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Enhancements of luminescent properties of $CaZrO_3:Eu^{3+}$ by A^+ (A = Li, Na, K)

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ABSTRACT

$CaZrO_3$:5%molEu^{3+} and $CaZrO_3$:5%molEu^{3+}/5mol%A^+ (A = Li, Na, K) phosphors were synthesized by a solid state reaction. Effects of codoped alkali ions on luminescent properties of $CaZrO_3$:5%molEu^{3+} was investigated. The XRD and FTIR measurements show that the all of synthesized phosphors have the same phase with pure $CaZrO_3$. The excitation and emission spectra indicate that the codoped alkali ions enhance the Eu^{3+} emission intensity significantly. Moreover, the decay lifetime is also prolonged by the addition of alkali ions. The enhancements of luminescent properties for $CaZrO_3$:5%molEu^{3+} can be attributed to the charge compensation and decrease of Ca^{2+} vacancies induced by the addition of alkali ions.

1. Introduction

In recent years, white light diodes (WLEDs) based on ultraviolet (UV) or near UV (NUV) chip are in focus of many investigations due to their advantages of high tolerance to UV or NUV chip color variation and remarkable color-rendering index [1–5]. More narrowly, this type of WLED uses the UV or NUV chip as excitation source and consists of phosphors with red, green and blue emissions. For phosphors, they should be sensitive to UV or NUV in a long wavelength region and have high emission efficiency. Due to the emissions in UV-infrared region originating from 4f to 4f or 5d to 4f transitions, lanthanide ions doped phosphors are widely investigated for the WLED applications [6]. As one of lanthanide ions, Eu^{3+} is widely investigated due to its characteristically red emission corresponding to $^5D_0 \rightarrow {}^7F_j$ (j = 0, 1, 2, 3, 4) transitions [7,8].

Perovskites with the formula of ABO_3 are interesting materials because of their reputably chemical and physical properties, as well as widely potential applications in various fields [9–12]. As a member of perovskite ABO_3 family, $CaZrO_3$ was found to be a good host of lanthanide ions and a number of Eu^{3+} doped phosphors were synthesized in recent years [12–21]. The structure of $CaZrO_3$ is made up of a three dimensional sublattice of corner-connected ZrO_6 octahedron, in which Ca^{2+} locates in 8-fold coordination with O^{2-} [18]. According to the report of Kumar at al., Eu^{3+} substitutes Ca^{2+} rather than Zr^{4+} in $CaZrO_4$ [21]. As a result, crystal defects are formed in $CaZrO_3:Eu^{3+}$ because of different valence between Eu^{3+} with Ca^{2+}, which act as quenching centers and influence the luminescent properties of $CaZrO_3:Eu^{3+}$. To keep charge balance in these phosphors, alkali ions (Li^+, Na^+, K^+) are widely used since alkali ions have small ionic radius and easy accommodation in host matrices [22].

Although there are some reports about Eu^{3+} doped phosphors in recent years, we cannot find reports about $CaZrO_3:Eu^{3+}$ phosphors codoped with alkali ions. As discussed above, since the substitution of Ca^{2+} by Eu^{3+} leads to the generation of crystal defects due to different valence and alkali ions are widely used to keep charge balance, the luminescent properties of $CaZrO_3:Eu^{3+}$ phosphors can probably be improved by codoping alkali ions. In this article, we report the synthesis and luminescent properties of $CaZrO_3:Eu^{3+}/A^+$ (A = Li, Na, K) phosphors. The Eu^{3+} mono-doped and Eu^{3+}/A^+ (A = Li, Na, K) codoped $CaZrO_3$ phosphors were synthesized by a solid state reaction. The luminescent properties of $CaZrO_3:Eu^{3+}$ were enhanced by codoping alkali ions (Li^+, Na^+, K^+) ions. The mechanism of the enhancements of luminescent properties was investigated.

2. Materials and methods

$CaZrO_3$:5%molEu^{3+} and $CaZrO_3$:5%molEu^{3+}/5mol%A^+ (A = Li, Na, K) phosphors were synthesized by a solid state reaction. Chemical reagents of $CaCO_3$ (99.9%), ZrO_2 (99.9%), Eu_2O_3 (99.99%) and A_2CO_3 (A = Li, Na, K) (99.99%) were used as raw materials in the solid state synthesis of $CaZrO_3:Eu^{3+}/A^+$ phosphors. In a typical synthesis, stoichiometrical amount of chemical reagents were weighted and ground in an agate mortar. Subsequently, the mixed reagents were added into a crucible and calcined at 1400 °C for 5 h in a muffle furnace. Finally, the

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products were collected after the furnace cooled to room temperature naturally and ground for the next measurements.

