

# Enhancement of optical transparency in  $Bi<sub>2</sub>O<sub>3</sub>$ -modified  $(K_{0.5}Na_{0.5})_{0.9}Sr_{0.1}Nb_{0.9}Ti_{0.1}O_3$  ceramics for electro-optic applications

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**Abstract** Transparent relaxor ferroelectrics,  $(K_{0.5}Na_{0.5})_{0.9-}$  $Sr_{0.1}Nb_{0.9}Ti_{0.1}O_3-x\%Bi_2O_3$  ( $x=0$ , 0.5, 1.0, 1.5, and 2, abbreviated as KNSNT-10 $x$ ), were fabricated using a pressureless sintering method. With the modification of  $Bi<sub>2</sub>O<sub>3</sub>$ , the crystal phase of KNSNT ceramics transformed from tetragonal to cubic-like symmetry, and dielectric behaviors became more relaxor like. These changes could reduce the light scattering arisen from birefringence and long-range ordering structure, thus enhancing the optical properties. For KNSNT-10 transparent ceramics, fingerprint morphological nanodomains were observed in the transmission electron microscope image, which made the ceramics sensitive to electric field. Therefore, a large effective linear electro-optic coefficient of 26.1 pm/V was obtained for the KNSNT-10 ceramics, and it is higher than the value (19.9 pm/V) for  $LiNbO<sub>3</sub>$  single crystal.

## Introduction

High-quality optical materials with a large electro-optic (EO) response are highly desirable for various optical applications, such as light shutters, modulators, and color

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filter devices  $[1-3]$ . LiNbO<sub>3</sub> single crystal is the industry benchmark of EO materials [[4,](#page-7-0) [5](#page-7-0)]. However, the small available size, high cost, long growth time, and low EO response make it difficult for a wide range of applications. Compared with the  $LiNbO<sub>3</sub>$  single crystal, transparent ceramics have apparent advantages, e.g., ceramic ruggedness, easy fabrication, low fabrication cost, large available size, and stronger EO responses [\[1](#page-7-0), [6](#page-7-0)].

Currently, lead-based transparent ceramics are widely studied [\[6–10](#page-7-0)], such as  $(Pb_{1-x}La_x)(Zr_xTi_{1-y})_{1-x/4}O_3$ ,  $Pb(Mg_{1/3}Nb_{2/3})O_3-PbTiO_3$ , and  $Pb(Zn_{1/3}Nb_{2/3})O_3-PbTiO_3$ system. The lead-based materials have a major drawback, that is their high lead content (more than 60 wt%). In order to protect environment, there is a need of replacing the lead-based materials by environmental friendly lead-free materials.  $K_0$ <sub>5</sub>Na<sub>0.5</sub>NbO<sub>3</sub> is one of the most promising candidates for lead-free piezoelectric ceramics and has been studied extensively  $[11–17]$  $[11–17]$ . The sintering behaviors and piezoelectric properties of the ceramics can generally be enhanced by the addition of different ions or the formation of new solid solutions with other ferroelectrics, such as  $Li^+$ ,  $Bi^{3+}$ ,  $Ta^{5+}$ ,  $BaTiO_3$ , and  $SrTiO_3$ . However, there are few works to report on enhancing optical properties of the ceramics. The early paper with regard to  $K_{0.5}Na_{0.5}NbO<sub>3</sub>$  translucent ceramics was reported by Kosec et al. [\[17](#page-7-0), [18](#page-7-0)]. Owing to the fine-grained and highdensity microstructure,  $0.8K_{0.5}Na_{0.5}NbO<sub>3</sub>-0.2SrTiO<sub>3</sub>$ ceramics with a pseudo-cubic perovskite structure became translucent; and their quadratic EO property also has been measured. Unfortunately, Curie temperature of the  $0.8K_0$ ,  $Na_0$ ,  $NbO_3$ – $0.2SrTiO_3$  (about 230 K) is below the room temperature, resulting in a weak ferroelectricity, so that the quadratic EO coefficient is one order of magnitude smaller than that of the commercial PLZT ceramics. Recently, Kwok et al. [\[19](#page-7-0), [20](#page-7-0)] employed the hot isostatic

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pressing sintering technique to obtain transparent  $(K_0, \,$  $Na<sub>0.5</sub>)<sub>1-x</sub>Li<sub>x</sub>Nb<sub>1-x</sub>Bi<sub>x</sub>O<sub>3</sub>$  ceramics, which exhibited a high linear EO coefficient. These results indicate that the  $K_{0.5}$  $Na<sub>0</sub>5Nb<sub>3</sub>$  lead-free material is a good candidate to replace the lead-based transparent ceramics.

