Electrical properties and luminescence properties of $0.96(\text{K}_{0.48}\text{Na}_{0.52})(\text{Nb}_{0.95}\text{Sb}_{0.05})-0.04\text{Bi}_{0.5}(\text{Na}_{0.82}\text{K}_{0.18})_{0.5}\text{ZrO}_3-x\text{Sm}$ lead-free ceramics

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Abstract: In this paper, Sm-doped $0.96(\text{K}_{0.48}\text{Na}_{0.52})(\text{Nb}_{0.95}\text{Sb}_{0.05})-0.04\text{Bi}_{0.5}(\text{Na}_{0.82}\text{K}_{0.18})_{0.5}\text{ZrO}_3$ (abbreviated as KNSN–0.04BNKZ) lead-free piezoelectric ceramics were prepared by conventional solid-state sintering method and the effects of Sm_2O_3 on the phase structure, microstructure, electrical and luminescent properties of KNSN–0.04BNKZ potteries were studied. Results revealed that a single solid solution phase with pseudo-cubic perovskite structure was formed between KNSN–0.04BNKZ and Sm_2O_3 . Existence of weak dielectric/ferroelectric properties with a diffuse dielectric anomaly and slim P – E hysteresis loops of the Sm-doped KNSN–0.04BNKZ demonstrated the ferroelectric relaxor behavior of the KNSN–0.04BNKZ– $x\text{Sm}$ ceramics. Accordingly, the temperature stability and fatigue behavior of the modified ceramics were significantly improved. It was found that the KNSN–0.04BNKZ ceramics with 0.002 mol Sm addition exhibited nearly temperature independent properties and fatigue-free behavior. Moreover, Sm-modified KNSN–0.04BNKZ exhibits a bright photoluminescence with a strong orange emission under visible light irradiation. As a material with both electrical and luminescent properties, it has good application prospect in future optoelectronic components by integrating its luminescent and electrical properties.

Keywords: lead-free piezoelectric ceramics; potassium–sodium niobate; phase structure; ferroelectricity; luminescent

1 Introduction

Piezoelectric ceramics have the ability to perform direct conversion between mechanical energy and electrical energy, and these materials are of great value to the

society [1–10]. In the past 60 years, $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ (PZT) has been paid attention to because of its excellent performance and wide applications [10,11]. However, these materials contain large quantity of Pb element [12]. As is known to all, Pb is toxic and it causes serious harm to environment and the body of people, especially young children [5,13]. Therefore many countries have begun to find environmentally friendly materials to replace Pb-based piezoelectric

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materials [10,14]. Nowadays, lead-free piezoelectric materials have gradually become perfect alternative materials in piezoelectric industry [5–16].

The potassium–sodium niobate ($\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$, KNN) lead-free material has caused widespread international concern because of its superior electrical performance [5–7,10,11,16–19]. In recent years, KNN-based piezoelectrics have been greatly developed. From 2014 to the present, the piezoelectric properties of KNN-based ceramics are constantly improving, where the piezoelectric constant as high as 490–570 pC/N is achieved [6,20–23], rendering that KNN-based piezoelectric ceramics become one of the most promising candidate materials replacing traditional PZT-based ceramics and [15,24]. Even so, other methods that can further optimize the performance of KNN-based materials are also under continuous research [25–27]. Researchers found that, ion doping as a more prominent one in these methods can optimize the performance of KNN-based piezoelectric materials. In the method of ion doping, the mechanism for the increase of the piezoelectric activity lies in forming a phase boundary. In 2016, Qin *et al.* [11] reported high piezoelectric response with a d_{33} of 460 pC/N in $(\text{K}_{0.48}\text{Na}_{0.52})(\text{Nb}_{0.96}\text{Sb}_{0.04})\text{O}_3\text{--Bi}_{0.50}(\text{Na}_{0.82}\text{K}_{0.18})_{0.50}\text{ZrO}_3$ system which has a boundary of rhombohedral tetragonal (R–T) phase. Recently, Wu *et al.* [6] made strides in enhancing the piezoelectric activity of KNN-based materials. In addition, rare-earth ions doping can endow KNN-based ceramics with the attractive optical properties besides the enhanced piezoelectric properties [13,16,17,28–34]. For instance, Wu's group reported Er-doped KNN-based lead-free ferroelectric transparent ceramics with excellent piezoelectric and optical multifunctional performances. Owing to piezoelectric/optical multifunctional characteristics, these materials are promising candidates in the application of color-tunable solid-state lightings and electrical-optical coupling devices [13,16,17]. Hao *et al.* [31] prepared reddish orange-emitting $0.948(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3\text{--}0.052\text{LiSbO}_3\text{--}x\text{mol}\%\text{Sm}_2\text{O}_3$ ($\text{KNN}\text{--}5.2\text{LS}\text{--}x\text{Sm}_2\text{O}_3$) lead-free piezoelectric materials with good piezoelectric properties. Wei *et al.* [32] proposed rare earth Pr^{3+} doped KNN lead-free material which exhibited excellent piezoelectric and photoluminescence properties. Furthermore, polarization-induced luminescence enhancement is observed in Pr^{3+} doped KNN material. The phenomenon was also observed in Er/Yb co-doped $0.94(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3\text{--}0.06\text{LiNbO}_3$ and Pr^{3+} -modified $0.93(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3\text{--}$

