

Preparation and Tunable Luminescence of Eu Doped KNN Ceramics

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Abstract: Rare-earth doped inorganic ferroelectrics are considered as novel photochromic materials, with potential applications for optical switch and information storage ($K_{0.5}Na_{0.5}NbO_3$ (KNN: x Eu) ceramics were prepared by high temperature calcination, with precursor powder obtained by hydrothermal method. Strong red emission at 615 nm was observed which corresponds to the ${}^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} under excitation of 465 nm. Under UV light irradiation for 3 min, the color of the ceramics turned from milky white to dark gray. The colored samples returned to the original color when heated at 200 °C for 10 min, showing strong photochromic behavior. Meanwhile, the luminescence intensity of Eu^{3+} can be tuned without obvious degradation by alternating UV light and heat stimulus. Upon UV light irradiation, large luminescence modulation ratio (ΔR_t) up to 83.9% was achieved for KNN:0.06Eu, indicating good luminescence switching behavior. A possible mechanism for non-radiative energy transfer from the luminescent center to the color center was proposed according to their luminescent behavior.

Key words: $K_{0.5}Na_{0.5}NbO_3$ (KNN); luminescence; photochromism

Photochromic (PC) materials, changing color between the coloring state and bleaching state upon light irradiation, have aroused increasing attention with great potential applications in photo-switching and related optoelectronic devices^[1-4]. Compared with traditional organic PC system, inorganic materials exhibit better thermal stability, higher chemical and fatigue resistance^[5-7]. Some inorganic materials have been reported for their PC behaviors, such as WO_3 , TiO_2 , and V_2O_5 ^[7-9]. However, the luminescence modulations of these materials are extremely poor, which limit their potential application for optical data storage. Recently, rare-earth element doped ferroelectric ceramics, including $K_{0.5}Na_{0.5}NbO_3$ (KNN), $Na_{0.5}Bi_{2.5}Nb_2O_9$ (NBN) and $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ (NBT), have been reported to show good luminescence switching behaviors^[10-11]. Rare earth doped ferroelectrics are capable of combining ferroelectric energy storage and optical memories, which make them fascinating candidates as high density information storage media^[12].

$K_{0.5}Na_{0.5}NbO_3$ (KNN) lead-free piezoelectric ceramics have been considered as the substitute for lead zirconate titanate (PZT) due to the large piezoelectric coefficient (d_{33}) and high Curie temperature (T_C)^[13-14]. Now, KNN:Er³⁺ and KNN:Er³⁺/Yb³⁺ display the upconversion

luminescence modulation performance^[15-17]. With visible light irradiation, the luminescent switching contrast (ΔR_t) up to about 60% is observed in KNN:Sm³⁺ ceramics^[18]. Eu^{3+} doped inorganic materials have also been proved to possess excellent photochromic behavior under UV irradiation, like $Sr_2SnO_4:Eu^{3+}$, $BaMgSiO_4:Eu^{3+}$, $Sr_3SnMO_7:Eu^{3+}$ ^[19-21]. The underlying mechanism may be various from the valence state transition of Eu^{3+} to volatilization-induced photochromism^[19]. Upon to now, photoluminescence and ferroelectric property of KNN:Eu³⁺ have been studied, while its luminescence based on PC reactions has not been reported^[22-23].

In this study, Eu^{3+} doped $K_{0.5}Na_{0.5}NbO_3$ (KNN: x Eu) powder with uniform morphology was fabricated by the hydrothermal method. KNN: x Eu ceramics were obtained by calcining the precursor powder at high temperature. Hydrothermal method displays many merits in regulating the grains size, distribution and lower preparation temperature. Upon UV light irradiation and thermal stimulus, KNN: x Eu ceramics display both photochromic reaction and tunable luminescence behavior with excellent reversibility. High value of ΔR_t (up to 83.9%) is achieved for KNN:0.06Eu. Possible luminescence switching mechanism was also proposed, regarding the energy

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transfer between luminescence center and color center.