The XRD patterns of the synthesized phosphors were checked by a Rigaku-Dmax 2500 diffractometer, operated at 45 kV and 40 mA. Diffraction data were collected in the step-scan mode, with a step size of 2θ = 0.033° and an accumulation time of 1 s per step. Fourier Transform Infra-red spectroscopy (FTIR) spectra were measured by a Perkin-Elmer 580B infrared spectrophotometer with the KBr pellet technique. The morphology of the samples was inspected by an FESEM-4800 field emission scanning electron microscope (SEM, Hitachi). The UV–Vis diffuse reflectance spectra (DRS) were recorded using a Hitachi U-4100 UV–Vis spectrophotometer. The excitation and emission spectra were obtained by an Edinburgh Instrument FLS920 spectrophotometer. 30 mg amount of the powder sample was mixed with 3 mL of methanol and pasted over the quartz slide (1 cm × 1 cm) and dried in the ambient condition. Both the excitation and emission slits were set at 2.5 nm. The thermal stability of the luminescence was examined using the spectrometer in combination with a heating apparatus, operated in an air environment. The phosphor was filled into a bronze sample cell. After heating to an objective temperature and keeping balance for 5 min, the emission and excitation spectra were recorded. The heating rate is less than 1 °C/min and the precision of temperature control is less than 0.1 °C. The electroluminescence (EL) emission spectrum of the packaged LED device was monitored by multi-channel spectroradiometer (OL 770).

3. Results and discussions

XRD technique was used to determine the phase of the synthesized $CaZrO_3:Eu^{3+}/A^+$ phosphors. Fig. 1 provides the XRD patterns of the synthesized $CaZrO_3$:5%molEu^{3+} and $CaZrO_3$:5%molEu^{3+}/5mol%A^+ (A = Li, Na, K) phosphors, as well as the standard data of JCPD card no. 35-0790 (orthorhombic $CaZrO_3$). The diffraction peaks of the synthesized phosphors are well accordance with the standard data of orthorhombic $CaZrO_3$. And there are no diffraction peaks corresponding to impurity. These results suggest the acquisition of Eu^{3+} mono-doped and Eu^{3+}/A^+ (A = Li, Na, K) codoped $CaZrO_3$ phosphors with a single phase. The groups on the surface of the synthesized phosphors were confirmed by the FTIR technique. Fig. 2 provides the FTIR spectra of the synthesized $CaZrO_3:Eu^{3+}/A^+$ phosphors. All of FTIR spectra consist of three broad absorption bands. The absorption bands in the range of 3200–3600 cm^{-1} and 1260–1700 cm^{-1} are induced by the absorbed water on the surface of the synthesized phosphors [23]. The band in the

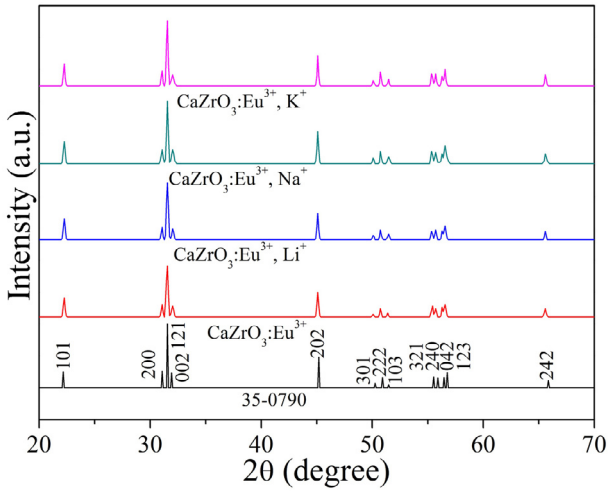

Fig. 1. XRD patters of $CaZrO_3$:5%molEu^{3+} and $CaZrO_3$:5%molEu^{3+}/5mol%A^+ (A = Li, Na, K) phosphors, as well as the standard data of JCPDs card no. 35-0790.