0.07BaTiO_3 ceramics [33,34]. Based on the above, through proper design with rare earth doping, new functional KNN-based luminescence/piezoelectric materials can be synthesized. In this work, high performance $0.96(\text{K}_{0.48}\text{Na}_{0.52})(\text{Nb}_{0.95}\text{Sb}_{0.05})\text{--}0.04\text{Bi}_{0.5}(\text{Na}_{0.82}\text{K}_{0.18})_{0.5}\text{ZrO}_3$ (abbreviated as KNSN–0.04BNKZ) composition [21] was chosen as the base matrix, and Sm_2O_3 was as the dopant. Then, a novel environmentally friendly luminescent ferroelectric material was fabricated by introducing trivalent Sm^{3+} as the activator into KNSN–0.04BNKZ ceramics.

2 Experimental

We prepared $0.96(\text{K}_{0.48}\text{Na}_{0.52})(\text{Nb}_{0.95}\text{Sb}_{0.05})\text{--}0.04\text{Bi}_{0.5}(\text{Na}_{0.82}\text{K}_{0.18})_{0.5}\text{ZrO}_3\text{--}x\text{Sm}$ (abbreviated as KNSN–0.04BNKZ– $x\text{Sm}$) samples by traditional solid phase synthesis method. Raw materials of K_2CO_3 (99%, Sinopharm Chemical Reagent), Na_2CO_3 (99.8%, Sinopharm Chemical Reagent), Nb_2O_5 (99.9%, Alfa Aesar), Bi_2O_3 (99.975%, Alfa Aesar), ZrO_2 (99%, Sinopharm Chemical Reagent), Sb_2O_3 (99%, Tianjin Kemiou Chemical Reagent), and Sm_2O_3 (99.9%, Alfa Aesar) were weighed and ground in the ZrO_2 ball with alcohol for 15 h. Then the dried mixture was calcined for 6 h under 850 °C. After the calcination, $x/2$ mol Sm_2O_3 ($x = 0.0005, 0.001, 0.002$, and 0.004) dopants were added into the KNSN–0.04BNKZ powders. Then the mixture was ground again for 15 h with alcohol as a medium. The powders are mixed with polyvinyl alcohol (PVA) and pressed into a sheet. At 550 °C, the subsequent PVA was burned for 5 h. Finally, the samples were sintered at 1200–1220 °C for 3 h. For the electric measurements, silver paste was applied to the surface of the polished samples. After sintered at 650 °C for 10 min, the electrode was formed.

The crystal structure of the ceramics was analyzed by the X-ray powder diffractometer (XRD, Bruker D8 Advance, Germany), and the scanning range was 20°–60°. Using field-emission scanning electron microscope (FE-SEM, Carl Zeiss, Merlin Compact), the microscopic appearances of the ceramics were observed. Using broad frequency dielectric spectrometer (Concept 80, Novocontrol Inc., Germany), the dielectric constant and dielectric loss of ceramics with the change of temperature were analyzed. Using broad frequency dielectric spectrometer, the impedance spectroscopies were analyzed (Concept80, Novocontrol Inc., Germany).

Using the aix-ACCTTF2000FE-HV ferroelectric test unit (aix-ACCT Inc, Germany), we measured the hysteresis loop, bipolar strain curve, and unipolar strain curve. Using the spectrofluorometer (FLS920, Edinburgh Instruments, UK), the photoluminescence (PL) spectra and photoluminescence excitation (PLE) spectra at room temperature were measured.

3 Results and discussion

Figure 1 reveals the surface micrographs of KNNS–0.04BNKZ– x Sm ($x = 0.0005, 0.001, 0.002$, and 0.004) ceramics sintered under the best sintering conditions. All ceramics have relative dense microstructure with homogeneous grains. With the increase of Sm content, the average grain size changes slightly, as illustrated in Fig. 2 (grain size distributions of KNNS–0.04BNKZ– x Sm samples). In the present work, the grain size of the samples was calculated by the software of Nano Measurer. As seen from Figs. 1 and 2, the average grain size shows very subtle change with the addition of Sm content. However, the proportion of small grains increases, confirming that the role of Sm in the KNN-based system involves grain growth inhibitor [31]. During sintering, partial Sm^{3+} may accumulate near the grain boundaries and reduce their densification mobility. The reduction in the mobility of the grain boundary weakens the mass transport, and thus inhibits the grain growth to some extent.