1 Experimental

The Eu^{3+} doped $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ (KNN: $x\text{Eu}$) ($x=0, 0.02, 0.04, 0.06, 0.08, 0.10$) precursor powder was prepared by the hydrothermal method. Sodium hydroxide (NaOH), potassium hydroxide (KOH), niobium pentoxide (Nb_2O_5) and europia (III) oxide (Eu_2O_3) served as raw materials. First, KOH and NaOH were weighed according to K^+/Na^+ ratio of 3:1. They dissolved in distilled water to form a solution in which the concentration of OH^- changed from 10 mol/L to 12 mol/L. Thereafter, Nb_2O_5 was added to the above solution and stirred for 30 min. The obtained suspension was placed in a 100-mL reaction kettle up to 70% of the total volume. Then the reaction kettle was sealed in a stainless-steel tank and heated at 200 °C for 12 h. The resulting products were obtained by centrifugation, washing and drying. The synthesized powders were granulated with 6wt% polyvinyl alcohol (PVA) binder, and then pressed into 12 mm disk-shaped pellets. KNN: $x\text{Eu}$ ceramics were prepared by calcination at 1140 °C for 4 h.

The crystal structure was characterized by powder X-ray diffraction (D/max-2400, Rigaku, Japan) using a $\text{Cu K}\alpha$ radiation. The microstructures of the ceramics were analyzed by scanning electron microscopy (S-4800, Hitachi, Japan). The UV-VIS-NIR spectrophotometer (Cary 5000, Agilent) were used to test the diffuse reflectance spectra. The coloration of the ceramics was carried out under the UV-light ($\lambda < 400$ nm) output of a 300 W Xe lamp (PLS-SXE300, Beijing Zhongjiaojinyuan Technology Co. Ltd). The luminescence spectra and luminescence quenching behavior (at 300, 350, 390, 407 and 450 nm) were characterized by a fluorescence spectrophotometer (F-7000, Hitachi, Japan).

2 Results and discussion

Fig. 1(a) shows the XRD patterns of the KNN precursor powder synthesized at 200 °C for 12 h ($\text{K}^+/\text{Na}^+=3:1$) with $[\text{OH}^-]$ concentration from 10 mol/L to 12 mol/L. When $[\text{OH}^-]$ was 10 mol/L, small amount of NaNbO_3 was observed in the sample, except for the main perovskite phase of KNN (PDF #77-0038). With the increase of $[\text{OH}^-]$ from 11 mol/L to 12 mol/L, the NaNbO_3 phase gradually disappeared. This result indicates that slight increase of $[\text{OH}^-]$ concentration can speed up the reaction process and facilitate the formation of pure KNN phase. Fig. 1(b) shows XRD patterns of the KNN: $x\text{Eu}$ ($x=0.02, 0.04, 0.06, 0.08, 0.10$) powders obtained by the hydrothermal method. Pure KNN phase has

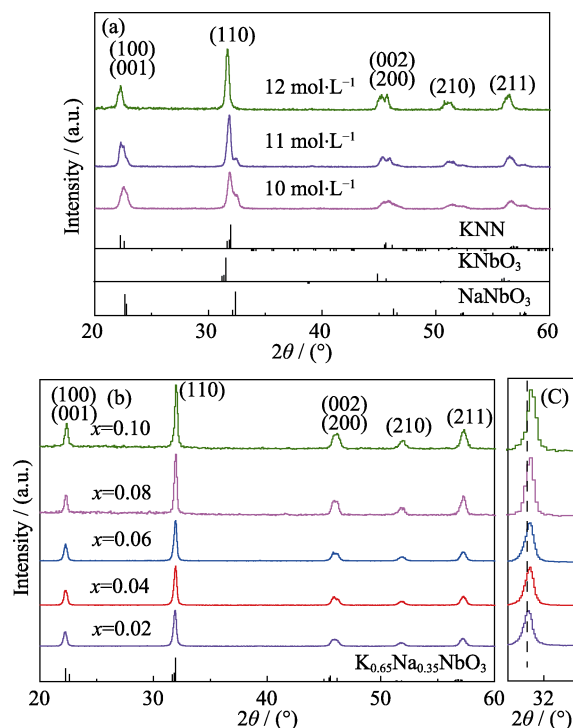


Fig. 1 XRD patterns of the precursor powders synthesized at 200 °C for 12 h ($\text{K}^+/\text{Na}^+=3:1$) with different $[\text{OH}^-]$ concentrations (a), XRD patterns of KNN: $x\text{Eu}$ ($x=0.02, 0.04, 0.06, 0.08, 0.10$) powders synthesized at 200 °C for 12 h ($\text{K}^+/\text{Na}^+=3:1$, $[\text{OH}^-]=11$ mol/L) (b) and zoomed XRD patterns from (b) within 30°–33° (c)

