Eu-doped $K_{0.5}Na_{0.5}NbO_3$ -(Ba,Sr)TiO₃: A novel lead-free luminescent ferroelectric transparent ceramic with reversible photochromism*

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Photochromic (PC) luminescent ferroelectric materials have aroused great interest because of their potential applications in optical information memories, optical switches and bio-imaging. However, those materials are basically opaque. In this work, we prepared a PC luminescent $K_{0.5}Na_{0.5}NbO_3$ -based ferroelectric transparent ceramic by modifying with Eu^{3+} , Ba^{2+} , Ti^{4+} and Sr^{2+} , which not only have good optical transmittances ($\sim 60\%$ at 900 nm), moderate ferroelectric properties and down-conversion photoluminescence (PL) properties, but also exhibit reversible PC behavior. After the illumination by xenon lamp, the colors of the ceramics change from pale green to gray, and then reversibly recover to their initial state via thermal stimulus (200°C for 10 min). Interestingly, both the optical transmittances and PL intensities can be effectively tailored by controlling the PC reaction process. The results suggest that the ferroelectric transparent ceramics are promising for the modulation of photoenergy and the design of optoelectronic devices.

Keywords: Ferroelectric ceramics; optical transmittance; Eu-KNNBST; photochromism; photoluminescence.

1. Introduction

With the explosion of information and technology in “photonics” industry, photoelectric devices based on optoelectronic materials have attracted extensive interest for the applications of information storage, photoswitches, optical sensing and smart windows.¹ Photochromic (PC) materials have been widely studied with regards to their ability of reflectivity and photoluminescence (PL) modulations in response to external stimulation. Photochromism phenomenon describes a process where the color of specimen can be changed (i.e., the coloration state and the decoloration state) via alternating visible/ultraviolet light irradiation, heat, or even electric field.^{2,3} Among all the PC materials, inorganic solid oxides own outstanding thermal stability, mechanical strength and chemical resistance.^{4,5} To date, RE-doped inorganic ferroelectrics, such as $Na_{0.5}Bi_{2.5}Nb_2O_9$,⁶ $Na_{0.5}Bi_{0.5}TiO_3$ (NBT)⁵ and $(K_{0.5}Na_{0.5})NbO_3$ (KNN),⁷ have been found to exhibit reversible PL modulation behavior based on PC reaction. However, the functionality of them is restricted as the ferroelectric performance can hardly be connected with the PC characteristics and the underlying PC mechanism is ambiguous. Hence, it is of great significance to explore new ferroelectrics with excellent PC properties and investigate the intrinsic kinetic process of PC reaction.

Environment-friendly lead-free KNN-based ceramics have been regarded as the most promising alternative to toxic lead-based piezoelectric materials, owing to their moderate dielectric constant, optimum piezoelectric response and good ferroelectricity.^{8–13} Recently, RE-doped KNN ceramics have been verified to have both PC and PL modulation behaviors induced by vacancy-related defects (e.g., K/Na/O vacancies),^{2–7} expanding the electrical applications to optoelectronic areas. Generally, pure KNN ceramics own poor relative density ($\sim 95\%$), low symmetry structure (orthorhombic phase) and large grain size ($1\text{--}2\ \mu\text{m}$).¹⁴ After using highly purified raw chemicals, tailoring the host composition and doping suitable ions, KNN-based ceramics could be fabricated into transparent ones, such as $(1-x)(K_{0.5}Na_{0.5})O_3$ - $xBa(Sc_{0.5}Nb_{0.5})O_3$ (KNN- x BSN),¹⁵ $(K_{0.5}Na_{0.5})_{1-x}Li_xNb_{1-x}Bi_xO_3$ (KNN- x LB)¹⁶ and $(1-x)(K_{0.5}Na_{0.5})NbO_3$ - $xSrTiO_3$ (KNN- x ST),¹⁷ exhibiting high relative density (over 98%), high symmetry (cubic or cubic-like phase) and fine grain size (below 500 nm). In addition, RE (e.g., Er or Ho)-doped KNN-based transparent ceramics are promising due to the coexistence of superior di-/piezo-/ferro-electric, optical, up-conversion PL and electro-optic properties, which can be adopted in interdisciplinary studies. It is well known that KNN-based materials have potential in the application of

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ferroelectric storage. It can be predicted that if the PC behavior can be realized in KNN-based ferroelectric transparent ceramics, the information storage will boost because of the combination of both ferroelectric and optical memories in the single entity.