Figure 3 presents the XRD patterns for KNNS–0.04BNKZ– x Sm samples in the 2θ range of 20° – 60° . All samples show pure perovskite phase with no second phase. In the present work, the Sm doping

Fig. 1 SEM micrographs of KNNS–0.04BNKZ– x Sm ($x = 0.0005, 0.001, 0.002$, and 0.004) ceramics.

Fig. 2 Grain size distributions of KNNS–0.04BNKZ– x Sm ($x = 0.0005, 0.001, 0.002$, and 0.004) ceramics.

Fig. 3 XRD patterns of KNNS–0.04BNKZ– x Sm ($x = 0.0005, 0.001, 0.002$, and 0.004) ceramics.

content is very small (≤ 0.004 mol), and such a small amount of impurity phase induced by Sm may hardly be observed in the XRD pattern, due to the detection limit of conventional X-ray diffraction techniques. While when compared with pure KNNS–0.04BNKZ (Fig. S1 in the Electronic Supplementary Material), the diffraction peaks shift to higher angle as the Sm doping level increases, which indicates a slight shrinkage

of the lattice due to the smaller ionic radii of Sm^{3+} (1.24 Å, CN = 12) than K^+ (1.64 Å, CN = 12) and Na^+ (1.39 Å, CN = 12). This indicates Sm^{3+} ion has diffused into the host lattice, and this can be further supported by the change of phase structure induced by Sm^{3+} . As shown in the evolution of (200) characteristic peak around 2θ of 45° , peak splitting (only for pure KNNs–0.04BNKZ sample) disappears after Sm doping. Pure KNNs–0.04BNKZ sample is reported to form rhombohedral–tetragonal coexisted phases [35], while all the studied Sm-modified samples favor a single pseudo-cubic (or tetragonal) phase. This means Sm doping induced a phase transition from rhombohedral–tetragonal coexisted phases to a single pseudo-cubic (or tetragonal) phase.

Figure 4 shows the (a) P – E hysteresis loops and (b) bipolar S – E loops of KNNs–0.04BNKZ– $x\text{Sm}$ ceramics with different Sm content recorded at room temperature and 10 Hz. It is generally believed that P – E hysteresis loop is the typical characteristic of ferroelectric materials [36]. In this study, slim P – E hysteresis loops show the ferroelectric relaxation behavior of KNNs–0.04BNKZ– $x\text{Sm}$ samples. When the amount of Sm is 0.002 mol, the remnant polarization P_r achieves its maximum and the coercive field E_c reaches the minimum, showing the enhanced ferroelectric properties induced by the proper amount of Sm. In addition, we found the S – E loops are quite asymmetrical with distinct strains at positive and negative electric fields, which may be caused by the “poling effect” during the application of AC measuring field. As we know, KNN-based ceramics usually exhibit “soft” behavior with low coercive field. Even with the application of AC field during the S – E measurement, they can easily be poled before the final test field applied. The electric dipoles are not random while show a certain orientation before the final electric

field applied, leading to asymmetrical S – E loops during testing. Figure 4(c) shows the unipolar strain curves of KNNs–0.04BNKZ– $x\text{Sm}$ samples, which show a perfect linear state. This means that the piezoelectric effect is the main contribution of strain [37]. The unipolar values are 0.11%, 0.10%, 0.09%, and 0.095% at 55 kV/cm, respectively, for ceramics with $x = 0.0005$, 0.001, 0.002, and 0.004, equivalently a large singal d_{33} of 200, 182, 164, and 173 pm/V, respectively. Meanwhile, the small singal d_{33} is 50, 55, 80, 60 pC/N, respectively.

When transferring the materials into application, the materials’ stability issues are of paramount importance [38]. In this work, we studied reliability characteristics of the materials, which include temperature stability and cyclic electrical stability (fatigue behavior). Figure 5 shows the (a) P – E hysteresis loops, (b) bipolar S – E , and (c) unipolar S – E curves of KNNs–0.04BNKZ– $x\text{Sm}$ ($x = 0.002$) ceramics at different temperatures (23–150 °C). Figure 5(d) shows the remnant polarization P_r and unipolar strain S_{uni} as a function of temperature of KNNs–0.04BNKZ– $x\text{Sm}$ ($x = 0.002$) ceramics. It can be obtained from Figs. 5(a)–5(c) that the P – E hysteresis loops and the S – E curves of KNNs–0.04BNKZ– $x\text{Sm}$ ($x = 0.002$) ceramics change slightly with increasing temperatures (23–150 °C). The loops show no significant deformation in the whole range of the measuring temperatures. Meanwhile, the remnant polarization P_r and unipolar strain S_{uni} show very slight changes with temperature. These results indicate that the Sm-doped KNNs–0.04BNKZ ceramics exhibit relatively good temperature stability in the measured temperature range.