been obtained with $[\text{OH}^-]$ of 11 mol/L, indicating that Eu^{3+} is helpful for the formation of pure KNN phase. In Fig. 1(c), with increasing Eu^{3+} concentration, (110) diffraction peak moves slightly to a higher angle, suggesting that Eu^{3+} has partly replaced K^+ and Na^+ of the KNN matrix. The ion radius of Eu^{3+} (0.112 nm) is smaller than those of Na^+ (0.139 nm) and K^+ (0.164 nm), resulting in the shrink of the crystal lattice^[22].

Fig. 2 displays the surface morphology of the KNN:0.06Eu ceramics calcined at 1140 °C. Regular grains with cubic shape are well crystallized, with average size of about 0.3 μm . This grain size is very similar

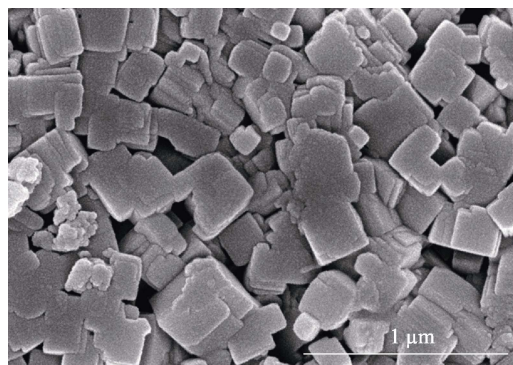


Fig. 2 SEM image of KNN:0.06Eu ceramics synthesized at 1140 °C for 4 h

to those of hot-press sintered KNN ceramics and solid-state sintered KNN:Er ceramics^[15, 24]. Rare earth (like Er³⁺ and Eu³⁺) may inhibit the grain growth of KNN ceramics^[15]. According to the EDS analysis, the molar ratio of K⁺ and Na⁺ of the ceramics is almost 0.78, which is different from the initial composition. The radius of K⁺ (0.164 nm) is much bigger than that of Na⁺ (0.139 nm), so it is much more difficult for K⁺ to diffuse into the crystal lattice^[25].

Fig. 3(a) shows the photoluminescence excitation (PLE) spectra of the KNN:0.06 ceramic and photoluminescence (PL) spectra of KNN:*x*Eu ceramics. The PLE spectrum monitored at 618 nm reveals three characteristic absorption peaks, wherein the band at 395 nm corresponding to the ⁷F₀→⁵L₆ transition, the 465 nm band corresponding to the ⁷F₀→⁵D₂ and the 526 nm band corresponding to the ⁷F₀→⁵D₁. The emission spectra excited at 465 nm of KNN:*x*Eu ceramics consists of a group of intense and sharp characteristic lines ranging within 570–750 nm, which mainly result from the characteristic f-f transition from the excited states ⁵D₀ to the ground state ⁷F_{*J*} (*J*=0–4) of Eu³⁺ ions^[23]. The strongest red emission at 615 nm comes from the ⁵D₀→⁷F₂ of Eu³⁺. The positions of emission peak and line shape of the emission spectra maintain the same, but the emission intensity of Eu³⁺ is a function of its doping concentration. With the increase of

Eu³⁺ concentration, the red emission intensity gradually increased and reached maximum when *x*=0.08. The intensity decreases gradually beyond this critical concentration.

The dynamic decay curves on Eu³⁺ concentrations for KNN:Eu ceramics under 465 nm excitation are shown in Fig. 3(b). The lifetimes are well fitted by using second-order exponential as follows:

$$I(t)=I_0+A_1\exp(-t/\tau_1)+A_2\exp(-t/\tau_2) \quad (1)$$

Where *I*₀ is the emission intensity at *t*₀, *A*₁ and *A*₂ are constant, τ_1 and τ_2 are the lifetimes of the exponential component.

$$\tau=(A_1\tau_1^2+A_2\tau_2^2)/(A_1\tau_1+A_2\tau_2) \quad (2)$$

With Eu³⁺ concentration increasing, the average lifetime gradually increases and reaches maximum when *x*=0.08, which is mainly related to the radiative energy transfer between Eu³⁺ neighbor ions. With Eu³⁺ concentration further increasing, the ion distance between Eu³⁺-Eu³⁺ becomes shorter, possibly resulting in the decrease of average lifetime^[26-27].

