

Rapid Communication

Photoluminescence of new red phosphor $\text{SrZnO}_2:\text{Eu}^{3+}$

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Abstract

$\text{SrZnO}_2:\text{Eu}^{3+}$ has been synthesized by solid-state reaction and its photoluminescence in ultraviolet (UV)–vacuum ultraviolet (VUV) range was investigated. The broad bands around 254 nm are assigned to CT band of $\text{Eu}^{3+}-\text{O}^{2-}$. With the increasing of Eu^{3+} concentration, Eu^{3+} could occupy different sites, which leads to the broadening of CT band. A sharp band is observed in the region of 110–130 nm, which is related to the host absorption. The phosphors emit red luminescence centered at about 616 nm due to Eu^{3+} ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ both under 254 and 147 nm, but none of Eu^{2+} blue emission can be observed.

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1. Introduction

The luminescence of materials doped with rare-earth ions has been of a subject for investigations in the field of display for decades. The development of displays, such as liquid crystal displays (LCDs), field emission displays (FEDs), plasma display panels (PDPs) and thin film electro-luminescent devices (TFEL), has always been accompanied by improvements in the phosphor used. Great efforts have been made to discover new host materials as well as activators with high performance for phosphor applications [1–4]. Trivalent europium ions based phosphors play an important role, because Eu^{3+} -doped inorganic phosphors show potential applications in optical displays due to strong red emission from Eu^{3+} [5,6]. So a novel phosphor, Eu^{3+} -activated SrZnO_2 , may provide another red phosphor choice for these applications.

The crystal structure of SrZnO_2 was reported by Schnering and Hoppe [7]. SrZnO_2 belongs to the orthorhombic system with the space group $Pnma$. In SrZnO_2 , the ZnO_4 tetrahedrons share edges with each other and form waved layer. The Sr atoms are surrounded by seven oxygen atoms and locate at the cavity between the layers. To this structure, there is one site for the Sr atom, one for the Zn

atom, and two for the O atoms. Shunichi et al. [8] reported a new luminescent material, $\text{SrZnO}_2:\text{Ba}^{2+}, \text{Mn}^{2+}$, which emitted yellow color under 281–283 nm excitation. Yu et al. [9] reported $\text{SrZnO}_2:\text{Tb}^{3+}$, which may form two types of luminescence centers in blue and green color regions due to occupying different crystallographic sites. All results proved that SrZnO_2 could be a promising candidate for luminescent host lattice. In this present paper, $\text{SrZnO}_2:\text{Eu}^{3+}$ phosphors were synthesized by solid-state reaction, and their luminescence properties under ultraviolet (UV) and vacuum ultraviolet (VUV) excitation have been studied for fundamental interest and application in Hg-free lamp, PDPs and back lighting source.

2. Experimental

The starting materials for the preparation of $\text{SrZnO}_2:\text{Eu}^{3+}$ were SrCO_3 (99.5%), ZnO (99%) and Eu_2O_3 (99.99%). All powder samples were prepared by conventional solid-state techniques. Stoichiometric proportion of the starting materials was intimately mixed together and sintered at 1000 °C in platinum crucible in air for 2 h, then quenched to room temperature.

The phase of powder samples were identified by using Rigaku D/max-2400 X-ray diffractometer with Ni-filtered $\text{CuK}\alpha$ radiation (XRD). The morphology of the powders was examined by JEOL-5600 scanning electron microscope

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(SEM). Excitation and emission spectra were measured by Edinburgh Instruments FLS-920T with VM-504 vacuum monochromator using a deuterium lamp as the light source. The excitation spectra were corrected with sodium salicylate.

3. Results and discussion

All the powders have a white color in body. Fig. 1 illustrates XRD pattern of un-doped SrZnO₂ sintered at 1000 °C for 2 h. From the XRD pattern, it is found that the orthorhombic structure of SrZnO₂ with space group *Pnma* is well formed and all the peaks are due to SrZnO₂ single phase (JCPDF 41-0551). The lattice parameters of the sample are $a = 0.5848(5)$ nm, $b = 0.3361(6)$ nm and $c = 1.1418(2)$ nm. Furthermore, a series of phosphors SrZnO₂: x Eu³⁺ ($0.025 \leq x \leq 0.125$; x means Eu³⁺ doping concentration in SrZnO₂) were prepared in the same condition and second phase as well as obvious shifting of the diffraction peaks were not observed as Eu³⁺ doping concentration increasing, which means that when Eu³⁺ were introduced into the lattice, the crystal structure does not change largely.

Fig. 2 shows the typical SEM micrograph of the prepared SrZnO₂:Eu³⁺. All the sample particles prepared by the solid-state reaction have an elliptical shape with a diameter of about 1–3 μm, and slight agglomeration appears.