To further study the long-term stability of the samples, we also performed fatigue testing of the samples. Figure 6 shows the bipolar fatigue behavior of (a) P – E and (b) S – E for KNNs–0.04BNKZ– $x\text{Sm}$ ($x = 0.002$) ceramics recorded at 10 Hz for 10^5 cycles. Figure 7

Fig. 4 (a) P – E hysteresis loops, (b) bipolar strain curves, (c) unipolar strain curves of KNNs–0.04BNKZ– $x\text{Sm}$ ($x = 0.0005$, 0.001, 0.002, and 0.004) ceramics measured at room temperature and 10 Hz.

Fig. 5 (a) P - E hysteresis loops, (b) bipolar S - E curves, (c) unipolar strain curves of KNSN-0.04BNKZ- x Sm ($x = 0.002$) ceramics at different temperatures; (d) the unipolar strain values for the above sample at different temperatures.

Fig. 6 Bipolar fatigue behavior of (a) P - E and (b) S - E for ergodic relaxor KNSN-0.04BNKZ- x Sm ($x = 0.002$) ceramics, at 10 Hz for 10^5 cycles. (c) Unipolar strain values for the above sample as a function of switching cycle. (d) Remanent polarization P_r for the above sample as a function of switching cycle.

Fig. 7 (a) P - E hysteresis loops, (b) bipolar S - E curves, and (c) unipolar strain curves of KNSN-0.04BNKZ- x Sm ($x = 0.002$) ceramics before fatigue and after 10^5 fatigue cycles.

shows the changes of the P - E and S - E loops before and after fatigue. It can be observed from Figs. 6 and 7 that the KNSN-BNKZ- x Sm ($x = 0.002$) ceramics exhibits fatigue-free behavior, whereupon P_r and S are found to have almost no change under 10^5 switching cycles. The phenomenon suggests the samples have excellent long-term stability. Combined with the results of Figs. 5–7, the material has excellent stability characteristics, which makes the material promising for electromechanical actuator applications.

Figure 8 shows the temperature dependence of dielectric properties of the KNSN-0.04BNKZ- x Sm ($x = 0.0005, 0.001, 0.002, \text{ and } 0.004$) ceramics tested at 100 kHz. As reported, pure KNN sample has two dielectric peaks, one corresponding to the phase transition of orthorhombic to tetragonal (T_{O-T}) at about 200 °C and the other one corresponding to the phase transition of tetragonal to cubic phase (T_c) at about 420 °C [35]. In the studied KNSN-0.04BNKZ- x Sm system, only a broadening dielectric peak was detected within the test temperature range, confirming the tetragonal (pseudo-cubic) phase in Sm-modified samples. In addition, the diffuse dielectric anomaly suggests the relaxor behavior. To further characterize the relaxor behavior of the Sm-modified samples, empirical formula proposed by Uchino and Nomura [39] was introduced, $1/\varepsilon - 1/\varepsilon_m = (T - T_m)^\gamma / C$, where ε_m is the value of dielectric constant corresponding to the highest point of the curve and T_m is the corresponding value of temperature. The value of C is invariable, and γ is a parameter called relaxation index between 1 and 2. In the case of obeying the equation Curie-Weiss law, $\gamma = 1$, which corresponds to the case of normal ferroelectric, whereas $\gamma = 2$ corresponds to the ideal relaxor ferroelectric. The logarithmic plots of equation regarding to the KNSN-0.04BNKZ- x Sm ($x = 0.0005, 0.001, 0.002, \text{ and } 0.004$) ceramics are shown in Fig. 9.

All ceramics show linear relationship and the fitting values are around 1.7, which indicates the generation of the relaxor behavior [40]. The dielectric relaxation in the studied KNSN-0.04BNKZ- x Sm system was mainly affected by the thermal motion of oxygen ions/vacancies as discussed in Fig. 10.