The lead-free  $(K_{0.5}Na_{0.5})_{0.9}Sr_{0.1}Nb_{0.9}Ti_{0.1}O_3$  solid solution exhibits proto-typical relaxor ferroelectric behavior and Curie temperature near 148 °C  $[21, 22]$  $[21, 22]$  $[21, 22]$  $[21, 22]$ . In this work, we prepared transparent  $(K_{0.5}Na_{0.5})_{0.9}Sr_{0.1}Ti_{0.1}Nb_{0.9}O_3$  $x\%$ Bi<sub>2</sub>O<sub>3</sub> EO ceramics, the effects of Bi<sub>2</sub>O<sub>3</sub> on their microstructure, optical and electrical properties were investigated.

## Experimental

Ferroelectric ceramics,  $(K_0, N_{0.5}Na_0, S_0, S_{0.1}Nb_0, T_{0.1}O_3$  $x\%Bi_2O_3$  (x = 0, 0.5, 1.0, 1.5 and 2.0, abbreviated as KNSNT-10 $x$ ), were prepared using the conventional solidstate reaction route. Stoichiometric raw oxides of  $K_2CO_3$ ,  $Na<sub>2</sub>CO<sub>3</sub>$ ,  $Nb<sub>2</sub>O<sub>5</sub>$ ,  $S<sub>2</sub>CO<sub>3</sub>$ ,  $TiO<sub>2</sub>$ , and  $Bi<sub>2</sub>O<sub>3</sub>$  (Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) were mixed and then milled using a zirconia ball medium with ethanol for 12 h. After ball milling, the mixtures were dried and then calcined at 900  $\degree$ C for 2 h. The precursor powders were ball milled for 24 h again, dried, and cold isostatically pressed into pellets at 300 MPa. The pressed pellets were sintered at  $1200 \degree C$  for 2 h without any pressure. The obtained pellets with a diameter of 8 mm were finally polished (with 5 nm diamond paste) to a thickness of 0.5 mm for optical property measurements.

Optical transmittance of the KNSNT- $10x$  ceramics was measured in the range of 300–850 nm using an UV–Vis spectrophotometer (UV-2550, Shimadzu Co., Tokyo, Japan). Refractive index of the ceramics was measured at 633 nm using a prism coupler (Model 2010, Metricon, Pennington, NJ). Crystal structures of the ceramics were detected using X-ray diffraction (XRD; X'Pert PRO MPD, Philips, Eindhoven, The Netherlands) with  $Cu K<sub>\alpha</sub>$  radiation at room temperature; and their microstructures (thermally etched surface performed at  $1100 \degree C$  for 30 min) were obtained using a field emission scanning electron microscope (FE-SEM; JEOL-6700F, Japan Electron Co., Tokyo, Japan) operated at 20 kV. Electron diffraction patterns of the ceramics were observed using a transmission electron microscope (TEM; Tecnai F30, FEI, Hillsboro, OR) operated at 300 kV accelerating voltage. Raman scattering experiments were performed with an instrument (LabRAM HR800, Horiba JobinYvon, Lyon, France) in a backward scattering geometry (the exciting source was the 514.5 nm line from an argon ion laser). Weak-field dielectric responses of the ceramics were measured with a precision impedance analyzer (4294A, Agilent, Santa Clara, CA) associated with a temperature controller (TP94, Linkam, Surrey, UK) over a temperature range of 293–773 K at a heating rate of 3 °C/min. Dependence of ferroelectric polarization (P) and longitudinally field-induced strain  $(S_{33})$  were measured at 10 Hz, using a ferroelectric test unit (TF-2000, aix-ACCT, Aachen, Germany). Before EO test, the transparent ceramics were polarized under an electric field of 4 kV/mm for 30 min and then measured with a transverse geometry using a modified Sénarmont method [\[23](#page-8-0)]. The testing samples had a thickness of  $t = 0.5$  mm, distance between electrodes of  $d = 1.0$  mm, testing modulation frequency of  $f = 1$  kHz, and a wavelength of  $\lambda = 633$  nm.

