A red oxide phosphor, $Sr_2ScAlO_5:Eu^{2+}$ with perovskite-type structure, for white light-emitting diodes*

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$Sr_2ScAlO_5:Eu^{2+}$, a red oxide phosphor with a perovskite-type structure, has been synthesized through a solid-state reaction and its luminescence properties have been investigated. An absorption band centering at 450 nm is observed from the diffuse reflection spectra and the excitation spectra, indicating that the phosphor can match perfectly with the blue light of InGaN light-emitting diodes. A broad red emission band at 620 nm is found from the emission spectra, originating from the $4f^6 5d$–$4f^7$ transition of the Eu^{2+} ions. The best doping content of Eu in this material is about 5%. $Sr_2ScAlO_5:Eu^{2+}$ is a highly promising red phosphor for use in white light-emitting diodes.

Keywords: luminescence, red phosphor, $Sr_2ScAlO_5:Eu^{2+}$, perovskite

PACC: 7855H, 6110M, 3250F

1. Introduction

White light-emitting diode (LED) has been studied extensively as a new light source because of its energy-saving, long lifetime, low operating voltage, compactness and environment friendly properties.[1] The white light can be generated by using an LED chip-phosphor system, in which the phosphor strongly absorbs ultraviolet (UV)-blue light (370–460 nm) from LED chip and efficiently re-emits red, or green, or yellow part of the visible spectrum. A current commercial white LED is composed of a blue LED and a yellow $YAG:Ce^{3+}$ phosphor.[2] However, this type of white light has a low colour rendering index (CRI) because $YAG:Ce^{3+}$ phosphor has a relatively weak emission in the red spectral region. To improve the CRI of white LED, the extensive efforts have been made to develop new red phosphors for blue-pump LED applications. Eu^{2+}-doped phosphors have attracted much attention because absorption and emission bands from the $4f^7 \leftrightarrow 4f^6 5d$ transition of Eu^{2+} ions can be tuned by the host lattice. Generally speaking, the centres of absorption and emission bands shift to long-wavelength region with the increase of covalency between the Eu^{2+} ion and the anion ligands (i.e., nephelauxetic effect).[3] For most of halide and oxide hosts, luminescence of Eu^{2+} is found to lie in the wavelength region from near UV to blue. Currently, orange–yellow emissions were reported in some of Eu^{2+}-doped oxides and oxynitrides, such as SiAlON,[4,5] $Sr_3SiO_5:Eu^{2+}$,[6] and $LiSrBO_3:Eu^{2+}$.[7] Meanwhile, some red phosphors have been discovered in the Eu^{2+}-activated nitrides and sulfides, such as $CaAlSiN_3:Eu^{2+}$,[8,9] $M_2Si_5N_8:Eu^{2+}$ (M=Ca, Sr),[10–13] and MS:Eu^{2+} (M=Sr, Ca).[14] However, the sulfide-based phosphors are thermally unstable and very sensitive to moisture. Therefore, the nitride-based phosphors have received significant attention because of their red emission for white LEDs, although their synthesis needs rigorous preparation conditions (high temperature and high nitrogen pressure). Until now, only one red phosphor excited by blue light, $Sr_3Al_2O_6:Eu^{2+}$, has been reported in Eu^{2+}-doped oxides;[15] this phosphor also is very sensitive to moisture.

In the present work, we introduce a new red oxide phosphor, $Sr_2ScAlO_5:Eu^{2+}$ with a perovskite-type structure. This phosphor has a strong excitation band

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centering at ∼ 450 nm and a broad emission band at ∼ 620 nm, potentially applicable to white LED assemblies. Sr_2ScAlO_5 is a chemically stable compound. As a phosphor, Sr_2ScAlO_5:Eu^{2+} has not been reported before, although the host material, Sr_2ScAlO_5, is well known to be a solid ionic conductor rather than phosphor.[16]

