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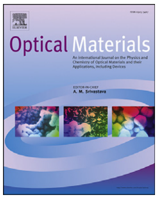

Unraveling the distinct luminescence thermal quenching behaviours of A/B-site Eu^{3+} ions in double perovskite $Sr_2CaMoO_6:Eu^{3+}$

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ABSTRACT

Eu^{3+}-doped Sr_2CaMoO_6 phosphors have a broad excitation band at around 350–425 nm, which meets the demand of Near-ultraviolet (NUV, 365–410 nm) absorption when applied in NUV-excitable phosphor-converted white light emitting diodes (WLEDs). The luminescence thermal quenching effects of Eu^{3+} ions at A/B sites (612 nm/593 nm) in Sr_2CaMoO_6 might be distinct with resultant emission colour variation, which is less studied but of significance for a scientific perspective. This research investigates on the temperature-dependent luminescence and decay curves of the nominal $Sr_{1.9}Li_{0.05}Eu_{0.05}CaMoO_6$ and $Sr_2Ca_{0.9}Li_{0.05}Eu_{0.05}MoO_6$ phosphors. Results indicate that the luminescence of B-site Eu^{3+} ions is quenched more easily than that of A-site Eu^{3+} ions, directly evidenced by the fast and slow decay components in the decay curves. A distortion of B-site octahedron with elevating temperature and strong coupling with phonons may be partially responsible for the relatively poor thermal quenching behaviors of B-site Eu^{3+} ions. The research gives perspective on the thermal quenching of emissive lanthanide ions at different sites in phosphors.

1. Introduction

White light emitting diodes (WLEDs) have attracted enormous attention for their low energy consumption, robustness and environmental friendliness [1–3], which is considered as a most promising general illumination light source. Near-ultraviolet (NUV, 365–410 nm) excitable WLEDs, fabricated by coating the NUV emissive LED chip with red, green and blue phosphors, have advantages in high colour rendering index, tunable colour temperature and superior colour uniformity [4–9]. Red phosphor is one of the vital components for such WLEDs. The $Y_2O_2S:Eu^{3+}$ phosphor is currently the common commercial phosphor as the red component for UV excitation, but it suffers from the drawbacks of poor absorbance in NUV region and chemical instability during work [10–14]. Thus, red phosphors with enhanced absorbance in NUV region and good chemical stability are still expected. The Eu^{3+}-doped Sr_2CaMoO_6 double perovskite red phosphor is reported to have a broad excitation band at around 350–425 nm [15–18], which is ascribed to the charge transfer band (CTB) of MoO_6 octahedron and matches the NUV GaN-based chips well [1,15–18]. Most of the research work on the Eu^{3+}-doped Sr_2CaMoO_6 phosphors focus on the room temperature luminescence, but the working temperature of LED devices is almost around or even above 370 K [19–21]. For the phosphors used in WLEDs, poor thermal stability would lead to a change of Commission Internationale de I'Eclairage (CIE) coordinates and colour rending index (CRI) of the device [20,22,23]. Therefore, the thermal performance of phosphors is an important technological consideration for the WLEDs devices. Thus the study of thermal stability and the thermal quenching mechanism of Eu^{3+}-doped Sr_2CaMoO_6 phosphor is of significance for a scientific perspective. For Eu^{3+}-doped Sr_2CaMoO_6 phosphor, there are 12-coordinated A sites and 6-coordinated B sites to accommodate Eu^{3+} ions [16,17]. When Eu^{3+} ions occupy the A sites without inversion centre, the forced electric dipole transition $^5D_0$-$^7F_2$ at ~612 nm of Eu^{3+} ion is effective. While Eu^{3+} ions enter into the B sites with centrosymmetry, the magnetic dipole transition $^5D_0$-$^7F_1$ at ~593 nm of Eu^{3+} ion is dominant. The luminescence thermal quenching of these two types of Eu^{3+} ions may be different and the variation of emission colour takes place. Furthermore, the B sites with centrosymmetry may be distorted with elevating temperature and lead to a degeneration of symmetry. While the symmetry of A sites is originally low (without inversion centre). The distinct local

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structure variation of A site and B site with elevating temperature may impose different influence on the luminescence of A/B-site Eu^{3+}. Since Raman spectroscopy is sensitive to the change of local structure [24], it may be helpful to unravel the origin of thermal quenching difference of Eu^{3+} luminescence at A site and B site. In this research, the temperature-dependent emission spectra, temperature-dependent decay lifetimes and temperature-dependent Raman spectra are investigated in detail to reveal the respective luminescence thermal quenching effect of A/B-site Eu^{3+} ions in the Sr_2CaMoO_6: Eu^{3+} phosphors.