At different test temperatures (425, 450, 475, 500, and 525 °C), the impedance spectra of the ceramics are recorded and shown in Figs. 10(a)–10(d). In this study, we observed two semicircles in all ceramics, suggesting two time constants ($\tau = RC$) in the impedance spectrum. The two semicircles are attributed to grain contribution (R_g) and grain boundary contribution (R_{gb}). The larger semicircle in the higher frequency range is ascribed to the grain effect (modeled by an equivalent circuit $R_b C_b$), whereas the grain boundary response (modeled by an equivalent circuit $R_{gb} C_{gb}$) contributes to the smaller semicircle in the lower frequency range [31]. It can be seen from Fig. 10 that the center of the semicircular arcs was above the real (Z') axis, suggesting an appearance of non-Debye type relaxation. Here, we noted the radius of the arc gets

Fig. 8 Dielectric permittivity ε_r as a function of temperature for the KNSN-0.04BNKZ- x Sm ($x = 0.0005, 0.001, 0.002, \text{ and } 0.004$) ceramics.

Fig. 9 Plot of $\log(1/\varepsilon - 1/\varepsilon_m)$ as a function of $\log(T - T_m)$ for the KNNS-0.04BNKZ- x Sm ($x = 0.0005, 0.001, 0.002$, and 0.004) ceramics at 10 kHz.

Fig. 10 Complex impedance plots for the KNNS-0.04BNKZ- x Sm ($x = 0.0005, 0.001, 0.002$, and 0.004) ceramics at various temperatures and Arrhenius plots of σ_{dc} conductivity of the KNNS-0.04BNKZ- x Sm ceramics.

smaller and smaller with the increase of temperature, suggesting the materials have more defects or carriers to lead the increase of conductivity. The phenomenon is a negative temperature coefficient of resistance (NTCR) behavior [34]. Activation energy (E_a) and conductivity (σ) are related as follows: $\sigma = \sigma_0 \exp(-E_a/kT)$. Seen from Fig. 10(e), the logarithm of the conductivity ($\ln\sigma$) of ceramics is well fitted with a linear curve of $1000/T$. The E_a of KNSN-0.04BNKZ- x Sm ($x = 0.0005, 0.001, 0.002$, and 0.004) ceramics is 0.74, 0.84, 0.66, and

0.92 eV, respectively. As reported that the values of E_a for A- and B-site cations in ABO_3 perovskite materials are approximately 4 and 12 eV, respectively [41]. For oxygen vacancies, it varies from 0.5 to 2 eV, depending on their concentration [42]. This can be related to the E_a of ceramics, which is in the range of 0.66–0.92 eV; this E_a is closely related to oxygen ion/vacancy migration [42]. Therefore, oxygen vacancies dominate the conductive properties of the KNSN-0.04BNKZ- x Sm ceramics from 425 to 525 °C.

In perovskite-type compounds, short-range motion of oxygen vacancies is a common phenomenon which contributes to high-temperature relaxation. The activation energy for the thermal motion of oxygen ions/vacancies is about 1 eV in different perovskite oxides at the high-temperature region where the diffuse dielectric anomaly is observed [41]. However, in the present work, the conductivity activation energy E_a is about 0.66–0.92 eV, lower than this value. According to Kang *et al.* [41], there might be a loose site for oxygen vacancies that needs less activation energy in order to make a motion or hopping, since all lattice sites are not ideally equivalent as we know. Therefore, in the present work, even E_a is lower than 1 eV, a short-range motion of oxygen vacancies still exists, producing high-temperature relaxation and diffuse dielectric anomaly as illustrated in Figs. 8 and 9.

Figure 11(a) shows PLE monitored at 597 nm and PL spectra excited at 407 nm for KNNS–0.04BNKZ– x Sm ($x = 0.0005$) ceramics. Seen from Fig. 11, four absorption peaks appear at 407, 420, 464, and 479 nm; from the energy level scheme of Sm^{3+} ions (Fig. 11(b)), the four absorption peaks are due to the f–f transitions [43]. In addition, the absorption peak around 407 nm corresponds to $^6\text{H}_{5/2} \rightarrow ^4\text{G}_{7/2}$. The absorption peak around 420 nm corresponds to $^6\text{H}_{5/2} \rightarrow ^4\text{P}_{5/2}$. And the absorption peaks around 464, 479 nm correspond to $^6\text{H}_{5/2} \rightarrow ^6\text{P}_{5/2}$, $^6\text{H}_{5/2} \rightarrow ^4\text{I}_{11/2}$ transitions, respectively [44,45]. In 563, 597, and 645 nm, the PL spectra exhibit three peaks by 407 nm excitation. The three emission peaks correspond to the f–f transition emissions of Sm^{3+} at 563 nm ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$), 597 nm ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$), and 645 nm ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$), respectively. Figure 12(b) shows the CIE chromaticity diagram of samples excited at 450 nm. It

Fig. 11 (a) Photoluminescence excitation (PLE) spectra and photoluminescent (PL) emission of KNNS–0.04BNKZ– x Sm ($x = 0.0005$) ceramics. (b) Energy level diagram of Sm^{3+} ions.