# Results and discussion

Figure 1 shows the photographs of the KNSNT-10 $x$ ceramics with a thickness of 0.5 mm. It can be observed that the  $Bi<sub>2</sub>O<sub>3</sub>$  content plays an important role in optical transparency. With increasing x content, the KNSNT-10 $x$ ceramics are transformed from translucence to optical transparency. The enhancement in optical transparency is also observed in the optical transmittance spectra (Fig. [2](#page-2-0)). The optical transmittance  $T$  increases as the  $x$  content increases from 0 to 1.0 and then decreases rapidly with  $x > 1.0$ . For the  $x = 1.0$  ceramic, a high optical transmittance of 51.5 % at the 633 nm wavelength is obtained. For transparent ceramic with a thickness  $t$ , transmittance  $T$  can be expressed as follows [[24\]](#page-8-0):

$$
T = (1 - R)^2 \exp(-\beta t), \quad R = \frac{(n - 1)^2}{(n + 1)^2}, \tag{1}
$$

where  $R$  is the reflectivity,  $n$  is the refractive index of the ceramic,  $\beta$  is the scattering coefficient neglecting the absorption (generally extinction coefficient), and  $t$  is the sample thickness. For KNSNT-10 ceramic, the refractive index measured at 633 nm is 2.253, then about 29 % optical reflection loss could be calculated resulting from



Fig. 1 Photographs of the KNSNT-10x transparent ceramics

<span id="page-2-0"></span>

Fig. 2 Optical transmittance spectra of the KNSNT-10 $x$  ceramics

twice air/ceramic interface reflection. If a proper antireflection coating is applied, the transmittance of the KNSNT-10 ceramic will be further improved to  $\sim 81$  %.

EO effect describes the change in the refractive index  $\Delta n$  due to an applied electric field E. For polarized ferroelectric ceramics, we have [[4\]](#page-7-0)

$$
\Delta n(E) = \frac{1}{2} n^3 r_c E. \tag{2}
$$

Using a modified Sénarmont method  $[23]$  $[23]$ , the effective EO coefficient can be calculated as

$$
r_c = \frac{\lambda d}{\pi L n^3} \frac{\Gamma_m}{V_m}, \quad \Gamma_m = \frac{2\sqrt{2}V_{rms}}{V_{p-p}},
$$
\n(3)

where  $\lambda$  is the testing wavelength, *n* is the refractive index,  $r_c$  is the effective linear EO coefficient, d is the electrode spacing of the sample,  $L$  is the length along the light path,  $V<sub>m</sub>$  is the peak-to-peak value of the applied *ac* electric field, and  $\Gamma_{\rm m}$  is the phase shift degree. Besides,  $V_{\rm p-p}$  is the maximum voltage output of the ceramic without electric field; and  $V_{\rm rms}$  is the maximum voltage output under an applied electric field. Figure 3a shows responded voltage of the photo-detection system as a function of analyzer angle of the  $x = 1.0$  ceramic.  $V_0$  is corresponding to the voltage output of the ceramic without electric field; and the  $V_{\text{p}-\text{p}}$  value can be found from this curve.  $V_{\text{E}}$  is the voltage of the ceramic under an electric field, from which the  $V_{\rm rms}$ can be obtained. Figure 3b shows phase shift  $(\Gamma_{\rm m})$  as a function of applied voltage  $V_{\text{m}}$ . It exhibits a remarkably linear behavior with the applied voltage. The effective EO coefficients can be determined from the slope of the curves associated with Eq.  $(3)$ . A summary of  $r_c$  for the KNSNT-10x ceramics is presented in Table [1.](#page-3-0) It can be found that the  $x = 1.0$  transparent ceramic has an EO coefficient of 26.1 pm/V, which is higher than that of single crystal  $LiNbO<sub>3</sub>$  (19.9 pm/V) [\[4](#page-7-0)]. Besides, the EO coefficients are



Fig. 3 a Responding voltage of the photo-detection system as a function of analyzer angle for the  $x = 1.0$  ceramic, **b** phase retardations as a function of ac applied field for the KNSNT-10x ceramics

41.8 and 14.9 pm/V for the  $x = 0.5$  and  $x = 1.5$ , respectively.