Lately, our group first discovered the photochromism phenomenon in Er-doped $(\text{K}_{0.5}\text{Na}_{0.5})_{0.95}\text{Li}_{0.05}\text{Nb}_{0.95}\text{Bi}_{0.05}\text{O}_3$ transparent ceramic, whose optical transmittance and up-conversion PL intensity can be effectively modulated through reversible PC reaction.¹⁸ Furthermore, it is necessary to develop other KNN-based transparent ceramics with PC behavior in the purpose of providing theoretical guidance for the development of luminescent ferroelectrics. In this work, a novel transparent ceramic, Eu-doped $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ -(Ba,Sr)- TiO_3 , possessing high optical transmittance and good down-conversion PL performance, is prepared by traditional solid-state synthesis. The results show that after the illumination by xenon lamp, the material not only owns decreased optical transmittance, but also exhibits remarkable PL modulation.

2. Experimental

According to the designed formula of x mol.% Eu^{3+} -doped $0.91\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ - 0.09BaSrTiO_3 (abbreviated as $x\text{Eu-KNNBST}$, $x = 0.25, 0.5, 1$), the ceramics were prepared by the solid-state reaction. Analytical-grade K_2CO_3 (99.99%), Na_2CO_3 (99.8%), SrCO_3 (99.8%), Nb_2O_5 (99.5%), Ti_2O_3 (99.8%), BaCO_3 (99.95%) and Eu_2O_3 (99.99%) raw chemicals were dried and weighed first. For each composition, the weighed powders were ball-milled for 12 h in ethanol, dried at 80°C , calcined at 850°C for 4 h and secondarily ball-milled for 10 h. After that, the obtained powders were mixed thoroughly with a 5 wt.% polyvinyl alcohol (PVA) binder solution and uniaxially pressed into disks (with the diameter of 12 mm and thickness of 1 mm) under the pressure of ~ 300 MPa. To completely burn out PVA and remove pores, the obtained pellets were heated to 800°C for 2 h at a slow rate of $0.5^\circ\text{C}/\text{min}$. Subsequently, the disk samples were finally sintered at 1205°C for 4 h in air for densification. All the as-prepared ceramics were polished to a thickness of ~ 0.3 mm to measure the optical and PL properties.

The optical transmittances of the ceramics were measured in the range of 300–950 nm by an ultraviolet-visible-infrared (UV-Vis-IR) spectrophotometer (PerkinElmer Lambda 950). The phase structure was characterized by X-ray diffraction (XRD, Rigaku Ultima III) with CuK_α radiation. The surface microstructures and element maps were performed by field emission scanning electron microscope (SEM, Zeiss Supra 55) and Energy Dispersive Spectrometer (EDS). The corresponding grain size distribution was determined by measuring 150 grains from the SEM micrographs using the linear intercept method based on the “Nano Measurer” software. The polarization-electric field (P-E) hysteresis loops were performed at 100 Hz by a ferroelectric test system (TF Analyzer 2000, aixACCT). The PL spectra were obtained using a

spectro-fluorometer (FluoroMax-4, HORIBA). The xenon lamp (PerkinElmer CEL-PE300L-3A, 300 W) with the wavelength ranging from 200 nm to 1100 nm was used as the light illumination source for the PC reaction.