Fig. 12 (a) PL spectrum intensity dependence of Sm concentrations excited at 407 nm and (b) calculated CIE chromaticity coordinates of KNNS–0.04BNKZ– x Sm ($x = 0.0005$) sample.

can be seen from Fig. 12(b) that orange fluorescence is emitted from the Sm-doped KNN-based ceramics. The coordinate is $x = 0.58$, $y = 0.41$ in the CIE chromaticity diagram. Figure 12(a) shows the effect of KNSN–0.04BNKZ– x Sm ceramic samples doped with different concentrations of Sm^{3+} on the luminescence spectrum under 407 nm excitation. Seen from Fig. 12(a), as the Sm^{3+} concentration increases, the intensity of the emission peak also increases. When the amount of Sm is 0.004 mol, the ceramics have the highest luminous intensity. In our previous work of KNN–5.2LS– $x\text{Sm}_2\text{O}_3$, the PL intensity reaches a maximum value when the Sm_2O_3 content is 0.4 mol%, and shows a decreasing tendency as Sm_2O_3 content further increases due to concentration-quenching effect [31]. In the present work, further increase Sm_2O_3 doping may further increase the PL intensity of the ceramics. However, considering the weakened electrical properties induced by enlarging Sm_2O_3 content, we did not carry out the study of luminescence properties in high Sm_2O_3 concentration.

4 Conclusions

In this work, solid-state sintering method was successfully applied to fabricate dense KNSN–0.04BNKZ– x Sm lead-free ceramics. Results revealed that Sm^{3+} diffuses into KNSN–0.04BNKZ to form a new solid solution, and all samples exhibit a single perovskite structure with pseudo-cubic phase at room temperature. Existence of slim P – E hysteresis loops with small remnant polarization values and the weak dielectric properties of the Sm-doped KNSN–0.04BNKZ demonstrates the ferroelectric relaxor behavior of the KNSN–0.04BNKZ– x Sm ceramics. The KNSN–0.04BNKZ ceramic with 0.002 mol Sm exhibited temperature-independent properties (23–150 °C) and fatigue-free behavior (up to 10^5 cycles). Moreover, Sm-doped KNSN–0.04BNKZ exhibits a bright photoluminescence with a strong orange emission under visible light irradiation. As multifunctional material with both ferroelectric and luminescent properties, KNSN–0.04BNKZ– x Sm ceramics may take an important role in multifunctional materials.

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Electronic Supplementary Material

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References

- [1] Matsubara M, Kikuta K, Hirano S. Piezoelectric properties of $(\text{K}_{0.5}\text{Na}_{0.5})(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_3$ – $\text{K}_{5.4}\text{CuTa}_{10}\text{O}_{29}$ ceramics. *J Appl Phys* 2005, **97**: 114105.
- [2] Liu WF, Ren XB. Large piezoelectric effect in Pb-free ceramics. *Phys Rev Lett* 2009, **103**: 257602.
- [3] Takenaka T, Sakata KO, Toda KO. Piezoelectric properties of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ -based ceramics. *Ferroelectrics* 1990, **106**: 375–380.
- [4] Rojac T, Bencan A, Malic B, *et al.* BiFeO₃ ceramics: Processing, electrical, and electromechanical properties. *J Am Ceram Soc* 2014, **97**: 1993–2011.
- [5] Saito Y, Takao H, Tani T, *et al.* Lead-free piezoceramics. *Nature* 2004, **432**: 84–87.
- [6] Wu JG, Xiao DQ, Zhu JG. Potassium–sodium niobate lead-free piezoelectric materials: Past, present, and future of phase boundaries. *Chem Rev* 2015, **115**: 2559–2595.
- [7] Shrout TR, Zhang SJ. Lead-free piezoelectric ceramics: Alternatives for PZT? *J Electroceram* 2007, **19**: 113–126.
- [8] Jeong CK, Park KI, Ryu J, *et al.* Nanogenerators: Large-area and flexible lead-free nanocomposite generator using alkaline niobate particles and metal nanorod filler. *Adv Funct Mater* 2014, **24**: 2565.
- [9] Jeong CK, Park KI, Son JH, *et al.* Self-powered fully-flexible light-emitting system enabled by flexible energy harvester. *Energ Environ Sci* 2014, **7**: 4035–4043.
- [10] Hao JG, Li W, Zhai JW, *et al.* Progress in high-strain perovskite piezoelectric ceramics. *Mat Sci Eng R: Rep* 2019, **135**: 1–57.
- [11] Qin YL, Zhang JL, Yao WZ, *et al.* Domain configuration and thermal stability of $(\text{K}_{0.48}\text{Na}_{0.52})(\text{Nb}_{0.96}\text{Sb}_{0.04})\text{O}_3$ – $\text{Bi}_{0.50}(\text{Na}_{0.82}\text{K}_{0.18})_{0.50}\text{ZrO}_3$ piezoceramics with high d_{33} coefficient. *ACS Appl Mater Interfaces* 2016, **8**: 7257–7265.
- [12] Cross E. Lead-free at last. *Nature* 2004, **432**: 24–25.
- [13] Lin JF, Xu J, Liu CW, *et al.* Effects of compositional changes on up-conversion photoluminescence and electrical properties of lead-free Er-doped $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ – SrTiO_3