2. Experimental

We intend to incorporate Eu^{3+} ions into A sites or B sites by replacing Sr^{2+} ions or Ca^{2+} ions (with the nominal formula of $Sr_{1.9}Li_{0.05}Eu_{0.05}CaMoO_6$ or $Sr_2Ca_{0.9}Li_{0.05}Eu_{0.05}MoO_6$). Such phosphors are synthesized by the solid-state reaction method. MoO_3 (analytical reagent, AR), $SrCO_3$ (AR), $CaCO_3$ (AR) Li_2CO_3 (99.99%) and Eu_2O_3 (99.99%) were used as raw materials. The stoichiometric amounts of raw materials were mixed in an agate mortar. Then the mixtures were sintered in corundum crucibles at 600 °C for 12 h, then at 900 °C for 12 h and finally at 1100 °C for 24 h, with several intermediate grindings.

X-Ray diffraction (XRD) patterns for checking phase purity were measured by Philips PW1830 X-ray diffractormeter with graphite monochromator and Cu target. The acceleration voltage and filament current were 40 kV and 40 mA, respectively. The excitation, emission spectra and decay curves were recorded on an Edinburgh FLS920 spectrometer, equipped with 450-W xenon lamp as excitation source for steady measurement and μF900 flash lamp as excitation source for decay curves measurement and a Hamamatsu R928 photomultiplier as detector. The temperature-dependent emission spectra and decay curves were detected by the same spectrometer equipped with a TAP-02 (Tian Jin Orient–KOJI instrument Co., Ltd., China) high temperature fluorescence accessory. The temperature-dependent Raman spectra were recorded by a Renishaw inVia Laser micro-Raman spectrometer with 633 nm laser beam as light source. To avoid fluorescence noise, sample without Eu^{3+} is used for the Raman measurement.

3. Results and discussion

3.1. Structural analysis

XRD patterns of the phosphors of $Sr_{1.9}Li_{0.05}Eu_{0.05}CaMoO_6$ and $Sr_2Ca_{0.9}Li_{0.05}Eu_{0.05}MoO_6$ are given in Fig. 1(a). It shows that the patterns are in good agreement with the standard card of Sr_2CaMoO_6 (JCPDS 48-0799), and no apparent impurity phase is observed for these phosphors. The schematic crystal structure of Sr_2CaMoO_6 (with $P2_1/n$ space group) [15] is shown in Fig. 1(b). Sr^{2+} cations locate at 12-coordinated A sites without inversion symmetry, while Ca^{2+} and Mo^{6+} cations are 6-coordinated at B sites with inversion centrosymmetry. B-site cations Mo^{6+} and Ca^{2+} in the lattice are arranged as a rock salt structure. Eu^{3+} ions can substitute both Sr^{2+} at A site and Ca^{2+} at B site with the preferred occupancy at B site owing to the ion radii difference, as the previous research reported [16].