3. Result and Discussions

3.1. Optical transmittance

The optical transmittances (T) of the $x\text{Eu-KNNBST}$ transparent ceramics are plotted in Fig. 1, ranging from 300 nm to 850 nm. With the increase of Eu^{3+} content (x), the T values just change slightly, suggesting that Eu-doping does not affect the transmittances of samples. As the wavelength increases, T rises rapidly at 400 nm and then gradually increases until reaching almost maximum in the near-infrared (NIR) region (900 nm). All the samples exhibit good optical transmittances from visible to NIR range, giving the T values of $\sim 35\%$ at 500 nm (green region), $\sim 45\%$ at 600 nm (red region) and $\sim 60\%$ at 900 nm (NIR region). The results are consistent with the optical transparencies of sample photographs, as shown in the set of Fig. 1. Not only Chinese characters under the samples are clearly visible, but the background objects (e.g., mobile phone case and stove) can be seen through the transparent ceramics. The T values of $x\text{Eu-KNNBST}$ are higher than those of non-RE doped KNN-based transparent ceramics, including KNN- $x\text{ST}$,¹⁷ $(1-x)\text{KNN-xSr}(\text{Al}_{0.5}\text{Nb}_{0.5})\text{O}_3$ ¹⁹ and $(1-x)\text{KNN-xSr}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$,²⁰ and are comparable to that of KNN- $x\text{LB}$.¹⁵ And novel transparent ceramics can be adopted in various functional applications, such as optical-electrical and magneto-optical integrated devices.²¹

3.2. Phase and microstructure

To uncover the reason of high optical transparency of $x\text{Eu-KNNBST}$ ceramics, phase structures and microstructures

Fig. 1. Optical transmittance spectra of the $x\text{Eu-KNNBST}$ transparent ceramics and the photographs of the ceramics with the thickness of ~ 0.3 mm (the insets).

Fig. 2. XRD patterns of the x Eu-KNNBST transparent ceramics.

were investigated. Figure 2 shows the XRD patterns of x Eu-KNNBST with different Eu^{3+} contents. All the samples possess almost pure perovskite structure (except for a small amount of impurity phases in the range of $20\text{--}30^\circ$ as marked in Fig. 2), suggesting that the modified ions (i.e., Eu^{3+} , Ba^{2+} , Sr^{2+} and Ti^{4+}) have diffused into the KNN host lattice. According to the ionic radius of K^+ (1.51 Å, coordination number CN = 12), Na^+ (1.18 Å, CN = 12), Eu^{3+} (0.96 Å, CN = 12), Sr^{2+} (1.326 Å, CN = 12), Ba^{2+} (1.68 Å, CN = 12), Nb^{5+} (0.69 Å, CN = 6) and Ti^{4+} (0.64 Å, CN = 6), $\text{Eu}^{3+}/\text{Sr}^{2+}$ may preferentially replace the Na-site, Ba^{2+} may occupy the K-site, while Ti^{4+} is more likely to substitute for the Nb-site. For the diffraction angle at around 45° , the first diffraction peak is lower than the second one, which indicates that the ceramics have a tetragonal phase structure at room temperature. Additionally, the generation of impurity phases can be due to the volatilization of alkali metal ions (K^+/Na^+) in the high-temperature sintering environment (i.e., 1205°C for 4 h) and then the stoichiometric deviation.^{22–24} From the perspective of crystal symmetry, compared with the orthorhombic phase of pure KNN, the tetragonal phase of x Eu-KNNBST is closer to cubic one, benefitting in reducing optical anisotropy and light scattering. Therefore, the optical transmittances of the x Eu-KNNBST ceramics significantly improve.

Figure 3 shows the SEM micrographs of free surfaces of the x Eu-KNNBST ceramics. All the samples have cubical grains although some pores inevitably exist. The columnar maps of grain size distributions are shown in the inset of Fig. 3, giving the average sizes of 137 nm (for $x = 0.25$), 164 nm (for $x = 0.5$) and 180 nm (for $x = 1$). The ceramics own superior homogeneity as the grains of each sample are evenly distributed. Induced by the modification of the doping ions Eu^{3+} , Ba^{2+} , Ti^{4+} , Sr^{2+} , the grain sizes of x Eu-KNNBST are much smaller than pure KNN ceramics ($1\text{--}2\text{ }\mu\text{m}$).¹⁰ The reduction of grains should be attributed to the donor/acceptor doping effect of the ions. According to the XRD analysis that $\text{Eu}^{3+}/\text{Sr}^{2+}/\text{Ba}^{2+}$ may preferentially