Fig. 4 shows the reflectance spectra and photochromic reaction of KNN:*x*Eu ceramics under UV irradiation and thermal stimulus. Fig. 4(a) gives the reflection spectra of KNN:0.06Eu ceramic irradiated under UV light for different time (0 s to 3 min). The reflection intensity decreases significantly in the region 400–750 nm with increasing irradiation time, indicating that the irradiated sample absorbs part of the visible light. The absorption ratio can be evaluated by comparing the difference of the reflective intensity before (RE₁) and after (RE₂) irradiation using the formula: $\Delta\text{abs} = \text{RE}_1 - \text{RE}_2$ (%)^[28]. Fig. 4(b) shows that KNN:0.06Eu has a broad absorption from 400 nm to 750 nm, with the absorption maximum at about 566 nm. In the inset of Fig. 4(b), upon UV light irradiation for 3 min, the color of the sample turns from milky white to gray as a colored sample. The colored sample recovered its initial stage when heated at 200 °C for 10 min (marked as Δ). In Fig. 4(c), KNN:0.06Eu ceramic shows the best photochromic behavior, which is indicated by the change of Δabs (at 566 nm) with Eu³⁺ concentration. KNN:0.06Eu ceramic is treated repeatedly with UV light irradiation (3 min) and thermal stimulus (200 °C for 10 min). As seen in Fig. 4(d), the reflectance intensity at 566 nm shows no obvious degradation for 10 cycles, showing good fatigue resistance of the color switching.

The photoluminescence spectra of KNN:0.06Eu ceramics before and after UV irradiation for 3 min are shown in Fig. 5(a). Upon UV light irradiation, the luminescence intensity decreases significantly, showing strong luminescence quenching effect. The quenching behavior may be explained by the parameter ΔR_t (luminescence

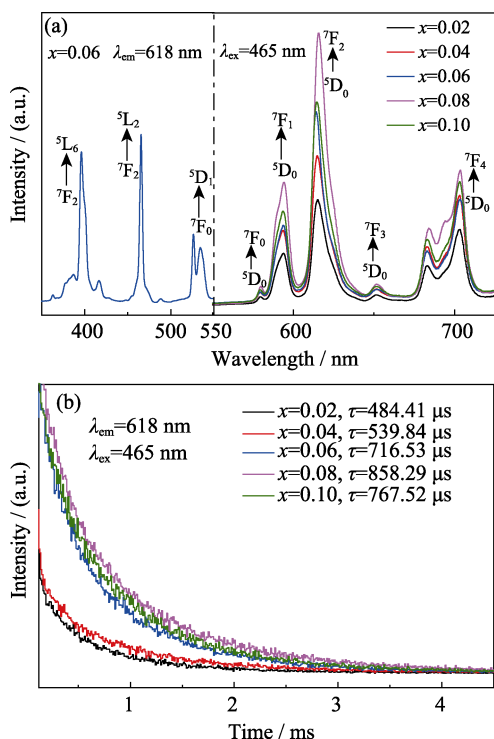


Fig. 3 Excitation ($\lambda_{\text{em}}=618$ nm) spectra of the KNN:0.06Eu ceramics and emission ($\lambda_{\text{ex}}=465$ nm) spectra of KNN:*x*Eu ceramics at room temperature (a) and the dynamic decay curves on Eu³⁺ concentrations for KNN:Eu samples under 465 nm excitation (b)

