Fluorescent and chromatic properties of visible-emitting phosphor KLa(MoO$_4$)$_2$:Sm^{3+}

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ABSTRACT

Sm^{3+} doped KLa(MoO$_4$)$_2$ phosphors were synthesized via a high-temperature solid-state reaction. The crystal structure of the phosphors was examined with XRD and a pure phase was confirmed. The photoluminescence (PL) spectra display dependence on both excitation wavelength and Sm^{3+} doping concentration. The concentration quenching behavior was studied and the possible relaxation channel for self-quenching of luminescence centers was discussed. The electric dipole–dipole interaction is confirmed to be the dominant mechanism for energy transfer between Sm^{3+} ions on the basis of both Van Uitert's and Dexter's models. The chromatic characteristics are also found to be dependent on both excitation wavelength and Sm^{3+} doping concentration.

1. Introduction

In recent decades, rare earth (RE) doped materials have attracted much attention due to their potential applications in the fields of lighting, display systems, laser media and optoelectronic devices etc [1–5]. In the field of solid-state lighting, the white light emitting diodes (W-LEDs), as a new generation of light sources, have many advantages such as low power consumption, environmental friendliness, long serving lifetime, and high luminous efficiency [6–9]. The phosphor-converted WLEDs (pc-WLEDs) provide a promising approach to achieve white light output via combining violet LEDs with tricolor emitting phosphors. However, the commercialized tricolor phosphors for fluorescent lamps cannot serve the device due to the excitation wavelength mismatch. Therefore tricolor phosphors with high luminescence performance have been extensively studied [10–12]. To date, great progress has been achieved in the development of blue- and green-emitting phosphors, but in contrast, works on the red phosphors are still lacking. The red component in phosphors is very important to improve the performance such as color rendering index and color temperature. The typical example is the commercial W-LED known as the combination of blue GaN-based LED with yellow-emitting phosphor YAG:Ce^{3+} whose lower color rendering index results in

a higher color temperature due to the lack of a red component in the spectra. Thus, exploring novel stable red phosphors which can be effectively excited by near UV light is of great significance. Beyond that, white light emitting glasses doped with rare earth ions can provide alternative approach to realize the W-LEDs [13].

The host material plays an important role in the performance of RE doped phosphors. Among various kinds of host materials, molybdates have attracted particular interest due to its easy preparation, low cost and excellent physical and chemical stability. The double molybdate, with a general formula of ALn(MoO$_4$)$_2$ (where A$^+$ is an alkali metal ion and Ln^{3+} is a lanthanide ion) has been extensively studied as the appropriate host for variety of inorganic phosphors [14–16]. The host ALn(MoO$_4$)$_2$ has a stable scheelite-type structure and can be doped with higher level of RE^{3+} concentration because of the existence of Ln^{3+} ions. RE^{3+} doped molybdates can be effectively excited by near UV light since the (MoO$_4$)$^{2-}$ group has intense absorption in the near UV region and the absorbed energy can be effectively transferred to the luminescent centers. As a red-emitting luminescence center, Sm^{3+} ion possesses some advantages such as lower cost, better color saturation, wider-ranged and more colorful spectra, compared with Eu^{3+} ion used in commercial red phosphors. Therefore cheap and easily synthesized KLa(MoO$_4$)$_2$:Sm^{3+} may be a promising candidate of red-emitting phosphors for W-LEDs.

In this work, we have studied on the fluorescent and chromatic properties of KLa(MoO$_4$)$_2$:Sm^{3+} phosphors. KLa(MoO$_4$)$_2$:Sm^{3+} phosphors with variant Sm^{3+} concentrations were synthesized via a

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simple high-temperature solid-state reaction. The X-ray diffraction and photoluminescence spectroscopy were used to characterize the samples. The energy transfer mechanism between Sm^{3+} ions is discussed on base of analyzing the concentration quenching behavior and the fluorescent decay process. The chromatic features of the phosphors are also discussed in detail.