- transparent ceramics. *J Alloys Compd* 2019, **784**: 60–67.
- [14] Li Y, Moon K, Wong CP. Electronics without lead. *Science* 2005, **308**: 1419–1420.
 - [15] Hussain A, Rahman JU, Ahmed F, *et al.* Plate-like $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ particles synthesized by topochemical microcrystal conversion method. *J Eur Ceram Soc* 2015, **35**: 919–925.
 - [16] Wang J, Luo L. Probing the diffusion behavior of polymorphic phase transition in $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ ferroelectric ceramics by Eu^{3+} photoluminescence. *J Appl Phys* 2018, **123**: 144102.
 - [17] Zhang Y, Luo L, Li K, *et al.* Large and reversible in-situ up-conversion photoluminescence modulation based on photochromism via electric-field and thermal stimulus in ferroelectrics. *J Eur Ceram Soc* 2018, **38**: 3154–3161.
 - [18] Yao Y, Li Y, Sun NN, *et al.* Enhanced dielectric and energy-storage properties in ZnO -doped $0.9(0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-0.06\text{BaTiO}_3)-0.1\text{NaNbO}_3$ ceramics. *Ceram Int* 2018, **44**: 5961–5966.
 - [19] Shen ZY, Shen WC, Li YM, *et al.* Effect of $(\text{Co}_{1/3}\text{Sb}_{2/3})$ complex doping on the structure and electrical properties of $0.96(\text{K}_{0.49}\text{Na}_{0.51})(\text{Nb}_{0.97}\text{Ta}_{0.03})\text{O}_3-0.04\text{Bi}_{0.5}\text{Na}_{0.5}\text{ZrO}_3$ lead-free piezoelectric ceramics. *J Mater Sci: Mater Electron* 2017, **28**: 137–141.
 - [20] Li FL, Gou Q, Xing J, *et al.* The piezoelectric and dielectric properties of sodium–potassium niobate ceramics with new multiphase boundary. *J Mater Sci: Mater Electron* 2017, **28**: 18090–18098.
 - [21] Wang XP, Wu JG, Xiao DQ, *et al.* Giant piezoelectricity in potassium–sodium niobate lead-free ceramics. *J Am Chem Soc* 2014, **136**: 2905–2910.
 - [22] Wu B, Wu HJ, Wu JG, *et al.* Giant piezoelectricity and high Curie temperature in nanostructured alkali niobate lead-free piezoceramics through phase coexistence. *J Am Chem Soc* 2016, **138**: 15459–15464.
 - [23] Xu K, Li J, Lv X, *et al.* Superior piezoelectric properties in potassium-sodium niobate lead-free ceramics. *Adv Mater* 2016, **28**: 8519–8523.
 - [24] Wu JG, Xiao DQ, Zhu JG. Potassium–sodium niobate lead-free piezoelectric materials: Past, present, and future of phase boundaries. *Chem Rev* 2015, **115**: 2559–2595.
 - [25] Fu J, Zuo R, Qi H, *et al.* Low electric-field driven ultrahigh electrostrains in Sb-substituted $(\text{Na}, \text{K})\text{NbO}_3$ lead-free ferroelectric ceramics. *Appl Phys Lett* 2014, **105**: 242903.
 - [26] Yao FZ, Patterson EA, Wang K, *et al.* Enhanced bipolar fatigue resistance in CaZrO_3 -modified $(\text{K}, \text{Na})\text{NbO}_3$ lead-free piezoceramics. *Appl Phys Lett* 2014, **104**: 242912.
 - [27] Men TL, Yao FZ, Zhu ZX, *et al.* Piezoelectric properties of $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3\text{--BaTiO}_3$ lead-free ceramics prepared by spark plasma sintering. *J Adv Dielect* 2016, **6**: 1650013.
 - [28] Sun HQ, Peng DF, Wang XS, *et al.* Green and red emission for $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3\text{:Pr}$ ceramics. *J Appl Phys* 2012, **111**: 046102.
 - [29] Wang J, Luo LH, Huang YP, *et al.* Strong correlation of the electrical properties, up-conversion photoluminescence, and phase structure in $\text{Er}^{3+}/\text{Yb}^{3+}$ -co-doped $(1-x)\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3\text{--}x\text{LiNbO}_3$ ceramics. *Appl Phys Lett* 2015, **107**: 192901.