Figure [4](#page-3-0) shows thermally etched surface micrographs of the KNSNT- $10x$  ceramics, along with the respective average grain size distribution diagrams.  $Bi<sub>2</sub>O<sub>3</sub>$  has an obvious effect on the microstructure of the ceramics, especially the grain size (Table [1\)](#page-3-0). The  $x = 1.0$  ceramic consists of faceted and cube-shaped grains, with an average grain size of  $0.21 \pm 0.04$  $0.21 \pm 0.04$  µm (Fig. 4c). For  $x = 2.0$ , the microstructure becomes loose and the grain size is decreased to  $0.16 \pm 0.03$  µm (Fig. [4](#page-3-0)d). It can be suggested that the addition of  $Bi<sub>2</sub>O<sub>3</sub>$  is effective in suppressing grain growth. The similar phenomenon has also been observed in other Bi-doped KNN systems, such as  $BiScO<sub>3</sub>-(K<sub>0.5</sub>)$  $Na<sub>0.5</sub>NbO<sub>3</sub>$  [[13\]](#page-7-0), BiFeO<sub>3</sub>–(Na<sub>0.515</sub>K<sub>0.485</sub>)<sub>0.95</sub>Nb<sub>0.8</sub>Ta<sub>0.2</sub>O<sub>3</sub> [\[16](#page-7-0)], and  $(Bi_{0.5}Na_{0.5})TiO<sub>3</sub>-(K<sub>0.5</sub>Na<sub>0.5</sub>)NbO<sub>3</sub>$  [[25\]](#page-8-0) ceramics. To understand the effect of  $Bi<sub>2</sub>O<sub>3</sub>$  on the microstructure of KNSNT- $10x$  ceramics, EDS mapping spectra of each element in KNSNT-10 ceramic are shown in Fig. S1 (see electronic supplementary material). All of the elements are homogeneously distributed through the ceramic. It have been reported that the addition of  $Bi<sub>2</sub>O<sub>3</sub>$  not only concentrated in grain boundaries to inhibit the grain growth during sintering process, but also diffused into the lattice by replacing A-site ions to compensate sintering loss of

<span id="page-3-0"></span>Table 1 Transmittance, linear EO coefficient  $r_c$  at 633 nm, and average grain size for the KNSNT-10x ceramics





Fig. 4 SEM micrographs of thermally etched surfaces of the KNSNT-10x ceramics.  $\mathbf{a} \times x = 0$ ,  $\mathbf{b} \times x = 0.5$ ,  $\mathbf{c} \times x = 1.0$ , and  $\mathbf{d} \times x = 2.0$ . The *insets* show the grain size distributions

alkaline elements  $[26, 27]$  $[26, 27]$  $[26, 27]$  $[26, 27]$  $[26, 27]$ . This induces a homogeneous distribution of Bi ions.

From the results of alumina and yttrium aluminum garnet transparency ceramics [[24,](#page-8-0) [28](#page-8-0), [29](#page-8-0)], grain size, grain boundary, and pores are generally considered as the main factors affecting the transmittance of ceramics, while optical scattering by pores in ceramics should be considered as the main factor when the crystal structure is isotropic. According to Eq. (1), the scattering coefficient  $\beta$ , assuming single scattering spherical pores, can be expressed as [[29\]](#page-8-0)

$$
\beta = \frac{p}{\frac{4}{3}\pi r^3} C_S,\tag{4}
$$

where  $p$  is the porosity volume fraction,  $r$  is the pore radius, and  $C<sub>S</sub>$  is the scattering cross section of the spherical pores. Pores can be frequency observed with a diameter of near 1 µm (Fig. [5](#page-4-0)a). As a result, the transmittance of the  $x = 0$ ceramic is as low as 11.4 % (Table 1). In comparison, the  $x = 1.0$  ceramic shows a high optical transmittance with a fully dense and poreless microstructure in the fracture morphology. Besides, fracture surface of the  $x = 1.0$ ceramic looks remarkably different. This also indicates that excess  $Bi<sub>2</sub>O<sub>3</sub>$  addition may influence the mass transportation during the sintering and thus obviously induce densification of the ceramics as well as suppress the grain growth process [\[27](#page-8-0)].