Fig. 3 shows excitation spectra of SrZnO₂: x Eu³⁺ ($0.025 \leq x \leq 0.125$) monitoring by 616 nm in UV region. The broad bands with the maximum at about 254 nm can be attributed to the charge transfer (CT) band from O²⁻ to Eu³⁺. The excitation peak at 395 nm is attributed to the ⁷F₀ → ⁵L₆ transitions of Eu³⁺, in addition to many other weak lines due to the various *f-f* transitions of Eu³⁺. With

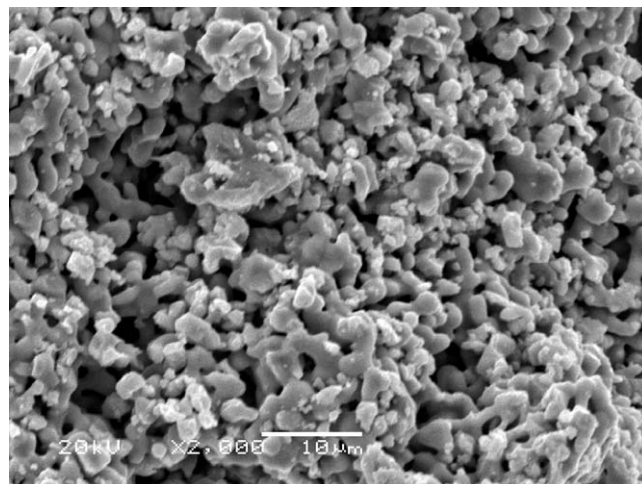


Fig. 2. SEM micrograph of SrZnO₂:Eu³⁺ particles.

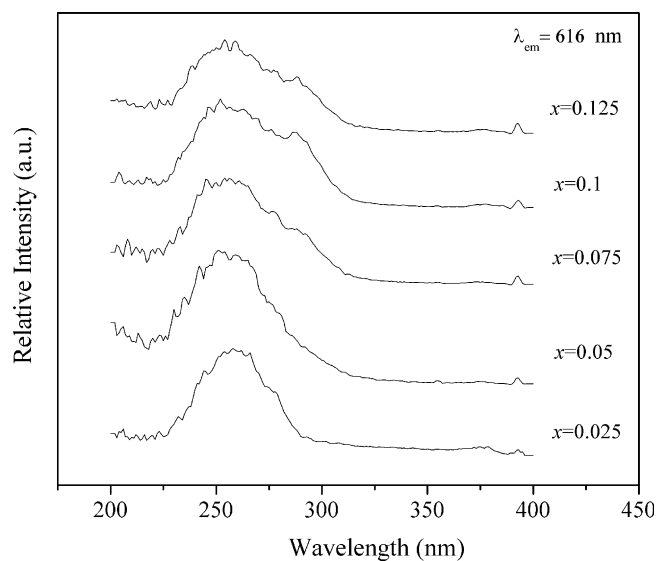


Fig. 3. Excitation spectra of SrZnO₂: x Eu³⁺ ($0.025 \leq x \leq 0.125$).

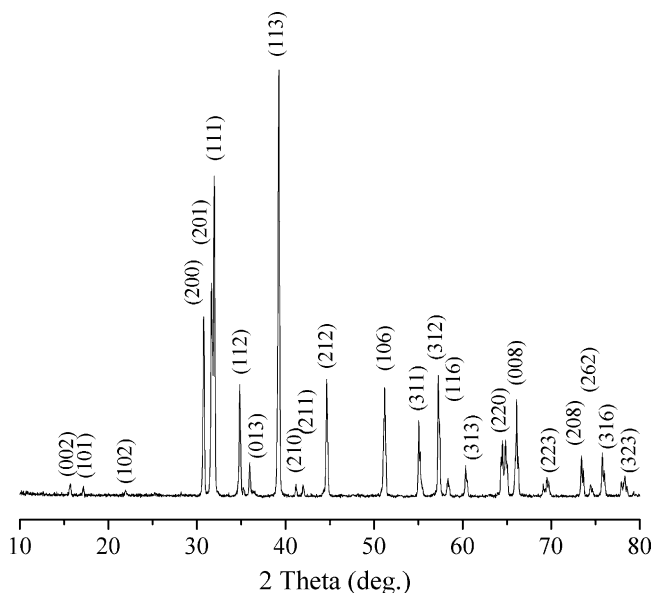


Fig. 1. XRD pattern of SrZnO₂ sintered at 1000 °C for 2 h.

