



A novel red phosphor $\text{NaLa}_4(\text{SiO}_4)_3\text{F}:\text{Eu}^{3+}$

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ABSTRACT

A novel red phosphor $\text{NaLa}_4(\text{SiO}_4)_3\text{F}:\text{Eu}^{3+}$ was synthesized by the conventional solid-state reaction at 950 °C for the first time. The luminescence properties of $\text{NaLa}_4(\text{SiO}_4)_3\text{F}:\text{Eu}^{3+}$ were investigated, and the critical concentration of the activator concentration (Eu^{3+}) was found to be 0.1 mol per formula unit. The phosphor presented red luminescence under the ultraviolet excitation of 254 or 395 nm, attributed to the transitions from $^5\text{D}_0$ excited states to $^7\text{F}_j$ ($J=0-4$) ground states of Eu^{3+} ions. The results indicated that this newly-developed phosphor could find applications in tricolor fluorescent lamp, phosphor-liquid crystal displays and white lighting devices utilizing GaN-based excitation in the near UV.

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1. Introduction

New rare earth activated phosphors are essential to lighting, imaging and display applications [1], because they can overcome the shortcomings that existing counterparts have [2]. In recent years, extensive research has been carried out on rare-earth-doped phosphors because of several important superior properties, such as luminescent characteristics, stability in vacuum, and corrosion-free gas emission under electron bombardment compared with traditional cathode ray tube used in current field emission displays [3,4]. Trivalent Eu ion, as one of the promising species that provide optical emission in red color regions, has been doped in various compounds [5–7]. Trivalent Eu ion has been expected as one of the promising species that provide optical devices in red color regions and many investigations have been conducted in various compounds [5–7]. However, to the best of our knowledge, there is no report on the research of $\text{NaLa}_4(\text{SiO}_4)_3\text{F}$ phosphor activated by rare earth or transition metal.

In this work, a new luminescent material $\text{NaLa}_4(\text{SiO}_4)_3\text{F}:\text{Eu}^{3+}$ was synthesized, its luminescence properties and the Eu^{3+} concentration dependence of the emission properties were investigated.

2. Experimental procedure

The starting materials La_2O_3 (A.R.), SiO_2 (A.R.), Eu_2O_3 (A.R.) and excess NaF (A.R.) were weighted as the nominal composition of $\text{NaLa}_{4-x}(\text{SiO}_4)_3\text{F}:\text{xEu}^{3+}$ ($x=0, 0.02, 0.04, 0.06, 0.08, 0.1, 0.12$). Then blended in agate mortar and sintered in an alumina crucible by

conventional solid state reactions at 950 °C for 2 h in air. Excess NaF (A.R.) was taken in order to compensate for the NaF evaporation. The amount of NaF needed was optimized by X-ray diffraction (XRD) and photoluminescence (PL) studies.

The structure of $\text{NaLa}_4(\text{SiO}_4)_3\text{F}:\text{Eu}^{3+}$ phosphors was identified by recording the powder X-ray diffraction (XRD) patterns using X'pert PRO X-ray diffractometer with $\text{Cu K}\alpha_1$ radiation ($\lambda=1.54056 \text{ \AA}$). Excitation and emission spectra were measured by using Hitachi F-4500 spectrofluorometer equipped with a 60 W Xenon lamp as excitation source. The chromaticity data were taken by using the PMS-50 spectra analysis system. All of the measurements were performed at room temperature.

3. Results and discussion

Fig. 1 shows the typical XRD patterns of the $\text{La}_{4-x}(\text{SiO}_4)_3\text{F}:\text{xEu}^{3+}$ samples with $x=0$ ($\text{NaLa}_4(\text{SiO}_4)_3\text{F}$) and $x=0.1$ ($\text{NaLa}_{3.9}(\text{SiO}_4)_3\text{F}:\text{0.1Eu}^{3+}$), respectively. Both of them match well with JCPDF files JCPDS (21-1364). No characteristic peaks of impurities are observed from the two samples. The calculated lattice constants of hexagonal $\text{NaLa}_4(\text{SiO}_4)_3\text{F}$ are: $a=9.689 \text{ \AA}$, $c=7.181 \text{ \AA}$, which are consistent with the JCPDS values, and the unit cell volume is 587.3 \AA^3 . In contrast, $\text{NaLa}_{3.9}(\text{SiO}_4)_3\text{F}:\text{0.1Eu}^{3+}$ presents a little smaller lattice constants and unit cell volume ($a=9.689 \text{ \AA}$, $c=7.1805 \text{ \AA}$, 583.8 \AA^3) due to the substitution of La^{3+} (the ionic radius of 0.122 nm) by Eu^{3+} with smaller ionic radius (0.113 nm).