3.2. Photoluminescence at room temperature and 10 K

The emission and excitation spectra for $Sr_{1.9}Li_{0.05}Eu_{0.05}CaMoO_6$ and $Sr_2Ca_{0.9}Li_{0.05}Eu_{0.05}MoO_6$ are presented in Fig. 2. When excited by 465 nm (the $^7F_0$-$^5D_2$ transition of Eu^{3+} ions), the main emission peak locate at 612 nm shown in Fig. 2(a), which is attributed to the $^5D_0$-$^7F_2$ transition of Eu^{3+} ions. Both the $^7F_0$-$^5D_2$ and $^5D_0$-$^7F_2$ transitions are forced electric dipole transition, which can only be effective for Eu^{3+} in non-centrosymmetry environment (A site). The intense 612 nm emission is ascribed to Eu^{3+} ions at A sites, namely A-site Eu^{3+} ions, in $Sr_{1.9}Li_{0.05}Eu_{0.05}CaMoO_6$ phosphor. The emission peaks in range of 580–600 nm corresponding to the $^5D_0$-$^7F_1$ transition are also observed but extreme weak. Two apparent emission peaks at 593 nm and 612 nm appear in emission spectra when excited by 350 nm. The emission peak at 593 nm is due to magnetic dipole transition and is effective in centrosymmetry environment (B site). The occurrence of apparent 593 nm emission suggests that part of Eu^{3+} ions enter B sites. Since 593 nm emission induced by A-site Eu^{3+} is negligible, the 593 nm emission excited by 350 nm is mainly caused by Eu^{3+} ions at B sites (so-called B-site Eu^{3+}). The excitation spectra monitored at 612 nm and 593 nm for $Sr_{1.9}Li_{0.05}Eu_{0.05}CaMoO_6$ are shown in Fig. 2(b). A strong sharp excitation line at 465 nm and a broad excitation band around 250–425 nm are observed when monitoring 612 nm emission. The former is correlated to the $^7F_0$-$^5D_2$ transition of Eu^{3+} ions and the latter is assigned to the charge transfer states (CTS) of MoO_6 groups. The significant inverse cases for their intensities ratio when monitoring 612 nm and 593 nm suggest that the 612 nm emission is mostly contributed by the A-site Eu^{3+} ions in $Sr_{1.9}Li_{0.05}Eu_{0.05}CaMoO_6$. In other words, the A-site Eu^{3+} ions could be excited by 465 nm efficiently and the B-site Eu^{3+} ions could not. The emission spectra of the nominal B-site substituent $Sr_2Ca_{0.9}Li_{0.05}Eu_{0.05}MoO_6$ phosphor are shown in Fig. 2(c). The 593 and 612 nm emission peaks are found to be weak when excited by 465 nm, hinting that there are only a few of Eu^{3+} ions located at A sites. The emission peak at 593 nm is dominant when excited by 350 nm, which suggests that most of Eu^{3+} ions locate at B sites. The other weak broad emission peaks at around 600–640 nm are mainly ascribed to the simultaneous excitations of non-centrosymmetry vibrational modes of the surroundings of Eu^{3+} ions (the so called vibronic transitions) and the $^5D_0$-$^7F_2$ electronic transition [16,25]. In the excitation spectra of $Sr_2Ca_{0.9}Li_{0.05}Eu_{0.05}MoO_6$, shown in Fig. 2(d), the weak 465 nm excitation peak also indicates that the amount of A-site Eu^{3+} ions is small. The broad CTS excitation band indicates these phosphors can absorb NUV light and the energy could transfer to Eu^{3+} ions at both A sites and B sites. To sum up, Eu^{3+} ions could enter both A and B sites in these phosphors, but mostly locate at A sites in $Sr_{1.9}Li_{0.05}Eu_{0.05}CaMoO_6$ and B sites in $Sr_2Ca_{0.9}Li_{0.05}Eu_{0.05}MoO_6$.

In order to confirm the location site of Eu^{3+} ions in host matrix, the emission spectra at 10 K are measured and presented in Fig. S1 in supplementary material. According to the previous research [26], there is significant variation for the $^5D_0$-$^7F_1$ transition in the range of 580–600 nm with single peak or splitting peaks when excited by different wavelength lights. It suggests that there are at least two sites in the Sr_2CaMoO_6 to accommodate the Eu^{3+} ions. Since the site-selective excitation data with precise excitation wavelength are lack, the emission spectra in Fig. S1 are always the mixture of both A-site and B-site Eu^{3+} emissions. Thus, it seems unable to analyze the $^5D_0$ -$^7F_0$ transition. The symmetry of this compound was reported to be $P2_1/n$ confirmed by neutron powder diffraction at room temperature [27], with A-site symmetry of C_1 and B-site symmetry of C_i. But the splitting of the peaks in Fig. S1 does not fully follow reference [26]. Since we don't know whether there is a phase transition or decomposition when temperature goes down to 10 K, we could not make the conclusion. However, it is pretty sure there are at least two sites for Eu^{3+}.

3.3. Temperature-dependent photoluminescence

3.3.1. Temperature-dependent emission spectra

The luminescence thermal quenching performance of