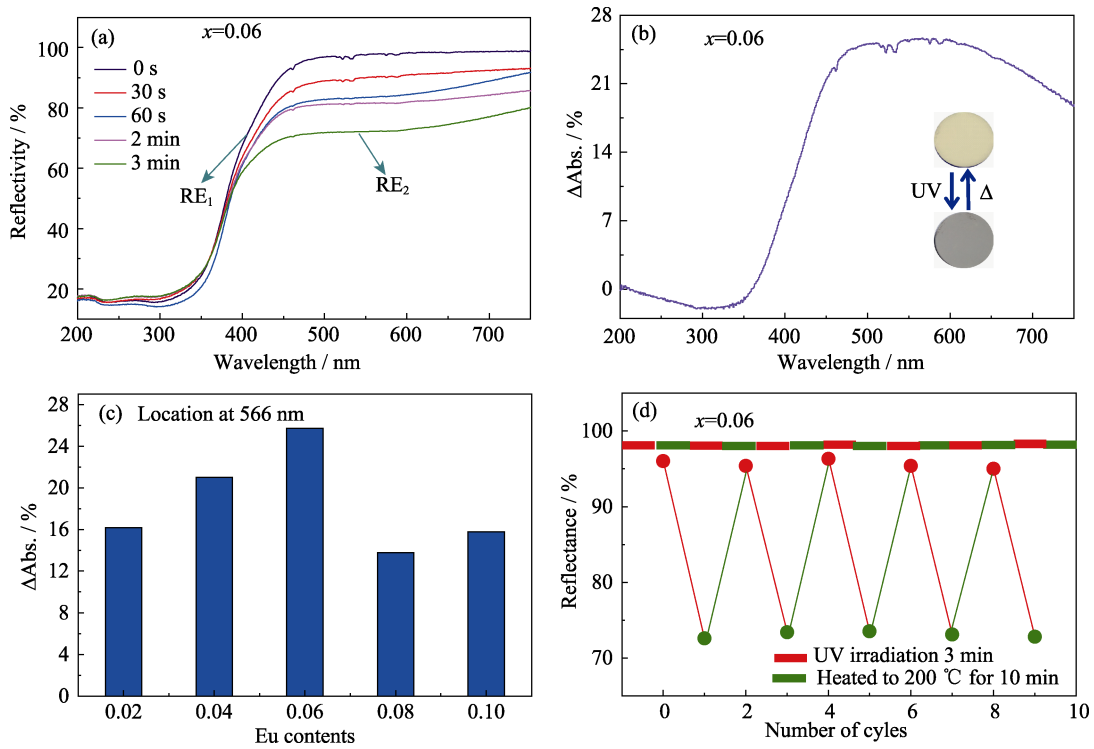


Fig. 4 Reflectance spectra for the KNN:0.06Eu by UV light irradiation (0 s, 30 s, 60 s, 2 and 3 min) (a), difference absorption (Δ abs) spectra for the KNN:0.06Eu by UV irradiation 3 min with inset showing photographs of color changes of ceramic before and after UV irradiation (b), the Δ abs vs Eu concentration (c) and reflectance intensity changes (d) of KNN:0.06Eu by alternating UV irradiation and heat treatment

modulation ratio) using the equation: $\Delta R_t = (R_0 - R_t) / R_0 \times 100$ (%), where R_0 and R_t are the luminescence intensity before and after light irradiation, respectively^[10,15]. Fig. 5(b) shows the change of ΔR_t at 615 nm as a function of Eu concentration. Upon UV light irradiation for 3 min, the emission intensities of all samples decreased significantly. The calculated ΔR_t values of the KNN: x Eu samples are 34.2% ($x=0.02$), 47.6% ($x=0.04$), 83.9% ($x=0.06$), 46.4% ($x=0.08$) and 48.3% ($x=0.10$), respectively. The maximum ΔR_t value (83.9%) is achieved for KNN:0.06Eu³⁺, which is comparably high among rare earth doped KNN ferroelectrics.

Furthermore, KNN:0.06Eu ceramic was subjected to

alternating UV light irradiation (3 min) and the thermal stimulus (200 °C for 10 min) for 7 cycles. For each cycle, the PL spectra were recorded immediately after UV light irradiation and the thermal stimulus. Accordingly, ΔR_t at 615 nm was calculated and the result was shown in Fig. 5(c). The decreased emission intensity after UV irradiation is able to almost recover its initial state upon heating treatment. ΔR_t has no obvious degradation for at least 7 cycles, illustrating good reversibility of the luminescence switching.