2. Experimental

2.1. Sample synthesis

A series of $KLa_{1-x}(MoO_4)_2:xSm^{3+}$ (x = 0.5, 1, 3, 5, 9, 15 and 20 mol%) phosphors were synthesized via a high-temperature solid-state reaction. In a typical synthesis, stoichiometric amounts of MoO_3 (99.99%), La_2O_3 (99.99%), Sm_2O_3 (99.99%), K_2CO_3 (99.99%) and NH_4HF_2 (AR) were mixed and finely ground together in an agate mortar. Here NH_4HF_2 was used as a flux to improve the chemical reaction. Then the mixture was transferred to an alumina crucible and calcined in a muffle furnace for 4 h at 1000 °C.

2.2. Sample characterization

X-ray powder diffraction (XRD) was performed on an XRD-6000 diffractometer (Shimadzu, Japan) with Cu $K\alpha_1$ as radiation source (λ = 0.15406 nm). The XRD data in the 2θ raging from 10° to 60° were collected under a scanning mode with the step size of 0.02° and the scanning rate of 2.0° min^{-1}. The photoluminescence (PL) emission/excitation spectra and fluorescence decays were measured with an F-4600 spectrometer (Hitachi, Japan) equipped with a 150 W xenon lamp as the excitation source. The spectral resolution was 0.1 nm. All measurements were carried out at room temperature.

3. Results and discussion

3.1. Crystal structure

The crystal structure of all the samples was examined by means of XRD and a very similar diffraction pattern for all the samples was observed. Fig. 1 shows the XRD patterns for two samples with high (a) and low (b) doping concentrations as representatives, and the pattern plotted by using the standard data (c) reported in the JCPDS card No. 40-0466 for comparison. It can be found that all the diffraction peaks for the samples with different doping concentrations are in good agreements with those appearing in the JCPDS card No. 40-0466. No additional peaks corresponding to other phases are found, indicating a relatively good purity and a single crystal structure of all the studied samples. In addition, no obvious change in the XRD patterns appears when the doping concentration of Sm^{3+} varies, which implies that the crystal structure of all the samples is independent from the doping concentration.
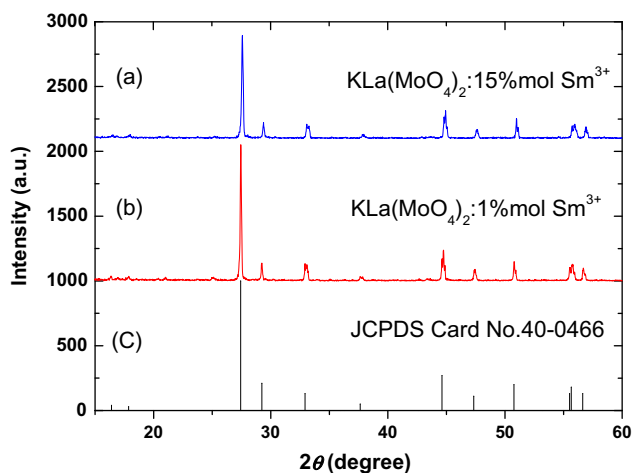

Fig. 1. XRD patterns for the phosphor $KLa_{1-x}(MoO_4)_2:xSm^{3+}$ (x = 0.01 and 0.15) and for the standard data reported in JCPDS card No. 40-466.