2. Experiment

A series of samples $(Sr_{1-x}Eu_x)_2ScAlO_5$ (x = 0–0.25) were prepared by a solid-state reaction. The starting materials were $SrCO_3$ (A.P.), Sc_2O_3 (A.P.), Al_2O_3 (A.P.) and Eu_2O_3 (A.P.). The raw powders were weighted according to the stoichiometric compositions, then mixed, abraded and pressed into pellets sequentially, and finally sintered at 1723 K for 4 h in a tube furnace under N_2/H_2 (9/1) atmosphere. The samples were investigated by x-ray powder diffraction (TTR III Rigaku) with Cu Kα radiation. Diffuse reflection spectra were measured on UV/Vis/NIR Jasco V570 spectrometer through using $BaSO_4$ as calibration. Emission and excitation spectra were recorded on an Edinburgh Instruments FLS 920 spectrophotometer equipped with a continuous (450 W) xenon lamp. For low-temperature measurements, samples were mounted on a closed cycle liquid helium cryostat (10 K–400 K, Advanced Research Systems DE202).

3. Results and discussion

The XRD results indicate that the samples are composed of Sr_2ScAlO_5 phase with a perovskite-type structure and a very small amount of Al_2O_3 (JCPDS No.: 10-0173) as impurity. A representative XRD pattern is shown in Fig. 1(a). The XRD data of $(Sr_{1-x}Eu_x)_2ScAlO_5$ (x=0–0.25) can be completely indexed on the basis of a cubic system with space group $Pa\bar{3}$. The lattice parameter, $\boldsymbol{a}$, of $(Sr_{1-x}Eu_x)_2ScAlO_5$ was derived from the rietveld refinement of the XRD data in a two-theta region of 10°–120°. The variation of the lattice parameter, $\boldsymbol{a}$, with Eu content is illustrated in Fig. 1(b). The lattice parameter decreases linearly with Eu content x increasing. This phenomenon conforms to the Vegard's law, since the ionic radius of Eu^{2+} (1.17 Å, 1 Å=0.1 nm) is smaller than that of Sr^{2+} (1.18 Å). This linear relation indicates that Eu^{2+} ions have been substituted for Sr^{2+} ions in the lattice.

Figure 2 shows diffuse reflection spectra of $(Sr_{1-x}Eu_x)_2ScAlO_5$ (x = 0, 0.02, 0.05, 0.15, 0.20, 0.25). For sample Sr_2ScAlO_5 (x = 0), only one absorption band appears at ∼ 280 nm, which corresponds to the absorption of host. For Eu-doped samples, two absorption bands centering at ∼ 280 nm and ∼ 450 nm are observed. The first one can be ascribed to the absorption of host compared with that of sample Sr_2ScAlO_5. The second is the absorption from $4f^7 \rightarrow 4f^65d$ transition of Eu^{2+} ions. With Eu^{2+} content increasing, the second absorption band is enhanced.

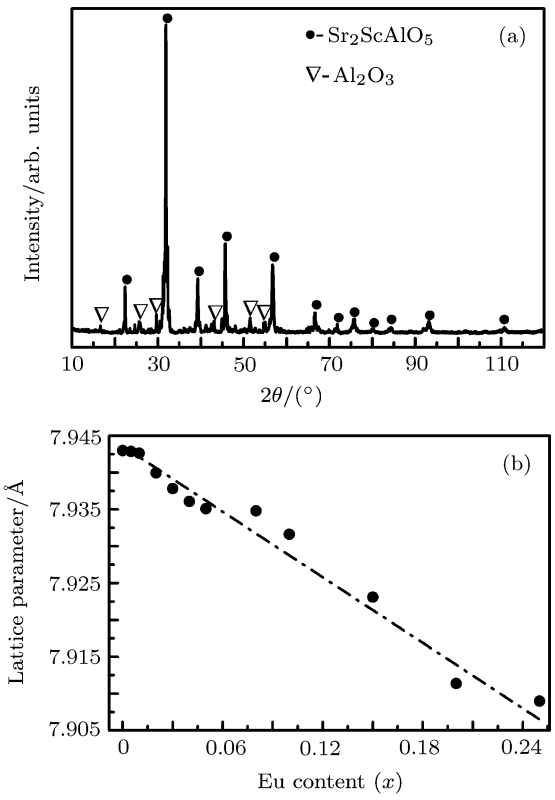


Fig. 1. The XRD pattern of $(Sr_{0.98}Eu_{0.02})_2ScAlO_5$ (a) and the variation of lattice parameter, $\boldsymbol{a}$, of $(Sr_{1-x}Eu_x)_2ScAlO_5$ with the Eu content (b).