Fig. 3. SEM micrographs of the x Eu-KNNBST transparent ceramics, (a) $x = 0.25$, (b) $x = 0.5$ and (c) $x = 1$. The inset of (a), (b) and (c) show the columnar map of the grain size distribution and mean size of the x Eu-KNNBST transparent ceramics.

occupy the site of Na^+ or K^+ (donor doping) and Ti^{4+} probably substitute for the site of Nb^{5+} (acceptor doping), both cation and oxygen vacancies (i.e., K/Na/O vacancies) will be created in the KNN matrix to maintain the charge

Table 1. Densities (ρ), theory densities (TD) and relative densities (RD) of the x Eu-KNNBST transparent ceramics.

Sample	ρ (g/cm ⁻³)	TD (g/cm ⁻³)	RD (%)
$x = 0.25$	4.636	4.832	95.95
$x = 0.5$	4.644	4.831	96.11
$x = 1$	4.659	4.83	96.45

balance. These vacancies are inclined to accumulate at the grain boundaries during grain growth, pinning the movement of grain boundaries and inhibiting the grain growth.^{19,20,25} Consequently, the grain sizes of x Eu-KNNBST ceramics greatly reduce. In addition, appropriate amount of rare earth (RE) oxides can serve as sintering additive to promote grain growth and improve the density of ceramics.^{19,26} As increasing the Eu^{3+} content, the grains marginally become larger (Figs. 3(a)–3(c)) and relative density slightly increases from 95.95% ($x = 0.25$) to 96.45% ($x = 1$) (Table 1). Furthermore, it can be observed that the mean grain size of each sample is far smaller than the wavelength of visible light. Thus, the scattering of the incident light by grain boundary can be effectively reduced, resulting in improving the optical transmittance. To analyze the elements, EDS analysis of the typical sample (x Eu-KNNBST with $x = 0.5$) is shown in

Fig. 4. All the elements (K, Na, Nb, O, Eu, Ba, Sr, Ti) can be observed and homogeneously distributed in the KNN-based matrix (Figs. 4(b) and 4(c)). However, it can be seen that the atomic percentage of K to Nb (K/Nb) is $\sim 37\%$ (Fig. 4(d)) and deviates from the theoretical ratio (i.e., 50%), indicating that the K element has volatilized under high sintering temperature (1205°C). While the atomic percentage of Na to Nb (Na/Nb) is close to 50%, suggesting that the volatilization of Na element is low at 1205°C. Combining with the XRD (Fig. 2) and SEM (Fig. 3) results, it can be concluded that high-optical transmittances of the x Eu-KNNBST ceramics are attributed to fine and uniform grains (< 200 nm), dense structure as well as improved crystal symmetry.

3.3. Ferroelectric properties

In order to investigate the electrical properties of the x Eu-KNNBST ceramics, P-E hysteresis loops were measured at 100 Hz under different electric fields, as shown in Fig. 5. The shapes of P-E loops of the x Eu-KNNBST ceramics are almost saturated. With increasing the electric fields, the maximum polarization (P_{max}) and remanent polarization (P_r) of them gradually increase. Interestingly, as x increases, the dielectric breakdown of the x Eu-KNNBST ceramics increases, from 46 kV/cm for $x = 0.25$ to 107 kV/cm for $x = 1$, which is

Fig. 4. Element analysis of the typical sample x Eu-KNNBST with $x = 0.5$, (a) SEM images, (b) and (c) K, Na, Nb, O, Ti, Sr, Eu, Ba elemental mappings and EDS spectrum, respectively, (d) Na/Nb and K/Nb atomic ratio.

Fig. 5. The P-E curves (100 Hz) of the x Eu-KNNBST transparent ceramics.

mainly related to the densities of the samples (Table 1). The ceramics with higher relative densities possess higher breakdown field strength. The P_r values are $3.18 \mu\text{C}/\text{cm}^2$ (for $x = 0.25$), $3.87 \mu\text{C}/\text{cm}^2$ (for $x = 0.5$) and $6.66 \mu\text{C}/\text{cm}^2$ (for $x = 1$). The above results indicate that the ceramics have moderate ferroelectric properties, which are related to the doping content of Eu^{3+} .