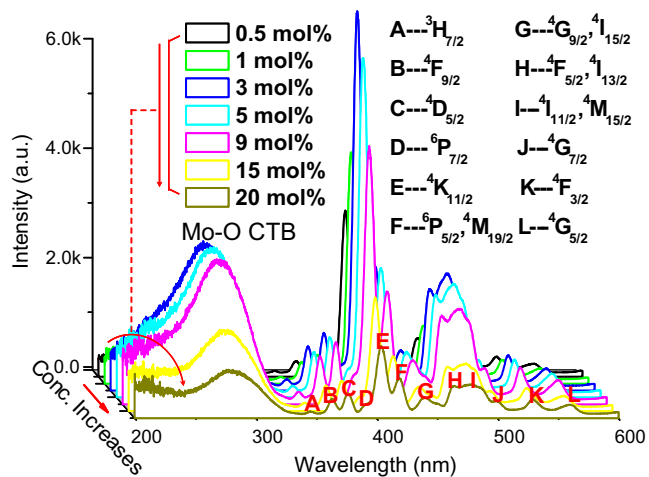**Fig. 2.** Excitation spectra of $KLa_{1-x}(MoO_4)_2:xSm^{3+}$ (x = 0.005–0.20) phosphors monitored at 646 nm.

3.2. Spectral properties

Excitation spectra of all the samples with different Sm^{3+} concentrations have been measured and shown in Fig. 2. The measurements were under the same conditions and the 646 nm emission corresponding to $^4G_{5/2} \rightarrow {}^6H_{9/2}$ transition of Sm^{3+} ion was monitored. The spectra of all the samples display a similar spectral profile as consisting of two parts. One part is a broad excitation band ranging from 200 to 340 nm with a maximum at around 280 nm corresponding to the Mo–O charge transfer absorption band (CTB). The existence of host absorption band in the excitation spectra of monitoring the Sm^{3+} emission indicates the occurrence of energy transfer process from MoO_4^{2-} groups to Sm^{3+} ions. The other part in the spectra is a series of sharp excitation peaks within the range from 340 to 580 nm, which can be attributed to the typical $f-f$ transitions of Sm^{3+} ion from the ground state $^6H_{5/2}$ to the excited states $^4G_{5/2}$, $^4F_{3/2}$, $^4G_{7/2}$, $^4I_{11/2}/{}^4M_{15/2}$, $^4F_{5/2}/{}^4I_{13/2}$, $^4G_{9/2}/{}^4I_{15/2}$, $^6P_{5/2}/{}^4M_{19/2}$, $^4K_{11/2}$, $^6P_{7/2}$, $^4D_{5/2}$, and $^4F_{9/2}$, and $^3H_{7/2}$ [17–21]. The most intense excitation peak is centered at 404 nm which matches the output of novel blue LEDs. It is obvious that the intensities of all the excitation peaks are dependent on the doping concentration. Each intensity increases until reaching a maximum value at 3 mol% of Sm^{3+}, and then decreases with the increasing concentration.

Emission spectra of all the samples were measured under 280 nm excitation corresponding to absorption of the host as shown in Fig. 3. All the emission spectra display a similar profile including a weak broad band emission and four sharp lines. The broad band originates from the MoO_4^{2-} groups, while four of the sharp lines being the typical emissions of Sm^{3+} ions originate from the transitions from the metastable energy level $^4G_{5/2}$ to the lower ^6H_J levels (J = 5/2, 7/2, 9/2 and 11/2) [20–22]. The presence of the typical emissions of Sm^{3+} ions under the selective excitation of MoO_4^{2-} groups indicates that an energy transfer process occurs from the MoO_4^{2-} groups to Sm^{3+} ions in $KLa(MoO_4)_2:Sm^{3+}$ samples. Among all the emission peaks of Sm^{3+} ions, the most intense one at around 646 nm corresponds to the transition $^4G_{5/2} \rightarrow {}^6H_{9/2}$. It is observed that the emission intensity changes with changing doping concentration of Sm^{3+}. It is worthwhile mentioning that the change in the intensity of the broad band is very slight but is obvious in that of the sharp lines, indicating the effective energy transfer from the MoO_4^{2-} groups to Sm^{3+} ions. The intensities of the emission peaks of Sm^{3+} ions initially increase, and then reach their corresponding maxima at the concentration around 3 mol% Sm^{3+}. The