNN-SMN ceramics has transformed into the pseudo-cubic phase. In ceramics of optically anisotropic crystals, an additional scattering of light arises occurs at the boundaries when the light travels from one grain to another. That is to say there is no new optical scattering center generated at grain boundary in ceramics with symmetric cubic phase because all refractive indexes are same, which efficiently maintains the transmittance. This is the reason why twinkle transparent ceramics and transparent laser ceramics generally have a cubic lattice structure, which is isotropic, such as MgO , Y_2O_3 , YAG, and MgAl_2O_3 ceramics.²⁷⁻³¹

Thus, it is reasonable to expect that the KNN-SMN ceramics with $x \geq 0.04$ show high transmittance. Besides, according to the obtained relationship between microstructure and transmittance, further exceeding the doping amount of SMN in KNN ceramics can cause a non-uniform grain size distribution in the obtained ceramics with lower densification, which will result in the weakening of transmittance for the KNN-SMN ceramics with higher x values. The relationship mechanism about two synergistic effects of microstructure and phase structure on transmittance

show that high densification, fine and small grains, uniform grain size distribution, and isotropic-optical pseudo-cubic structure are all considered as favorable factors for the excellent transparent performance.

Fig. 7(a) shows the temperature dependence of the dielectric constant and dielectric loss of KNN-SMN ceramics with different x measured from room temperature to 500 °C at a frequency of 100 kHz. It is found that two sharp dielectric peaks, similar to pure KNN, showed at 150°C and 370°C in the ceramics with $x \leq 0.03$, which correspond to the phase transitions from orthorhombic to tetragonal and from tetragonal to cubic, respectively. For ceramics with $x \geq 0.04$, the two peaks tend to merge into one peak, and finally only one peak is observed when $x \geq 0.06$, suggesting the crystal structure of the ceramics finally change into cubic structure. Moreover, the broader peaks are observed in KNN-SMN ceramics with $x \geq 0.04$, which can be called diffuse phase transition caused by heterogeneous doping, giving rise to the composition fluctuation. The similar results are also obtained in $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3\text{-(Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$ relaxor ceramics.³² In addition, the dramatic decrease in grain size also cause the ceramics with $x \geq 0.04$ possess the broadened and suppressed dielectric peaks.³³ Fig. 7(b) gives the dielectric constant, dielectric loss and T_c of the KNN-SMN ceramics measured at the frequency of 100 kHz as a function of x . It can be seen from Fig. 7(b) that T_c decreases gradually from 370 °C to 60 °C. The maximum dielectric constant ε_m also decreases with increasing x and the dielectric loss below 3% is obtained in all compositions.

Another typical characteristic for relaxor ferroelectrics is the frequency

dispersion of dielectric permittivity. The temperature dependence of dielectric constant for the KNN-SMN ceramics measured under various frequencies is plotted in Figs. 8(a-d). The nearly frequency-independent phenomenon and sharp dielectric peaks were observed for the ceramics with $x = 0.02$. Whereas for the ceramics with $x \geq 0.04$, a **strong diffuse phase transition was observed**, suggesting the ceramics show a relaxor-like characteristic. For a normal ferroelectric material, the dielectric constant as a function of temperature is described by the following equation:

$$\varepsilon = C/(T - T_m) \quad (3)$$

where C is the Curie–Weiss constant, T_m is the Curie–Weiss temperature. Deviation from the Curie–Weiss law can be defined by $\Delta T = T_B - T_m$, where T_B denotes the temperature from which the dielectric constant starts to follow the Curie–Weiss law, and T_m represents the temperature **where** the dielectric constant reaches the maximum. At $T < T_B$, the paraelectric phase transforms into the ergodic relaxor state and forms the polar nano-regions.³⁴ The plots of $1/\varepsilon$ versus T for the KNN-SMN ceramics are showed in Figs 9(a-d). It is found that with increasing x , the ΔT_m increases from 15 °C at $x = 0.02$ to 328 °C at $x = 0.08$, suggesting that a diffuse phase transition behavior has been enhanced **with increasing SMN amount**.