 - [30] Wu X, Lau CM, Kwok KW. Photoluminescence properties of Er/Pr -doped $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ ferroelectric ceramics. *J Am Ceram Soc* 2015, **98**: 2139–2145.
 - [31] Hao JG, Xu ZJ, Chu RQ, *et al.* Bright reddish-orange emission and good piezoelectric properties of Sm_2O_3 -modified $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ -based lead-free piezoelectric ceramics. *J Appl Phys* 2015, **117**: 194104.
 - [32] Wei YB, Wu Z, Jia YM, *et al.* Dual-enhancement of ferro-/piezoelectric and photoluminescent performance in Pr^{3+} doped $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ lead-free ceramics. *Appl Phys Lett* 2014, **105**: 042902.
 - [33] Wang J, Luo LH, Huang YP, *et al.* Effect of Yb codoping on the phase transition, and electrical and photoluminescence properties in KNLN:Er/xYb ceramics. *J Am Ceram Soc* 2016, **99**: 1625–1630.
 - [34] Yao QR, Wang FF, Xu F, *et al.* Electric field-induced giant strain and photoluminescence-enhancement effect in rare-earth modified lead-free piezoelectric ceramics. *ACS Appl Mater Interfaces* 2015, **7**: 5066–5075.
 - [35] Hao JG, Zhai JW, Li YX. Preparation of $(\text{K}_{0.50}\text{Na}_{0.50})\text{NbO}_3$ lead-free piezoelectric ceramics by mechanical activation assisted method. *Jpn J Appl Phys* 2011, **50**: 110207.
 - [36] Hao J, Xu Z, Chu R, *et al.* Good temperature stability and fatigue-free behavior in Sm_2O_3 -modified $0.948(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3\text{--}0.052\text{LiSbO}_3$ lead-free piezoelectric ceramics. *Mater Res Bull* 2015, **65**: 94–102.
 - [37] Hao J, Xu Z, Chu R, *et al.* Large electric-field-induced strain in SrZrO_3 modified $\text{Bi}_{0.5}(\text{Na}_{0.80}\text{K}_{0.20})_{0.5}\text{TiO}_3$ lead-free electromechanical ceramics with fatigue-resistant behavior. *J Alloys Compd* 2015, **647**: 857–865.
 - [38] Zhai YZ, Du J, Chen C, *et al.* Temperature stability and electrical properties of Tm_2O_3 doped KNN-based ceramics. *J Mater Sci: Mater Electron* 2019, **30**: 4716–4725.
 - [39] Uchino K, Nomura S. Critical exponents of the dielectric constants in diffused-phase-transition crystals. *Ferroelectrics* 1982, **44**: 55–61.
 - [40] Shi W, Feng Y, Lu T, *et al.* Photoluminescence and impedance properties of rare-earth doped $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ lead-free ceramics. *J Mater Sci: Mater Electron* 2019, **30**: 9–16.
 - [41] Kang BS, Choi SK, Park CH. Diffuse dielectric anomaly in perovskite-type ferroelectric oxides in the temperature range of 400–700 °C. *J Appl Phys* 2003, **94**: 1904–1911.
 - [42] Steinsvik S, Bugge R, Gjønnes J, *et al.* The defect structure of $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-y}$ ($x = 0\text{--}0.8$) investigated by electrical conductivity measurements and electron energy loss spectroscopy (EELS). *J Phys Chem Solids* 1997, **58**: 969–976.
 - [43] Zhang HW, Deng H, Chen C, *et al.* Chemical nature of giant strain in Mn-doped $0.94(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3\text{--}0.06\text{BaTiO}_3$ lead-free ferroelectric single crystals. *Scripta Mater* 2014, **75**: 50–53.

- [44] Brinkley SE, Lin YD, Chakraborty A, *et al.* Polarized spontaneous emission from blue-green m-plane GaN-based light emitting diodes. *Appl Phys Lett* 2011, **98**: 011110.
- [45] Yang XY, Liu J, Yang H, *et al.* Synthesis and characterization of new red phosphors for white LED applications. *J Mater Chem* 2009, **19**: 3771–3774.

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