

Luminescent properties of a novel reddish-orange phosphor Eu-activated KLaSiO₄

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A novel reddish-orange emitting phosphor Eu-activated KLaSiO₄ was synthesized by the conventional solid-state reaction at 1200 °C. The luminescence properties of KLaSiO₄:Eu phosphor were investigated, and the critical concentration of the activator ion (Eu³⁺) was established as 0.02 mol per formula unit. Chromaticity coordinates of a typical KLa_{0.98}SiO₄:0.02Eu phosphor were $x = 0.614$ and $y = 0.385$. The phosphor exhibited reddish-orange luminescence with dominating emission at 612 nm, corresponding to ⁵D₀ → ⁷F₂ of Eu³⁺. Furthermore, the phosphor was characterized by excellent thermal stability, implying its potential use in white light emitting diodes.

Keywords: *potassium lanthanum silicate; luminescence; reddish-orange phosphors; Eu³⁺*

1. Introduction

Rare earth ions have become good candidates for luminescent centers due to their special 4f intra-shell transitions [1]. In particular, europium ion has been considered as one of the promising species that provide optical devices in red or orange color regions and is widely used as a luminescent activator for a considerable number of phosphors [2–9]. Silicates are usually used as a phosphor matrix [2, 10–12], because of their stable crystal structure and high thermal stability [12].

Potassium lanthanum silicate (KLaSiO₄) is a very useful compound owing to its simple preparation conditions and excellent chemical stability [13]. In addition, the electric charge and ionic radius of lanthanum ion is similar to that of many rare earth ions, which makes it often to be the lattice substitution position by rare-earth ions. However, to the best of our knowledge, there is no report on the research on KLaSiO₄ phosphor activated by rare earth or transition metals.

In this work, a novel luminescent material KLaSiO₄:Eu was synthesized; its luminescence properties and Eu concentration dependence of emission properties were investigated.

2. Material and methods

The starting materials K₂CO₃ (AR), La₂O₃ (AR), Eu₂O₃ (AR) and SiO₂ (AR), were weighted according to the nominal composition of KLa_{1-x}SiO₄:xEu ($x = 0, 0.005, 0.01, 0.015, 0.02, 0.025, 0.03, \text{ and } 0.035$). Then, the compounds were blended in an agate mortar and sintered in an alumina crucible by conventional solid state reaction at 1200 °C for 2 h in air followed by an additional grinding.

The crystal structure as well as the phase purity of the as-prepared phosphors were identified by recording the powder X-ray diffraction (XRD) patterns using X'Pert PRO X-ray diffractometer with CuKα₁ radiation ($\lambda = 1.54056 \text{ \AA}$) at 40 kV and 30 mA. The XRD patterns were collected in the range of $20^\circ \leq 2\theta \leq 50^\circ$ (which is consistent with the PDF card of KLaSiO₄). Excitation and emission spectra as well as decay curves were measured by using Hitachi F-7000 spectrofluorometer with a 150 W xenon lamp as the excitation source. The chromaticity data were taken by using the PMS-50 spectra analysis system.

3. Results and discussion

The XRD patterns of undoped host lattice KLaSiO₄ (a) and KLa_{0.98}SiO₄:0.02Eu (b) are

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presented in Fig. 1. The peaks in all of these patterns are in excellent agreement with the pattern of potassium lanthanum silicate (KLaSiO₄) registered in the Joint Committee on Powder Diffraction Standards Card (JCPDS Card No. 49-0661) in terms of diffraction angle and intensity. Almost no characteristic peaks of impurities are observed from the two samples. There is no identifiable difference in diffraction peaks. Also no notable shift in the diffraction lines of the KLa_{0.98}SiO₄:0.02Eu and KLaSiO₄ powders is observed, indicating that no significant structural changes occurred by substituting La³⁺ with Eu³⁺ due to the same electric charge and similar ionic radii of Eu³⁺ (0.113 nm) [14] and La³⁺ (0.122 nm) [15]. In addition, the Eu³⁺ doping concentration investigated in this work is less than the interstitial position doping concentration of Eu³⁺ in KLaSiO₄ lattice.