For the relaxor ferroelectrics, the reciprocal of the dielectric constant and temperature obey the Uchino and Nomura function, a modified Curie–Weiss law:³⁵

$$1/\varepsilon - 1/\varepsilon_m = (T - T_m)^\gamma / C \quad (4)$$

where γ is called a diffusion coefficient ranging from a normal ferroelectric to an ideal relaxor ferroelectric, C is the Curie-like constant. The value of γ varies from 1 to

2, when γ changes from 1 to 2, representing the structure transform from normal ferroelectric to typical relaxor ferroelectric. Fig. 9(e) shows the plots of $\log(1/\varepsilon - 1/\varepsilon_m)$ as a function of $\log(T - T_m)$ at 100 kHz for KNN-SMN ceramics with different x . A linear relationship was observed for each specimens. The slope of the fitting curves was used to determine the γ value. The obtained γ value are 1.47, 1.49, 1.78, 1.82, 1.85, 1.87, and 1.90 for ceramics with $x = 0.02, 0.03, 0.04, 0.05, 0.06, 0.07$, and 0.08, respectively, indicating that the ceramics (particularly for those with $x \geq 0.04$) become more relaxor-like, e.g., closer to a relaxor ferroelectric. In typical relaxor ABO_3 compounds, either the A-sites or B-sites are occupied by two or more cations. It is known that a large difference in ionic radii of A-sites or B-sites is favorable for the formation of ordered structures. Owing to the different ionic radii of Sr^{2+} ions (1.18 Å) compared with those of Na^+ and K^+ (1.02 Å and 1.38 Å), the substitution of Sr^{2+} in the A-sites of KNN lattice should increase the A-site disordered degree and hence the local compositional fluctuation, giving rise to polar nano-regions (PNRs). The similar phenomenon also occurs at B-sites of KNN lattice, where Mg^{2+} (0.89 Å) and Nb^{5+} (0.64 Å) also possess the different ionic radii. Additionally, the influences from random-fields caused by the different valence among different ions in B-sites of KNN perovskite structure cannot be ignored. In KNN-SMN, the local electric fields and the elastic fields will give rise to the PNRs by hindering the long-range dipole alignment. Because the emergence of the large number of PNRs can result in the formation of the pseudocubic phase and decrease the optical anisotropy by weakening the scattering of light at the grain boundaries,

thus the optical transparenance increases. Therefore, the ceramics with $x \geq 0.04$ ($\gamma \geq 1.78$) may contain a large amount of PNRs and exhibit higher transmittance.

Raman spectroscopy is a useful technique to analyze the structure and composition of KNN-based systems. It is very sensitive to structural deformations caused by impurities or deficiencies on A-sites cations or B-sites and the molecular vibrations of crystal lattice in the short range ordering. To further reveal the relaxor behaviors of the KNN-SMN ceramics, Fig. 10(a) shows Raman spectra of the KNN-SMN ceramics with different x measured in the frequency range $100\text{-}1000\text{ cm}^{-1}$ at room temperature. The main vibration modes ($\nu_1\text{--}\nu_5$) are associated with the NbO_6 octahedron. The peaks below 200 cm^{-1} correspond to the translational mode of K^+/Na^+ cations and rotations of the NbO_6 octahedron. Fig. 10(b) demonstrates the ν_1 and ν_2 modes with the best fitting results using Gauss function. As shown in Fig. 10(b), the peak position of ν_1 mode, which can be assigned to the symmetric stretching mode of the NbO_6 octahedral corresponding to slightly different Nb-O band distances based on the model proposed by Jehng,³⁶ shifts to lower wavenumbers (Fig. 10(c)) with increasing of SMN due to the reduced distortion of NbO_6 octahedral, thus the crystal symmetry of the ceramics increases. Furthermore, the degree of relaxor dispersion can be manifested by the full width at half maximum (FWHM) of ν_1 mode. Fig. 10(d) shows the FWHM of ν_1 mode as a function of x . The ν_1 mode becomes broader with increasing SMN content from 0.02 to 0.08. As a result, the degree of relaxor dispersion of the KNN-SMN ceramics increases. The similar phenomenon also was found in Bi_2O_3 -modified $(\text{K}_{0.5}\text{Na}_{0.5})_{0.9}\text{Sr}_{0.1}\text{Nb}_{0.9}\text{Ti}_{0.1}\text{O}_3$ ceramics reported by