In order to further investigate the effect of irradiation wavelength on the tunability of luminescence, the emission spectra of KNN:0.06Eu ceramic ($\lambda_{ex}=465$ nm) under

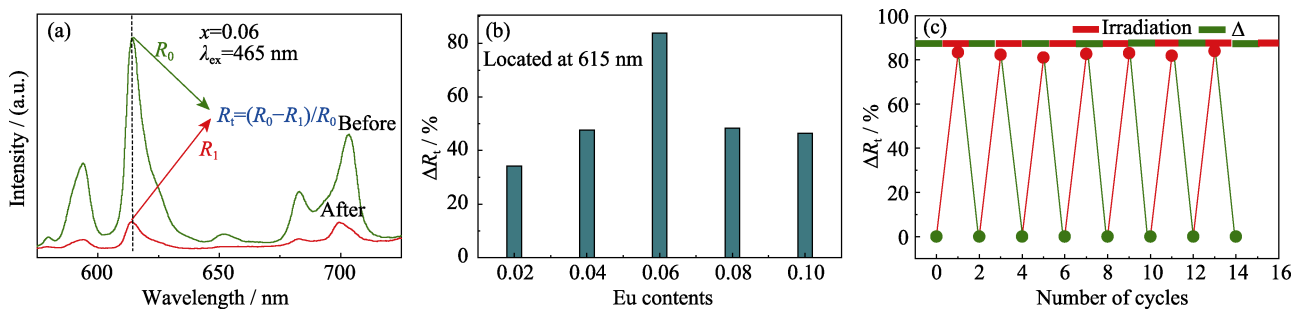


Fig. 5 Changes of emission spectra ($\lambda_{ex}=465$ nm) of KNN:0.06 Eu ceramics before and after UV irradiation for 3 min (a), luminescence switching ratio (ΔR_t) at 615 nm as a function of Eu concentration (b) and ΔR_t of KNN:0.06Eu ceramics by alternating UV light irradiation and thermal stimulus for 7 cycles (c)

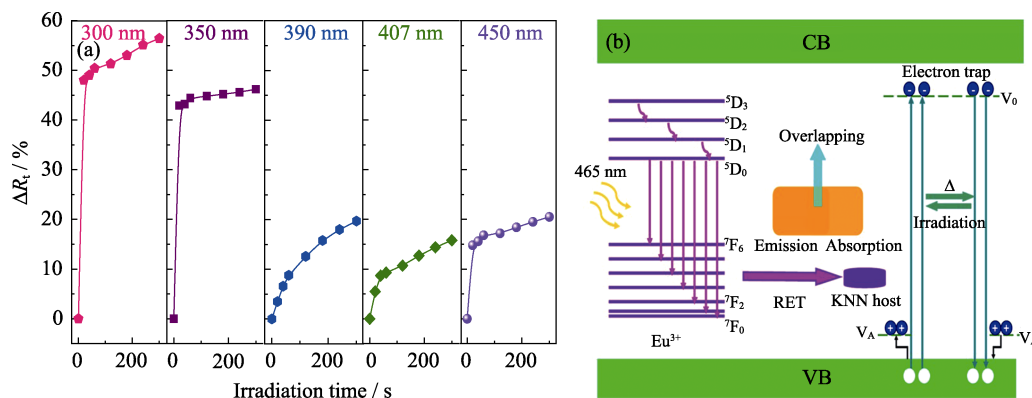


Fig. 6 Luminescence modulation ratio (ΔR_t) as a function of irradiation time under different irradiation wavelengths (a) and schematic diagram of luminescence modulation upon photochromic reactions for KNN: x Eu ceramics (V_O is oxygen vacancy, and V_A is K and Na vacancy) (b)

different wavelength irradiation (300, 350, 390, 407 and 450 nm) were measured, as shown in Fig. 6(a). For this experiment, a xenon lamp equipped with an F-7000 spectrometer acted as the irradiation light source. In Fig. 6(a), with irradiation time (20 s, 40 s, 1 min, 2 min, 3 min and 4 min) increasing, ΔR_t of the KNN:0.06Eu gradually increases. ΔR_t decreases dramatically with increasing irradiation wavelength, and the largest ΔR_t is obtained with irradiation wavelength of 300 nm. This result verifies that the luminescence of KNN:0.06Eu can be effectively tuned by UV light irradiation. There are some reports of Eu based photochromic materials which is also effectively excited by UV light, like $\text{Sr}_2\text{SnO}_4\text{:Eu}^{3+}$, $\text{BaMgSiO}_4\text{:Eu}^{3+}$, $\text{Sr}_3\text{SnMO}_7\text{:Eu}^{3+}$, although the origins of PC processes may be varied^[19-21].