 $XRD$  patterns of the KNSNT-10 $x$  ceramics are displayed in Fig. [6a](#page-4-0). All of the ceramics possess a single perovskite structure. KNN shows orthorhombic symmetry, and the KNSNT $(x = 0)$  is tetragonal at room temperature [\[21](#page-7-0), [22](#page-8-0)]. Notably, the addition of  $Bi<sub>2</sub>O<sub>3</sub>$  caused the two peaks to merge into a sharp peak (Fig. [6b](#page-4-0)), suggesting that they may transform into another phase with very similar lattice constants, e.g., pseudo-cubic phase. Similar results have been observed in other KNN-based ceramics, such as Bi-modified KNN  $[20]$  $[20]$ , KNN–SrTiO<sub>3</sub>  $[22]$  $[22]$ , and KNN–  $(Bi_{0.5}Na_{0.5})TiO_3$  [[25\]](#page-8-0). In addition,  $Bi^{3+}$  (0.138 nm,

<span id="page-4-0"></span>

Fig. 5 SEM micrographs of fracture surfaces of the KNSNT-10x ceramics.  $\mathbf{a} x = 0$  and  $\mathbf{b} x = 1.0$ 



Fig. 6 XRD patterns of the KNSNT-10 $x$  ceramics

 $CN = 12$ ) is close to  $K^{+}$  (0.164 nm,  $CN = 12$ ) and Na<sup>+</sup>  $(0.138 \text{ nm}, \text{CN} = 12)$ . This suggests that  $Bi^{3+}$  ions can diffuse into A-site of the KNSNT lattices to compensate the sintering loss of alkaline elements [[13,](#page-7-0) [30\]](#page-8-0).

Figure [7](#page-5-0) demonstrates temperature dependences of dielectric permittivity and dielectric loss (tan  $\delta$ ) of the KNSNT- $10x$  ceramics in the frequency range from 1 kHz to 1 MHz. KNN is a classical ferroelectric with two transition peaks: one is associated with the cubic-to-tetragonal phase transition at 428  $\degree$ C and the other with the tetrago-nal-to-orthorhombic phase transition at 206 °C (Fig. [7a](#page-5-0)). With the addition of  $Bi<sub>2</sub>O<sub>3</sub>$ , the ceramics exhibit a broadened cubic–tetragonal transition peak, which shifts to low temperature. In addition, the observed  $\varepsilon'$  decreases from 1583 to 828 at 10 kHz and 300 K as the content of  $Bi<sub>2</sub>O<sub>3</sub>$  is increased from 0 to 2.0 (Table [2\)](#page-5-0). Also, the temperatures  $(T<sub>m</sub>)$  of the maximum dielectric permittivity and the corresponding peak values  $(\epsilon'_m)$  at 10 kHz are decreased (Table [2](#page-5-0)). This result also indicates that Bi ions have diffused into the A-site of KNSNT ceramics. For the modified ceramics, an obvious diffuse phase transition can be observed, and the  $\varepsilon'$  decreases with increasing frequency, which is a typical characteristic for relaxor ferroelectrics.

For relaxor ferroelectrics, the reciprocity of the dielectric permittivity and temperature follow the Uchino and Nomura function, a modified Curie–Weiss law [\[31](#page-8-0)],

$$
\frac{1}{e'} - \frac{1}{e'_{\rm m}} = \frac{(T - T_{\rm m})^{\gamma}}{C},\tag{5}
$$