The fluorescence excitation spectrum (a) and emission spectra (b) of typical sample $\text{NaLa}_{3.9}(\text{SiO}_4)_3\text{F}:\text{0.1Eu}^{3+}$ were shown in Fig. 2.

The excitation spectrum (Fig. 2a) clearly indicates a broad absorption from 240 to 325 nm (with a maximum at 281 nm) and several excitation bands located at 362 nm ($^7\text{F}_0 \rightarrow ^5\text{D}_4$) [4,6], 382 nm ($^7\text{F}_0 \rightarrow ^5\text{L}_7$) [5,6], 395 nm ($^7\text{F}_0 \rightarrow ^5\text{L}_6$) [4–6], 413 nm ($^7\text{F}_1 \rightarrow ^5\text{D}_3$) [5] and

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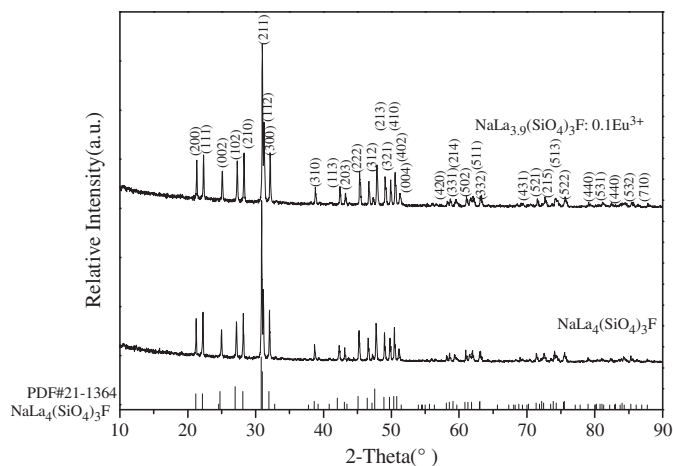
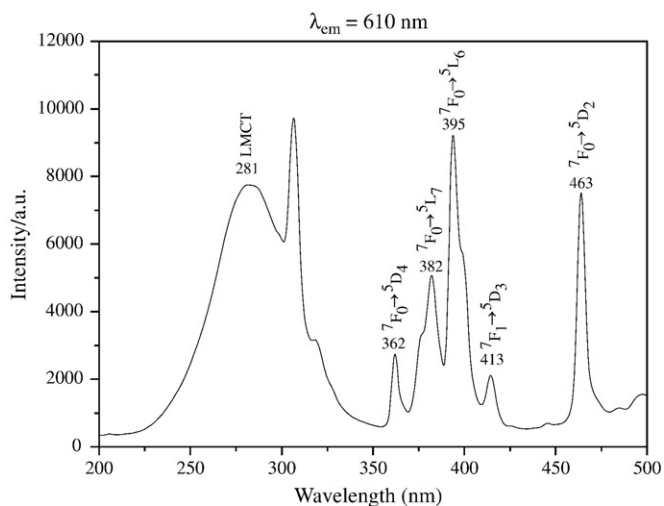
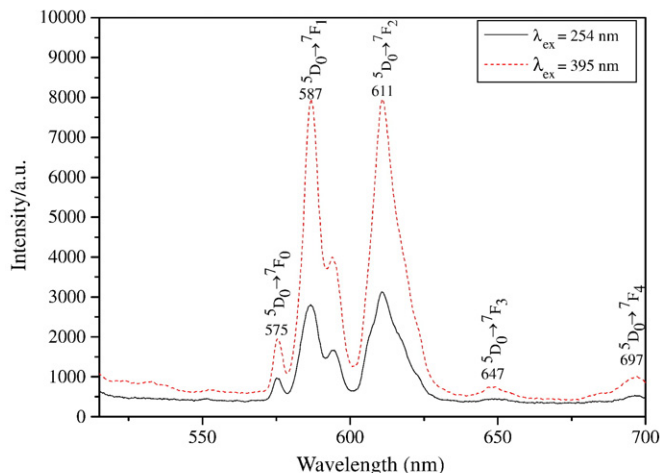


Fig. 1. X-ray diffraction patterns of $\text{NaLa}_4(\text{SiO}_4)_3\text{F}$ and phosphor $\text{NaLa}_{3.9}(\text{SiO}_4)_3\text{F}: 0.1\text{Eu}^{3+}$.

463 nm (${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$) [5,6], respectively. The broad absorption from 240 to 325 nm can be attributed to charge-transfer transition from negative ion (2p^6) to the empty state of 4f^7 of Eu^{3+} ion [ligand-to-metal charge-transfer (LMCT)] [6]. This phosphor can be excited with



(a) Excitation spectrum ($\lambda_{\text{em}} = 610 \text{ nm}$)



(b) Emission spectra ($\lambda_{\text{ex}} = 254 \text{ nm}$ and 395 nm)

Fig. 2. Excitation and emission spectra of the $\text{NaLa}_4(\text{SiO}_4)_3\text{F}: \text{Eu}^{3+}$ phosphor.