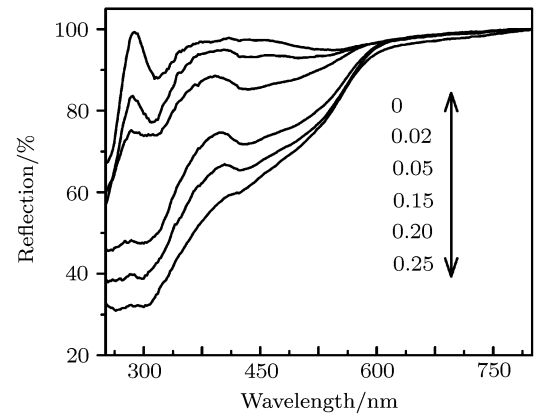


Fig. 2. Diffuse reflection spectra of $(Sr_{1-x}Eu_x)_2ScAlO_5$.

The excitation and emission spectra of $(Sr_{1-x}Eu_x)_2ScAlO_5$ samples show broad band features, corresponding to the $4f^7 \rightarrow 4f^6 5d$ transition of Eu^{2+} ions. The narrow emission lines from the Eu^{3+} intra-$4f^n$ shell transition ($^5D_0 \rightarrow {}^7F_J$) are not observed. These results indicate that Eu atoms behave as Eu^{2+} ions in the host lattice, and accord with the XRD results. The excitation spectra and the emission spectra of a typical sample, $(Sr_{0.98}Eu_{0.02})_2ScAlO_5$ phosphor, are shown in Fig. 3, in which those of standard commercial YAG:Ce^{3+} (Xiamen Quantum Star, YAG-3) are also plotted as comparison. The first excitation band peaking at $\sim$ 280 nm is attributed to the transition between the valence band and the conduction band of the host, and in accordance with the first absorption band of reflection spectra. The second one at $\sim$ 450 nm is attributed to the electric dipole-allowed transition from the $4f^7(^8S_{7/2})$ ground state to $4f^6(^7F)5d$ excited state of the Eu^{2+} ions. Correspondingly, the emission band at $\sim$ 620 nm is ascribed to the electric dipole-allowed transition from the $4f^6(^7F)5d$ excited state to the $4f^7(^8S_{7/2})$ ground state of the Eu^{2+} ions. The broad emission band peaks at 620 nm and covers the range from 570 nm to 670 nm, so the phosphor has a pure red emission. As a result, the intense red colour of powder samples is visible with the naked eye.

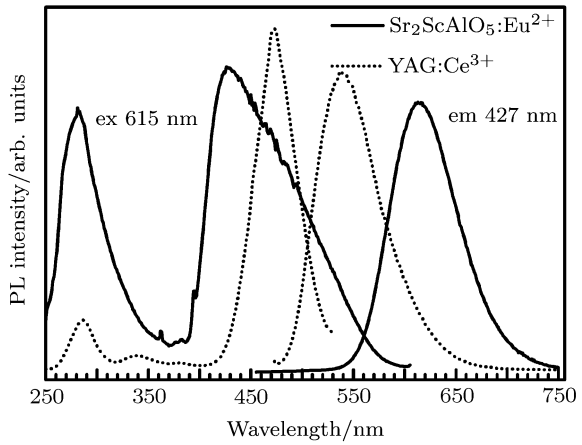


Fig. 3. The excitation and emission spectra of the $(Sr_{0.98}Eu_{0.02})_2ScAlO_5$.