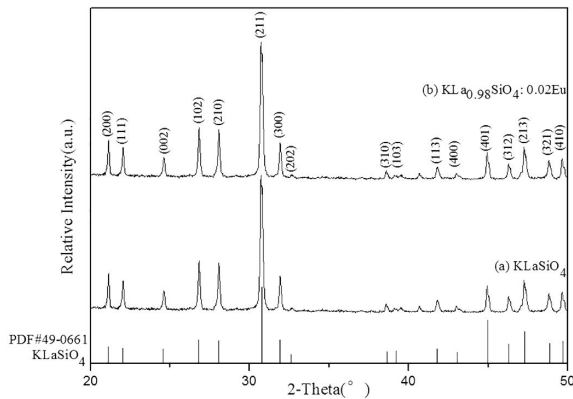


Fig. 1. X-ray diffraction patterns of KLaSiO₄ and KLa_{0.98}SiO₄:0.02Eu phosphor.

The excitation spectrum (a) and emission spectra (b) of a typical KLa_{0.98}SiO₄:0.02Eu sample are shown in Fig. 2.

The excitation spectrum (Fig. 2a) clearly indicates a broad absorption from 210 nm to 330 nm (with the maximum at 280 nm) and several excitation bands located at 362 nm ($^7F_0 \rightarrow ^5D_4$) [2, 3], 381 nm ($^7F_0 \rightarrow ^5L_7$) [4], 393 nm ($^7F_0 \rightarrow ^5L_6$) [2], 411 nm ($^7F_1 \rightarrow ^5D_3$) [5] and 463 nm ($^7F_0 \rightarrow ^5D_2$) [3], respectively. The broad excitation peak from 210 nm to 330 nm can be attributed to charge-transfer transition from negative ion (2p⁶) to the 4f⁷ state of Eu³⁺ ion (ligand-to-metal charge-transfer

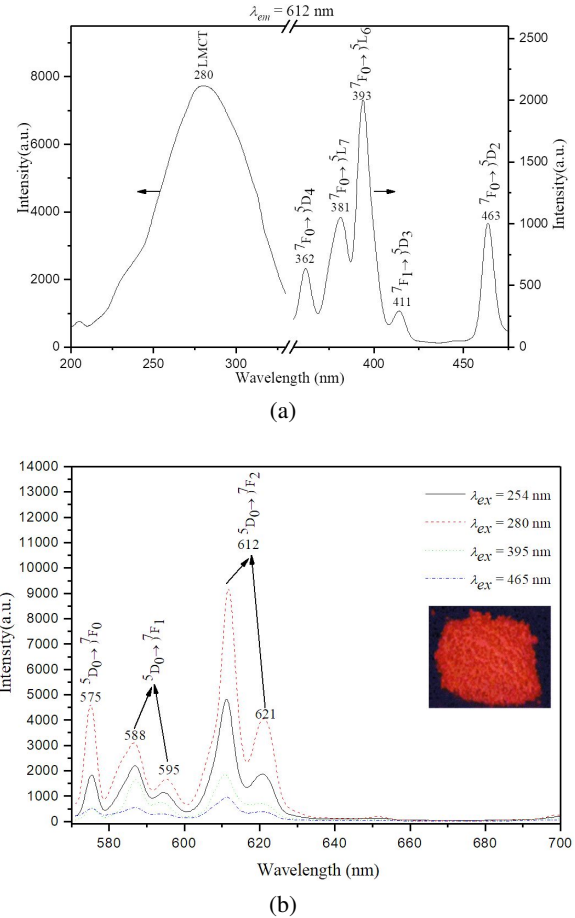


Fig. 2. Excitation and emission spectra of KLa_{0.98}SiO₄:0.02Eu phosphor: (a) excitation spectrum and (b) emission spectra.