Fig. 6(b) illustrates the possible mechanism of luminescence switching based on PC reactions. It may be explained by the free or trapped charge carrier and resonance energy transfer (RET) mechanism, which bases on the overlap of the emission band of Eu^{3+} ions and the absorption bands of photochromic KNN ceramics^[29-30]. Due to many vacancy-related defects in KNN host, additional defect energy levels form within the forbidden gap of KNN. Upon UV light illumination, the electrons from the valence band (Ev) are excited to higher energy level (defect level), and are trapped by the oxygen vacancies (V_O)^[10,15]. The excited holes are also trapped by the K and Na vacancies (V_A). Both of these defects are color centers which have a broad absorption band in the range from 400 to 700 nm (Fig. 4). The emission positions of Eu^{3+} overlaps with the absorption band range of these color centers (Fig. 3, 4 and 5). When Eu^{3+} is excited, the emission can be effectively absorbed by the color centers through the resonance energy transfer, resulting in the significant decrease of the Eu^{3+} luminescence intensity^[19]. When the ceramic is heated to 200 °C for 10 min, the

colored sample fade back into their original color state. Meanwhile, electrons can be released from the traps and the color centers disappears. Correspondingly, the emission intensities of Eu^{3+} are also recovered.

The luminescence mechanism of KNN: x Eu is similar with that of $\text{Sr}_3\text{SnMO}_7\text{:Eu}$ which is also irradiated by UV (254 nm) light^[19]. Other KNN based ceramics, like KNN:Er, KNN:Er/Yb, KNN:Ho/Yb and KNN:Sm, have been reported to show photochromic and luminescence switching behavior by visible light (407 nm) illumination^[16-18]. Furthermore, the emission intensity reached maximum for KNN:0.08Eu, while the largest luminescence switching ratio is achieved for KNN:0.06Eu. The luminescence switching ratio mainly relates to the energy transfer between luminescence centers and color centers. And the color centers relates to the traps or defects within the host lattice. The unique feature of KNN: x Eu is possibly caused by the varied trap depths or distributions of defects within this system, which will be systematically studied in the future.

3 Conclusions

Eu doped $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ (KNN: x Eu) precursor powders were hydrothermally synthesized at 200 °C for 12 h ($\text{K}^+/\text{Na}^+=3:1$, $[\text{OH}^-]=11$ mol/L). The phase-pure perovskite KNN: x Eu ceramics exhibit homogeneous morphology when calcined at 1140 °C for 4 h. KNN: x Eu ceramics show remarkable photochromic and luminescence switching behavior. Upon UV light irradiation, the sample colors change from the initial milky white to dark gray. By alternating UV irradiation and thermal stimulus, the luminescence modulation ratio (ΔR_t) of KNN:0.06Eu reach high values of 83.9%. These results indicate that KNN: x Eu system is a potential candidate for novel photo-electronic device.

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Eu 掺杂 KNN 陶瓷的制备及可调性发光研究

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摘要: 稀土离子掺杂铁电陶瓷是一类新型光致变色材料, 在光开关、光信息存储等领域具有潜在应用价值。本研究采用水热法制备了 $(K_{0.5}Na_{0.5})_{1-x}Eu_xNbO_3(KNN:xEu)$ 前驱体粉体, 随后利用高温烧结得到对应陶瓷样品。在 465 nm 激发下, 观察到 615 nm 处有强的红色发光, 对应于 Eu^{3+} 的 ${}^5D_0 \rightarrow {}^7F_2$ 跃迁。通过紫外光照射, KNN:Eu 陶瓷从乳白色变为深灰色。随后经过 200 °C 加热 10 min, 着色陶瓷又变回到初始颜色, 显示出良好的光致变色行为。紫外照射和反复加热循环可以有效调控该陶瓷的发光强度。且经过多次循环之后, 发光强度没有明显衰减。在紫外光照射下, KNN:0.06Eu 陶瓷发光强度的可调比(ΔR_I)高达 83.9%, 说明发光具有良好的可调性。进而结合发光中心和色心之间的能量转移, 对 KNN:Eu 陶瓷的光致变色和发光机理进行了解释。

关键词: $K_{0.5}Na_{0.5}NbO_3(KNN)$; 发光; 光致变色

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