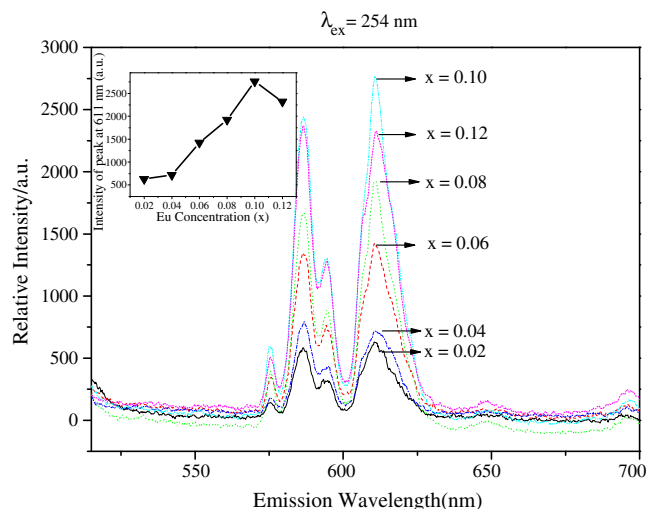


Fig. 3. Emission spectra of $\text{NaLa}_{4-x}(\text{SiO}_4)_3\text{F}: x\text{Eu}^{3+}$ ($x = 0.02, 0.04, 0.06, 0.08, 0.1, 0.12$) ($\lambda_{\text{ex}} = 254 \text{ nm}$).

different wavelengths due to its broad excitation from 240 to 325 nm, and its considerable emission intensity under 254 nm excitations along with the maximum excitation band at 395 nm makes it very attractive for such applications as the red component of tricolor luminescence materials [8], phosphor-liquid crystal displays [9] and white lighting devices utilizing GaN-based excitation in the near UV [10]. The emission spectra of $\text{NaLa}_{3.9}(\text{SiO}_4)_3\text{F}: 0.1\text{Eu}^{3+}$ phosphors under 254 nm and 395 nm excitation (Fig. 2b) show roughly the same position of emission peaks, except for the intensity. The emission intensity corresponding to the 254 nm excitation is remarkably lower than that of 395 nm because of the relatively lower absorption at this wavelength (Fig. 2a). Five emission peaks at about 575 nm, 587 nm, 611 nm, 647 nm, 697 nm are assigned to transitions of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ ($J = 0-4$) [6], respectively. The emission peak ascribed to the transition of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ is split while the others are not.

In general, the color of phosphor is represented by color coordinates. The $\text{NaLa}_{3.9}(\text{SiO}_4)_3\text{F}: 0.1\text{Eu}^{3+}$ phosphor has been found to have chromaticity coordinates of $x = 0.6168$ and $y = 0.3548$, which is depicted by reddish orange very near to "ideal red" in chromaticity diagram [11].

The change of emission intensity and wavelength of $\text{NaLa}_{4-x}(\text{SiO}_4)_3\text{F}: x\text{Eu}^{3+}$ as a function of Eu^{3+} concentration ($x = 0.02, 0.04, 0.06, 0.08, 0.1, 0.12$) was shown in Fig. 3. The highest integrated emission intensity is noted at the Eu^{3+} concentration of $x = 0.1$, which is taken as the critical concentration. Lower doping concentrations and excessive doping lead to weak luminescence and concentration quenching of the Eu^{3+} emission, respectively. Concentration quenching may occur because the excitation energy migrates about a large number of centers before being emitted. The excitation energy may transfer between the close Eu^{3+} ions by the exchange interaction. The decrease in the average distance between Eu^{3+} ions, owing to the increasing Eu^{3+} concentration, favors the energy transfer, and the critical concentration corresponds to a sufficient reduction in the average distance.

4. Conclusions

The novel red phosphors $\text{NaLa}_{4-x}(\text{SiO}_4)_3\text{F}: x\text{Eu}^{3+}$ were synthesized by the conventional solid-state reaction at 950°C for 2 h. The optimized phosphor with the composition of $\text{NaLa}_{3.9}(\text{SiO}_4)_3\text{F}: 0.1\text{Eu}^{3+}$ presents the broad absorption from 240 to 325 nm, and exhibits very good luminescence properties. Its considerable emission intensity under 254 nm excitations, along with the maximum excitation band at 395 nm, makes it potential candidate material for the red component

of tricolor luminescence materials, phosphor-liquid crystal displays and white lighting devices utilizing GaN-based excitation in the near UV.

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