(LMCT)) [3]. This phosphor can be excited at different wavelengths due to its broad excitation range of 210 nm to 330 nm, and its considerable emission intensity under 280 nm excitation along with the small excitation bands at 254 nm, 395 nm and 465 nm, which makes it very attractive for such applications as phosphor-liquid crystal displays [16] and white lighting devices utilizing GaN-based excitation in the near UV [17]. The emission spectra of KLa_{0.98}SiO₄:0.02Eu phosphor under 254 nm, 280 nm, 395 nm and 465 nm excitation (Fig. 2b) show roughly the same position of emission peaks, except for the intensity. The emission intensity corresponding to the 254 nm, 395 nm and 465 nm excitation is remarkably lower than that of 280 nm because of the remarkably lower absorption at these

wavelengths (Fig. 2a). The dominant peak in the emission spectrum is near 612 nm, which is assigned to the $^5D_0 \rightarrow ^7F_2$ transition [6] of Eu^{3+} . Emission bands at about 575 nm, 588 nm, 595 nm and 621 nm are assigned to transitions of $^5D_0 \rightarrow ^7F_0$ [3], $^5D_0 \rightarrow ^7F_1$ [7], $^5D_0 \rightarrow ^7F_1$ [4] and $^5D_0 \rightarrow ^7F_2$ [8], respectively. It is clearly seen that the transition $^5D_0 \rightarrow ^7F_1$ splits into two peaks at 588 nm and 595 nm, the transition $^5D_0 \rightarrow ^7F_2$ also splits into the peaks at 612 nm and 621 nm.

Normally, the luminescence properties of phosphor are known to be strongly affected by the concentration of the activator. The change in emission intensity of $\text{KLa}_{1-x}\text{SiO}_4:\text{xEu}$ as a function of Eu concentration ($x = 0.005, 0.01, 0.015, 0.02, 0.025, 0.03, 0.035$) under excitation of 280 nm is shown in Fig. 3. The highest integrated emission intensity is noted at the Eu^{3+} concentration of $x = 0.02$, which is taken as the critical concentration. Lower doping concentration as well as excessive doping lead to weak luminescence and concentration quenching of the Eu^{3+} emission, respectively. The decrease in emission efficiency at Eu^{3+} higher than 0.02 could be attributed to concentration quenching that usually occurs as a result of the nonradiative energy transfer among luminescent centers before being emitted. With increasing of Eu^{3+} concentration, the distance between two neighboring Eu^{3+} ions becomes short, and thus the probability of energy transfer increases. The critical concentration corresponds to a sufficient reduction in the average distance.

In general, the color of phosphor is represented by color coordinates. The $\text{KLa}_{0.98}\text{SiO}_4:0.02\text{Eu}$ phosphor has been found to have chromaticity coordinates of $x = 0.614$ and $y = 0.385$, which is shown in Fig. 4 and can be depicted by reddish orange.

Fig. 5 shows the $^5D_0 \rightarrow ^7F_2$ emission intensity changes of $\text{KLa}_{0.98}\text{SiO}_4:0.02\text{Eu}$ with the raising of temperature. When the temperature increased to 80 °C, the emission intensity of $\text{KLa}_{0.98}\text{SiO}_4:0.02\text{Eu}$ only dropped to 88.5 %. When the temperature increased to 120 °C, the emission intensity of $\text{KLa}_{0.98}\text{SiO}_4:0.02\text{Eu}$ still remained 78.5 %, indicating that the $\text{KLa}_{0.98}\text{SiO}_4:0.02\text{Eu}$ phosphor has a very good

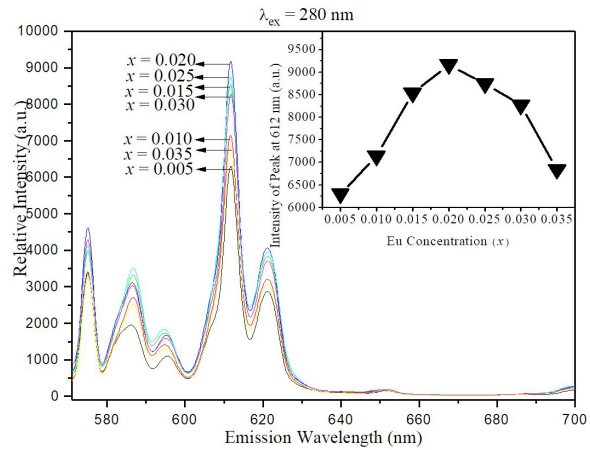


Fig. 3. Emission spectra of $\text{KLa}_{1-x}\text{SiO}_4:\text{xEu}$ phosphors ($x = 0.005, 0.01, 0.015, 0.02, 0.025, 0.03, 0.035$).