The dense densification, uniform fine-sized grains, and high symmetry of cubic structure associated with relaxor characteristic co-modulate the 0.95KNN-0.05SMN ceramics to exhibit excellent optical properties with highest transmittance in this work. Unfortunately, the decrease of T_c and increase of relaxor behavior are not benefit to enhance the ferroelectric and piezoelectric properties. The P - E hysteresis loops of KNN-SMN transparent ceramics with different KNN/SMN ratios measured at 1 Hz at room temperature are compared in Fig. 11. It is noticed that the shape of P - E loop becomes slimmer with increasing SMN content especially for compositions with $x \geq 0.04$. As shown in Fig. 11(b), the remnant polarization (P_r) of the KNN-SMN decreases from 12 $\mu\text{C}/\text{cm}^2$ to 2 $\mu\text{C}/\text{cm}^2$ when x increases from 0.02 to 0.08, suggesting that ferroelectric properties deteriorated seriously due to the increase of the crystal symmetry from orthorhombic to pseudo-cubic induced by the gradually intensive relaxor behavior. Fig. 11(c) shows the piezoelectric constant (d_{33}) of the KNN-SMN transparent ceramics with different x . The d_{33} dropped sharply from 125 pC/N to 22 pC/N when x increases from 0.02 to 0.08. Taking into account of both high transmittance and good electrical properties simultaneously, the 0.95KNN-0.05SMN ceramics with highest transmittance can be considered as a promising lead-free transparent ferroelectric candidates in this work: $\varepsilon_m = 2104$, $E_c = 7.5$ kV/cm, $P_r = 5.0$ $\mu\text{C}/\text{cm}^2$, and $d_{33} = 92$ pC/N, for which the electrical properties are much better than that of 0.975(K_{0.5}Na_{0.5})NbO₃-0.025LaBiO₃ reported in our previous work.

Conclusions

Lead-free transparent ferroelectric ceramics $(1-x)(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3\text{-}x\text{Sr}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (KNN-SMN, $x=0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08$) were successfully designed and fabricated by the pressure-less sintering procedure. The effects of SMN content on the optical properties, microstructure, phase transition, electrical properties and relaxor behavior were studied in detail to reveal the relationship among composition-structure-properties. It was found that the high densification, uniform fine-sized grains, and high symmetry of cubic structure associated with relaxor characteristic co-modulated the 0.95KNN-0.05SMN ceramics to exhibit excellent optical properties. With increasing SMN content, the phase structure transformed from orthorhombic to isotropic-optical pseudocubic symmetry, which efficiently maintains the transmittance because the optical scattering center generated at grain boundary were inhibited in symmetric cubic phase. The SEM results confirmed that the samples with high densification, small grain size, and uniform size distribution exhibited higher transmittance due to the reduced scattering by pores, grains, and grain boundaries. In addition, relaxor behavior was significantly enhanced by introducing SMN in KNN-based ceramics. The transparent and electric properties results indicated that the $0.95(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3\text{-}0.05\text{Sr}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ceramics exhibited higher transmittance (60% in the near-IR region) accompanied with better electrical properties ($\varepsilon_m = 2104$, $P_r = 5.0 \mu\text{C}/\text{cm}^2$, $d_{33} = 92 \text{ pC}/\text{N}$).

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Tab.1. Lattice parameters of KNN-SMN transparent ceramics

Samples	Lattice parameters			
	a(Å)	b(Å)	c(Å)	a/c
0.02	4.0007	3.8441	3.8305	1.0444
0.03	4.0082	3.9420	3.9017	1.0273
0.04	4.0106	3.9525	3.9826	1.0070
0.05	4.0115	3.9649	4.0018	1.0024
0.08	4.0144	3.9806	4.0067	1.0019