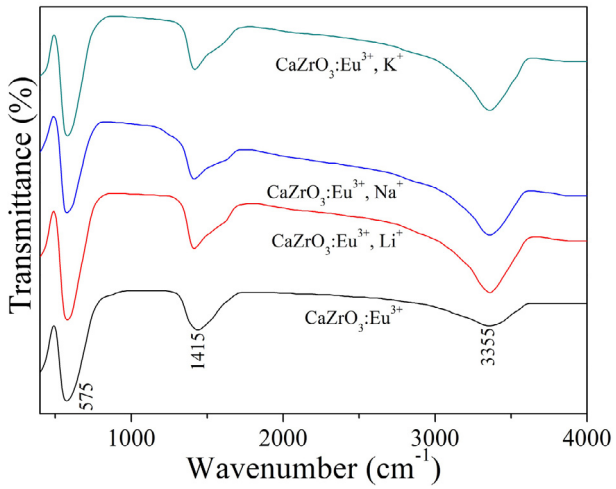

Fig. 2. FTIR spectra of $CaZrO_3$:5%molEu^{3+} and $CaZrO_3$:5%molEu^{3+}/5mol%A^+ (A = Li, Na, K) phosphors.

range of 500–650 cm^{-1} is a characteristic stretching band of $CaZrO_3$ [24]. Fig. 3 presents the SEM images of $CaZrO_3$:5%molEu^{3+} and $CaZrO_3$:5%molEu^{3+}/5mol%A^+ (A = Li, Na, K) phosphors. The synthesized phosphors have an irregular morphology and a wide size range, which are general for nano/micro crystals synthesized by the solid state reaction. The SEM images also show that the codoped A^+ ions do not influence the microstructure and size. It is well known that the intrinsic properties of inorganic materials are determined by their sizes, shapes, morphologies, compositions, and crystallinity. The XRD and SEM results demonstrate that the influence of size, shape, morphology, composition and crystallinity on the luminescence of phosphors can be ignored.

Fig. 4 gives the DRS of $CaZrO_3$ host and $CaZrO_3:Eu^{3+}/A^+$ phosphors. It can be seen that all of samples have a drop in reflection around 275 nm, which corresponds to the host absorption band of $CaZrO_3$. For Eu^{3+} doped phosphors, there are several weak absorption bands in the range of 350–600 nm, which results from the 4f to 4f absorption of Eu^{3+} ion [25]. Fig. 5 gives the excitation spectra of $CaZrO_3$:5% molEu^{3+} and $CaZrO_3$:5%molEu^{3+}/5mol%A^+ (A = Li, Na, K) phosphors. There are several of excitation bands in the wavelength range of 200–500 nm. The broad excitation band in the range of 200–350 nm and with a peak at about 278 nm results from the electron transfer from an O^{2-} 2p orbit to an empty 4f orbital of Eu^{3+}, namely charge transfer band (CTB). Other excitation bands in the range of 350–500 nm are induced by the f-f transitions of Eu^{3+}, which can be ascribed to the $^4F_0 \rightarrow {}^5D_4$, $^4F_0 \rightarrow {}^5G_4$, $^4F_0 \rightarrow {}^5L_6$, $^4F_0 \rightarrow {}^5D_3$ and $^4F_0 \rightarrow {}^5D_2$ transitions. In the excitation bands of Eu^{3+}, the excitation band with a peak at about 395 nm originating from the $^7F_0 \rightarrow {}^5L_6$ transitions is strongest. The excitation spectra of the synthesized phosphors indicate that they can be excited by UV, NUV and visible lights. Due to the forbidden nature of certain f-f transitions of Eu^{3+}, the excitation intensities of f-f transitions are weaker than the excitation intensity of CTB. From the DRS and excitation spectra, we can see that $CaZrO_3:Eu^{3+}/A^+$ phosphors have strong absorption to UV or NUV lights, meaning that they can be candidates for UV-LEDs. Fig. 6 shows the emission spectra of $CaZrO_3$:5% molEu^{3+} and $CaZrO_3$:5%molEu^{3+}/5mol%A^+ (A = Li, Na, K) phosphors. Under the excitation at 278 nm, the emission spectra of the synthesized phosphors consist of emission bands in the range of 575–625 nm corresponding to $^5D_0 \rightarrow {}^7F_j$ (j = 0, 1, 2, 3, 4) transitions. Among the emission bands, the emission peaks at about 615 nm originating from $^5D_0 \rightarrow {}^7F_2$ transition is strongest. The $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} is an electric dipole transition and will be strong when Eu^{3+} locates a site without inversion symmetry. The strongest emission band originating from $^5D_0 \rightarrow {}^7F_2$ transition suggests that Eu^{3+} locates an