3.4. PL properties

Figure 6 shows the PL excitation (PLE) spectrum monitored at the 592-nm emission and the PL emission spectra excited by 407 nm, taking x Eu-KNNBST with $x = 1$ as the representative example. The excitation spectrum consists of three strong absorptions bands centered at 407 nm, 460 nm and 530 nm, coming from the $^7\text{F}_0 \rightarrow ^5\text{L}_6$, $^7\text{F}_0 \rightarrow ^5\text{D}_2$ and $^7\text{F}_0 \rightarrow ^5\text{D}_1$ transitions of Eu^{3+} , respectively.²⁷ Among them, the blue emission peak at 465 nm is the strongest. Upon the excitation at 407 nm, the emission spectrum exhibits one weak emission band at 578 nm, and two strong ones centered at 592 nm and 615 nm, respectively. According to the energy level scheme of Eu^{3+} (inset of Fig. 6), these emission bands

are mainly from the characteristic $f-f$ transition emissions of Eu^{3+} at 578 ($^5\text{D}_0 \rightarrow ^7\text{F}_0$), 592 ($^5\text{D}_0 \rightarrow ^7\text{F}_1$) and 615 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$).⁶ Figure 7 shows the room temperature PL emission spectra of the x Eu-KNNBST ceramics with different Eu^{3+} concentrations. Three main emission bands with distinct intensities make x Eu-KNNBST emit reddish-orange light. The PL intensity gradually increases with x , indicating more effective energy transfer process at shorter inter-distance between two Eu^{3+} ions as x increases (below the quenching concentration, e.g., $x \leq 0.01$ in x Eu-KNNBST).

3.5. Transmittance modulations by PC reactions

When illuminated by a 300-W xenon lamp (with the wavelengths of 200–1100 nm) for 2 min, the colors of x Eu-KNNBST transparent ceramics become darker and their optical transparencies seem worse (Fig. 8(a)). And after thermal stimulus at 200°C for 10 min, both colors and transparencies can recover to the initial state, exhibiting excellent reversible capacity. The phenomenon is called reversible photochromism, based on vacancy-related defects caused by volatilization of alkali metal ions (i.e., K^+ and Na^+) and ion

Fig. 6. The PLE and PL spectra of 1Eu-KNNBST monitored at 592 nm and 407 nm, the inset is the energy level diagram of Eu^{3+} .

Fig. 7. The PL spectra of the x Eu-KNNBST transparent ceramics with different Eu^{3+} contents.

vacancies (i.e., K/Na/O vacancies) generated by ion doping.^{4,18} These vacancy-related defect levels locate between the conduction band (CB) and valence band (VB) of the x Eu-KNNBST ceramics. Under the illumination of xenon lamp, the electron-hole pairs are captured by the defect levels to form color centers, meanwhile the electron-hole pairs are separated. The presence of color centers increases the probability of light scattering, ultimately darkening the color and reducing the optical transmittance of the x Eu-KNNBST ceramics. After thermal stimulus, the trapped electrons absorb enough energy to detach from the holes (such as O vacancies), resulting in the disappearance of color centers and recovery of ceramic colors. Figure 6(b) shows the optical transmittance spectra before and after the illumination of xenon lamp for 2 min. The observed optical transmittances remarkably decrease ranging from 450 nm to 800 nm after illumination. In order to investigate the PC reaction induced change of T values, the modulation ratio of transmittance

(ΔAbs) is defined as

$$\Delta\text{Abs} = \frac{T_0 - T_1}{T_0} \times 100\%, \quad (1)$$

where T_0 and T_1 are the transmittance before and after illumination. The ΔAbs values at ~ 500 nm are about 26.2% ($x = 0.25$), 18% ($x = 0.5$), 22.8% ($x = 1$), respectively, comparable to that of Er-doped KNLNB transparent ceramics (28.2%).¹⁸