The Eu content dependence of the integrated photoluminescence (PL) intensity of Eu^{2+} emission bands is plotted in Fig. 4. The integral emission intensity increases quickly with Eu content x. The intensity reaches a maximum at $x = 0.05$, and then decreases by the effect of concentration quenching. For the excitation spectra the integral intensity shows a similar variation of PL intensity with the content of Eu. So the best doping content of Eu in $(Sr_{1-x}Eu_x)_2ScAlO_5$ is about 5%. The quantum output of sample with $x = 0.05$ is about 48% at room temperature. The quantum output may be increased further by adjusting synthesis method and conditions.

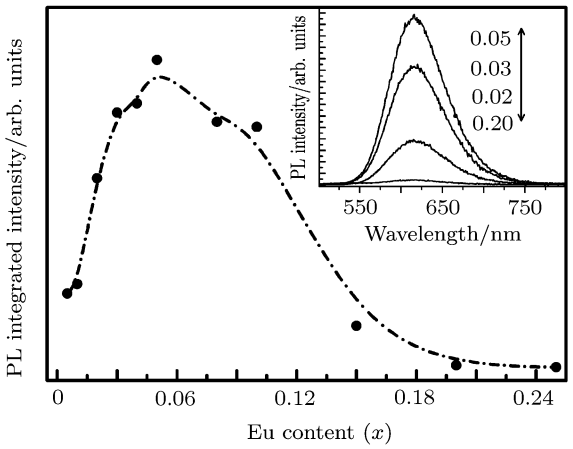


Fig. 4. Curves for PL intensity of $(Sr_{1-x}Eu_x)_2ScAlO_5$ versus Eu content, x.

The PL emission spectra of $(Sr_{0.95}Eu_{0.05})_2ScAlO_5$ between 10 K and 300 K with an interval of 50 K, excited at 427 nm by an xenon lamp, are shown in Fig. 5. The PL spectra were recorded under the same conditions except for changing the temperature; therefore, the relative intensities can be directly compared with each other. The temperature dependence of the total integrated PL intensity of Eu^{2+} emission bands, calculated from the inset, is plotted in Fig. 5. The integrated PL intensity monotonically decreases with temperature increasing. The probability of nonradiative transition increases with the temperature increasing, resulting in the decrease of the emission intensity.

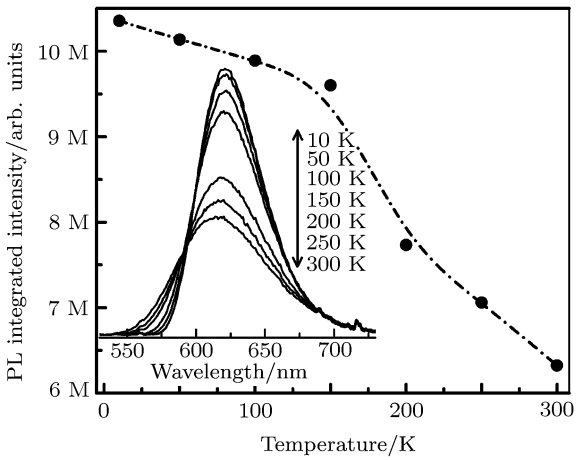


Fig. 5. PL spectra of $(Sr_{0.95}Eu_{0.05})_2ScAlO_5$ at different temperatures.

4. Summary

Sr_2ScAlO_5: Eu^{2+} phosphor has a perovskite-type structure. It is well known that perovskite-type oxides have a rich variation in chemical composition, structure and characteristics. This will provide a large possibility in further improving its luminescent properties through adjusting composition and lattice of host.

In summary, we have found a red oxide phosphor, Sr_2ScAlO_5:Eu^{2+} with a perovskite-type structure. This phosphor has a strong excitation band centering at 450 nm and a broad emission band at 620 nm, potentially applicable to white LED assemblies. In addition, the discovery of this phosphor will encourage us to explore new red phosphors for white LEDs in perovskite-type oxides.

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