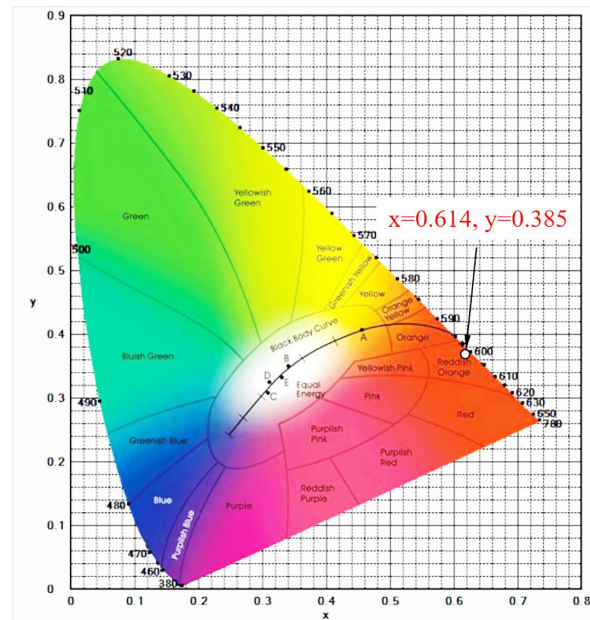


Fig. 4. CIE chromaticity coordinates of $\text{KLa}_{0.98}\text{SiO}_4:0.02\text{Eu}$ phosphor.

thermal stability compared with the commercial $\text{Y}_2\text{O}_3\text{S}:\text{Eu}^{3+}$ phosphor. Because of these advantages, $\text{KLa}_{0.98}\text{SiO}_4:0.02\text{Eu}$ phosphor could be a potential candidate for tricolor white LEDs.

Fig. 6 shows the emission decay curves of $\text{KLa}_{1-x}\text{SiO}_4:\text{xEu}$ ($x = 0.015, 0.02$ and 0.025) (monitored at 612 nm) upon 393 nm excitation. These decay curves can be well fitted into

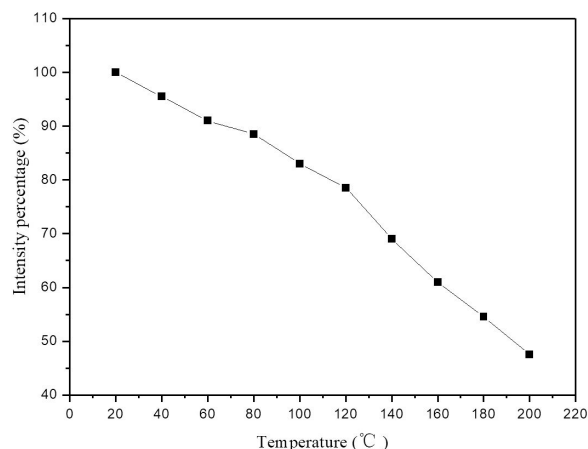


Fig. 5. The $^5D_0 \rightarrow ^7F_2$ emission intensity of Eu^{3+} in $\text{KLa}_{0.98}\text{SiO}_4:0.02\text{Eu}$ with raising temperature.

a single exponential function as $I = I_0 \exp(-t/\tau)$ (here I_0 is the initial emission intensity at $t = 0$ and τ is the decay constant of the emission center). The decay constants were obtained to be 0.82 ms, 0.78 ms, and 0.63 ms for $x = 0.015$, 0.02 and 0.025, respectively. Obviously, the decay time gets shorter and shorter with the increasing of Eu^{3+} concentration, as shown in the inset of Fig. 6. Such decline of $\text{Eu}^{3+}5D_0 \rightarrow ^7F_2$ state is due to the energy migration or interaction between Eu^{3+} ions. It is indicated that the Eu^{3+} ion in KLaSiO_4 host has a fast decay time.

4. Conclusions

In the present work, the novel $\text{KLa}_{1-x}\text{SiO}_4:x\text{Eu}$ phosphors were synthesized by the conventional solid-state reaction at 1200 °C for 2 h. The optimized phosphor with the composition of $\text{KLa}_{0.98}\text{SiO}_4:0.02\text{Eu}$ presents the broad absorption from 210 nm to 330 nm, and exhibits very good luminescence properties. The chromaticity coordinates of a typical sample $\text{KLa}_{0.98}\text{SiO}_4:0.02\text{Eu}$ phosphor have been found to be $x = 0.614$ and $y = 0.385$.