3.6. PL modulations by PC reactions

Figure 9 shows the PL modulation behavior of the typical sample x Eu-KNNBST with $x = 1$. The PL intensity obviously decreases with the extension of time (from 0 s to 140 s). And similar behavior can also be observed in other two samples (i.e., $x = 0.25$ and $x = 0.5$). It can be indicated that the PC behavior not only affects the optical transmittance of sample, but also changes the PL intensity. The mechanism is also related to vacancy-related defects. Upon 407-nm excitation, the luminescence center Eu^{3+} undergoes ground state transition, multi-phonon relaxation and finally radiation transition (i.e., emission). Due to the existence of the defect levels between CB and VB in x Eu-KNNBST, the active electrons of Eu^{3+} during transition are inevitably captured, decreasing the transition efficiency and then the PL intensity. The emission quenching degree (ΔR_t) can be well described by the following equation:

$$\Delta R_t = \frac{R_0 - R_1}{R_0} \times 100\%, \quad (2)$$

where R_0 and R_1 is the emission intensity at 615 nm before and after illumination, respectively. Figure 10 shows the variation of ΔR_t with illumination time for the x Er-KNNBST

(a)

(b)

Fig. 8. Transmittance modulations by PC reactions of the x Eu-KNNBST transparent ceramics. (a) Photographs of the x Eu-KNNBST transparent ceramics under the illumination by xenon lamp (200–1100 nm, 300 W, 2 min) and after the thermal stimulus (200°C, 10 min). (b) The optical transmittance spectra of the x Eu-KNNBST transparent ceramics before and after illumination.

Fig. 9. PL spectral changes of the typical sample $x\text{Eu-KNNBST}$ with $x = 1$ under the illumination by xenon lamp with different times of 10, 30, 60, 90, 120 and 140 s.

Fig. 10. The variation of luminescence quenching degree (ΔR_t) with illumination time for the $x\text{Er-KNNBST}$ transparent ceramics.

transparent ceramics. For the three samples, the ΔR_t values boost sharply from 0 s to 10 s, and then increase steadily until 140 s, suggesting that the illumination-induced PL quenching is dominating at first 10 s and then gradually becomes saturated. This PL quenching process is closely linked to the saturation of color centers. At the beginning of first 10 s illumination, numerous vacancy defects exist and a large number of color centers generate. Correspondingly, the PL intensity decreases rapidly at the first stage. Afterwards, sustained illumination can hardly bring more color centers, leading to the stabilization of PL intensity and saturation of ΔR_t values. At 140 s of illumination time, the 0.5Eu-KNNBST ceramic exhibits the maximum ΔR_t value of $\sim 38\%$, larger than the other two ones ($\sim 20\%$ for $x = 0.25$ and $\sim 32\%$ for $x = 1$). Besides, the PL intensities can also be well restored after the thermal stimulus (200°C , 10 min), similar to the reversible modulation of optical transmittances. The Eu-KNNBST transparent ceramics display outstanding noncontact optical modulations of both transmittance and PL intensity, which have potential in the application of optical sensors and memories.

4. Conclusions

The $x\text{Eu-KNNBST}$ transparent ceramics were synthesized by the solid-state reaction. The phase structures, microstructures, optical transmittances, densities, ferroelectric properties, PL and photochromism were studied. It is found that the modification of Eu^{3+} , Ba^{2+} , Ti^{4+} and Sr^{2+} ions in KNN ceramics can increase the crystal symmetry, reduce the grain size to below 200 nm and improve the densification. As a result, the ceramics can be made into transparent ones, giving the optical transmittances of $\sim 60\%$ at 900 nm. Due to the presence of emission center Eu^{3+} , $x\text{Eu-KNNBST}$ shows good down-conversion PL characteristics under the excitation of 407 nm. The transmittances and PL intensities can be effectively modulated based on the PC behavior. The photochromism is related to vacancy-related defects caused by ion doping and volatilization of alkali metal ions. The multifunctional $x\text{Eu-KNNBST}$ transparent ceramics enable the superposition of both ferroelectric and optical storages, which further enrich the versatility of KNN-based ferroelectric transparent ceramics and broadens their applications in optoelectronic areas.

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