where C is Curie constant and  $\gamma$  is the diffusion coefficient of value ranging from one (a normal ferroelectric) to two (an ideal relaxor ferroelectric). Figure [8](#page-5-0) shows  $ln(1/\varepsilon'-1/$  $\varepsilon'$ <sub>m</sub>) as a function of  $ln(T - T_m)$  at 10 kHz for the KNN,  $x = 0$ , 1.0, and 2.0, respectively. By least-squares fitting the experimental data according to the modified Curie– Weiss law,  $\gamma$  is determined, with results listed in Table [2](#page-5-0). It can be found that the maximum value of  $\gamma$  is 2.0 for  $x = 1.0$ . Correspondingly, the  $x = 1.0$  ceramic exhibits a much broader diffuse phase transition (Fig. [7](#page-5-0)c), suggesting that the ceramic is more relaxor like and contains more polar nanoregions [\[32](#page-8-0), [33](#page-8-0)]. However, for ceramics with  $x > 1.0$ , the diffusion coefficient  $\gamma$  is decreased. This may be partly due to the appearance of electronic conduction at high temperatures (the tan  $\delta$  shown in Fig. [7d](#page-5-0)).

To further reveal the relaxor behaviors of the KNSNT- $10x$  ceramics, Fig.  $9a$  shows Raman spectra of the ceramics at room temperature. The main vibration modes  $(v_1-v_5)$  are associated with the  $NbO<sub>6</sub>$  octahedra. The peaks at  $\sim$ 160 cm<sup>-1</sup> can be assigned to the K<sup>+</sup>/Na<sup>+</sup> translation and rotations of the  $NbO<sub>6</sub>$  octahedra [[21](#page-7-0), [34\]](#page-8-0). Figure [9](#page-5-0)b demonstrates the  $v_1$  and  $v_2$  modes with the best fitting results using Gauss function. Based on the model proposed by *Jehng* [\[35](#page-8-0)], the  $v_1$  mode can be assigned to the symmetric stretching mode of the  $NbO<sub>6</sub>$  octahedra, which corresponds to slightly different Nb–O bond distances. Consequently, the  $v_1$  mode is sensitive to the change of composition as well as phase structure. For the  $Bi<sub>2</sub>O<sub>3</sub>$ modified KNSNT ceramics, the  $v_1$  mode shifts to a lower frequency with the increase of  $Bi<sub>2</sub>O<sub>3</sub>$  content (Fig. [9c](#page-5-0)), due to the reduced distortion of  $NbO<sub>6</sub>$  octahedron, thus increasing the crystal symmetry of the ceramics. Furthermore, the degree of relaxor dispersion can be manifested

<span id="page-5-0"></span>



Table 2 Dielectric permittivity  $\varepsilon'$  at 300 K, the maximum dielectric permittivity  $\varepsilon'$ <sub>m</sub>, Curie temperature  $T$ <sub>m</sub>, diffusion coefficient  $\gamma$ , and field-induced strains  $S_{33}$  of the KNSNT-10x ceramics





Fig. 8  $\ln(1/\varepsilon'-1/\varepsilon_{\rm m})$  as a function of  $\ln(T-T_{\rm m})$  for the KNSNT-10x ceramics (the symbols experimental data, the solid lines fitting by the modified Curie–Weiss law)



Fig. 9 a Raman spectra of the KNSNT-10x ceramics, **b** the  $v_1$  and  $v_2$ modes fitting by Gauss function, c Raman shift of  $v_1$  mode as a function of x content, and **d** FWHM of  $v_1$  mode as a function of x content



 $(a)$ 

<span id="page-6-0"></span>

nanodomains superlattices [00]

Fig. 11 a Bright-field TEM image and b SAED pattern along the [001] zone axis of the KNSNT-10 ceramic

by the full width at half maximum (FWHM) of  $v_1$  mode [\[21](#page-7-0)]. Figure [9](#page-5-0)d shows the FWHM of  $v_1$  mode as a function of x content. As the content of  $Bi<sub>2</sub>O<sub>3</sub>$  is increased from 0 to 1.0, the  $v_1$  mode becomes broader. As a result, the degree of relaxor dispersion of the KNSNT-10 $x$  ceramics is increased. For the relaxor KNSNT-10 ferroelectric, the reduction of long-range ordering structure makes the light scattering to be reduced and thus the optical transparency is increased [[1\]](#page-7-0).