Acknowledgements

Thanks are due to Professor R.J. Zeng and Doctor Y.B. Chen of Xiamen University. This research is partially supported by National Natural Science Foundation of China (No. 51162013, 51362014), Major Discipline Academic

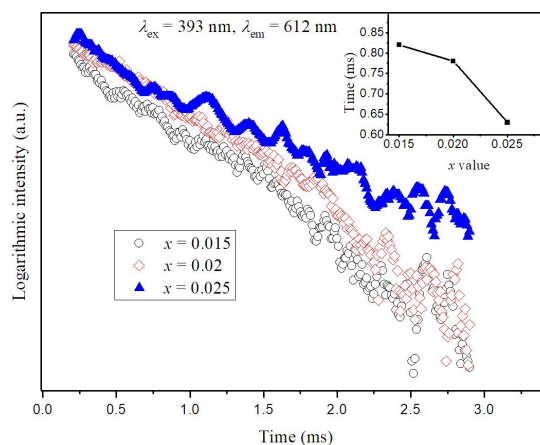


Fig. 6. Decay curves of $^5D_0 \rightarrow ^7F_2$ of Eu^{3+} in $\text{KLa}_{1-x}\text{SiO}_4:x\text{Eu}$ with different Eu^{3+} concentrations ($x = 0.015$, 0.02 and 0.025) ($\lambda_{\text{ex}} = 393$ nm, $\lambda_{\text{em}} = 613$ nm). The inset curve is the dependence of decay time on Eu^{3+} concentration.

and Technical Leader Training Plan Project of Jiangxi Province (No. 20113BCB22009), and Science and Technology Supporting Plan Project of Jiangxi Province (NO. 20111BBE50018), and post-doctoral researchers preferred funded projects of Jiangxi Province (No. 2013KY34), and Scientific Youth Project of Jiangxi Provincial Education Department (GJJ150892).

References

- [1] BLASSE G., GRABMAIER B.C., *Luminescent Materials*, 2nd Ed., Springer, Berlin, 1994.
- [2] FENG G., JIANG W.H., CHEN Y.B., ZENG R.J., *Mater. Lett.*, 65 (2011), 110.
- [3] FU J., *Electrochem. Solid State*, 3 (2000), 350.
- [4] SHIMOMURA Y., KIJIMA N., *Electrochem. Solid State*, 7 (2004), H1.
- [5] ZHANG J., WANG Y., *Electrochem. Solid State*, 13 (2010), J35.
- [6] KUANG J., LIU Y., YUAN D., *Electrochem. Solid State*, 8 (2005), H72.
- [7] XIN S., WANG Y., WANG Z., ZHANG F., WEN Y., ZHU G., *Electrochem. Solid State*, 14 (2011), H438.
- [8] SHIMOMURA Y., KIJIMA N., *Electrochem. Solid State*, 7 (2004), H18.
- [9] OH J.R., PARK H.K., DO Y.R., *Electrochem. Solid State*, 12 (2009), J58.
- [10] HAN L., WANG Y., ZHANG H., ZHANG J., *Electrochem. Solid State*, 14 (2011), J73.
- [11] PARK J.K., CHOI K.J., KANG H.G., KIM J.M., KIM C.H., *Electrochem. Solid State*, 10 (2007), J15.
- [12] KIM J.S., PARK Y.H., CHOI J.C., PARK H.L., *Electrochem. Solid State*, 8 (2005), H65.

- [13] AUNG Y.L., NAKAYAMA S., SAKAMOTO M., *J. Mater. Sci.*, 40 (2005), 129.
- [14] FANG T.H., HSIAO Y.J., CHANG Y.S., CHANG Y.H., *Mater. Chem. Phys.*, 100 (2006), 418.
- [15] WANG N., CHEN W., ZHANG Q.F., DAI Y., *Mater. Lett.*, 62 (2008), 109.
- [16] VECHT A., NEWPORT A.C., BAYLEY P.A., CROSSLAND W.A., *J. Appl. Phys.*, 84 (1998), 3827.
- [17] NEERAJ S., KIJIMA N., CHEETHAM A.K., *Chem. Phys. Lett.*, 387 (2004), 2.

Received 2019-01-16
Accepted 2019-02-11