 $50 \text{ nm}$ 

Ferroelectric hysteresis loops  $(P-E)$  of the ceramics are plotted in Fig. 10a. For the KNSNT-10x ceramic, the value of remnant polarization is significantly lower than the saturation polarization at high electric field, indicating that there is a strong relaxation of polarization in the ceramics. Besides, various electric field *P–E* loops of the  $x = 0$  and  $x = 1.0$ ceramics (Fig. S2 in electronic supplementary material) also indicate a typical characteristic for relaxor ferroelectrics [\[9](#page-7-0)]. It is noted that the remnant polarization drops gradually as the x content increases from 0 to 2.0 (Fig.  $10a$ ), implying that the increase of  $Bi<sub>2</sub>O<sub>3</sub>$  addition can degrade ferroelectric properties of the KNSNT ceramics. Figure 10b shows bipolar field-induced strains of the KNSNT-10x ceramics. A butterfly-type strain curve is observed for  $x = 0$ , and the strain value is 0.079 % at 60 kV/cm (Table [2\)](#page-5-0). With the  $Bi<sub>2</sub>O<sub>3</sub>$  content increasing to  $x = 1.0$ , the strain value decreases to 0.033 %. For ferroelectric ceramics, EO property originates from the microdomain movement under applied electric field [[1,](#page-7-0) [9](#page-7-0)]. The measured linear EO coefficients can be related to the spontaneous polarization as follows [\[36](#page-8-0), [37](#page-8-0)]:

<sup>110</sup>

010

$$
r_{\rm c} = 2\varepsilon_0 \varepsilon' g_{\rm c} P_{\rm s},\tag{6}
$$

where  $\varepsilon_0$  is the vacuum permittivity,  $\varepsilon'$  is the dielectric permittivity, and  $g_c$  is the polarization-related quadratic EO coefficient. From the equation, the changes of EO coefficient  $r_c$  should be related to the dielectric constant and spontaneous polarization. Indeed, as the content of  $Bi<sub>2</sub>O<sub>3</sub>$  is increased, both spontaneous polarization  $P_s$  and dielectric permittivity  $\varepsilon'$  decrease (Table [2](#page-5-0)). As a result, the EO response of the KNSNT-10x ceramics is weakened.

Figure 11 displays TEM image and selected area electron diffraction (SAED) pattern from the same area with a representative feature of the KNSNT-10 ceramic. In Fig. 11a, fingerprint morphology nanodomains with length

<span id="page-7-0"></span>shorter than 50 nm are clearly visible. According to the classical theory of ferroelectric domains, the domain wall can be considered as the layer that separates two domains with different but crystallographically equivalent directions of the polarization vector, and the domain wall energy is proportional to the squared value of the domain size. Therefore, the nanodomain wall energy is inherently lower in such nanodomains of the KNSNT-10 ceramic. As a result, the nanodomain can be easily reoriented under electric fields [[38,](#page-8-0) [39\]](#page-8-0). Ultimately, a high EO response is obtained for the KNSNT-10 ceramic (26.1 pm/V). Figure [11](#page-6-0)b shows the SAED pattern along the [100] zone axis, in which superlattice reflections are observed (marked by rings). From the fundamental perovskite reflections, these superlattice reflections originate from slight deviations of the ideal perovskite structure [\[40](#page-8-0)]. Combining with the results of Raman spectra (Fig. [9](#page-5-0)c), it is believed that the superlattice reflection dominates from the  $NbO<sub>6</sub>$  oxygen octahedral tilting in the relaxor ferroelectric.

### **Conclusions**

Lead-free transparent electro-optical KNSNT-10x ceramics  $(x = 0-2.0)$  have been fabricated using the conventional solid-state reaction route. The phase structure of the ceramics presented cubic-like symmetry with the addition of  $Bi<sub>2</sub>O<sub>3</sub>$ , and their average grain size decreased with the increasing  $Bi<sub>2</sub>O<sub>3</sub>$  concentration. As a result, optical anisotropy and birefringence of light of the grains were greatly reduced; a high transparency of 51.5 % at 633 nm wavelength was obtained for KNSNT-10 transparent ceramics. In addition, with increasing  $Bi<sub>2</sub>O<sub>3</sub>$  concentration ( $x \le 1.0$ ), the KNSNT ceramics became more relaxor like. For the KNSNT-10 ceramics, fingerprint morphological nanodomains with the length shorter than 50 nm were observed, which may be sensitive to electric field. Finally, a large effective linear electro-optical coefficient of 26.1 pm/V was obtained for the KNSNT-10 ceramics.

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