the increasing of Eu³⁺ concentration, the CT band of Eu³⁺–O²⁻ is broadening gradually, while other bands change little. When $x > 5$ mol%, the band in the region from 220 to 320 nm could be the overlap of two bands with maxima at about 253 and 285 nm, respectively. It has been reported that for SrZnO₂:Ba²⁺, Mn²⁺, Mn²⁺ ions prefer to substitute Zn²⁺ sites apparently due to their similar ionic radii [8]. In Tb³⁺-activated SrZnO₂, Tb³⁺ ions may occupy both Sr²⁺ and Zn²⁺ crystallographic sites, since the difference of radius of Tb³⁺ and Sr²⁺ is similar to that of Tb³⁺ and Zn²⁺ (the ionic radii of Sr²⁺, Zn²⁺ and Tb³⁺ are 112, 74 and 92.3 pm) [9]. The ionic radii of Eu³⁺ is 95 pm, which is closer to that of Sr²⁺, so Eu³⁺ likely prefer to occupy the Sr²⁺ sites. But with the increasing of Eu³⁺, partially Eu³⁺ may occupy the sites of Zn²⁺. Eu³⁺ occupies two different surroundings, which results in the broadening of excitation bands.

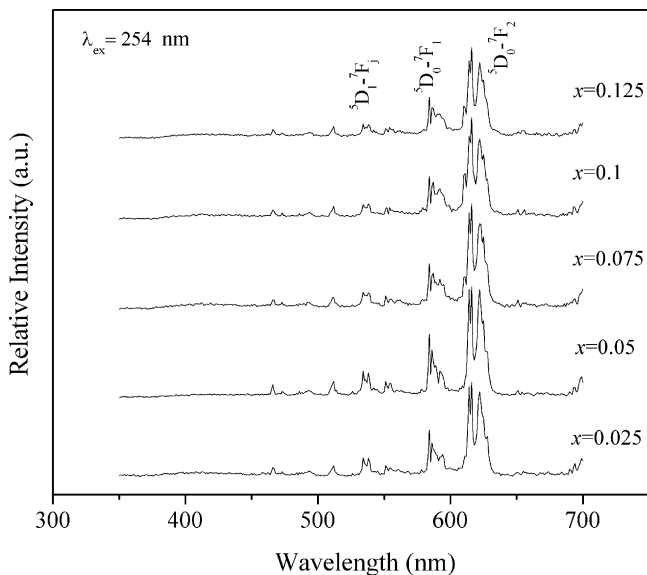


Fig. 4. Emission spectra of $\text{SrZnO}_2:x\text{Eu}^{3+}$ ($0.025 \leq x \leq 0.125$).

The phosphors of Eu^{3+} -activated SrZnO_2 are found to exhibit a red emission under UV excitation. Fig. 4 shows the emission spectra of $\text{SrZnO}_2:x\text{Eu}^{3+}$ ($0.025 \leq x \leq 0.125$) under 254 nm excitation. It can be seen from Fig. 4 that the spectra are dominated by the main lines at 616 nm due to the ${}^5D_0 \rightarrow {}^7F_2$ transition, and the peaks at 585 nm are due to the ${}^5D_0 \rightarrow {}^7F_1$ transition. The peaks from ${}^5D_0 \rightarrow {}^7F_2$ (electric-dipole transition) are stronger than that from ${}^5D_0 \rightarrow {}^7F_1$ (magnetic dipole transition), which indicates that Eu^{3+} occupies the sites with no inversion symmetry. In addition to that, there are some weak peaks in the range of 500–570 nm, which are assigned to the ${}^5D_1 \rightarrow {}^7F_j$ transitions. The emission spectra of phosphors enhance with the increased Eu^{3+} concentration up to $x = 5$ mol%, then decrease due to the concentration quenching. According to the structure of SrZnO_2 , the ZnO_4 tetrahedra form a layer, and the larger ions Sr^{2+} located at the cavity between the layers. The possible explanation is as follows: with increasing of Eu^{3+} concentration, Eu^{3+} partially substitutes the sites of Zn^{2+} , which can lead to the shortening of distances between Eu^{3+} and inducing the quenching of Eu^{3+} .

When Eu^{3+} is doped into SrZnO_2 , it could replace the X^{2+} (X represents Sr or Zn). In order to keep the charge balance, two Eu^{3+} should be needed to substitute for three X^{2+} . Hence, one vacancy defect represented as V_x'' with two negative charges and two positive defects of Eu_x^\bullet would be created. By thermal stimulation, the electrons in the vacancy defects of V_x'' would be transferred to Eu_x^\bullet sites and reduced Eu^{3+} to Eu^{2+} form. Former works have reported that some host lattice composed of the tetrahedral anion groups (PO_4 , BO_4 , AlO_4 and SiO_4) may reduce of $\text{Eu}^{3+} - \text{Eu}^{2+}$ in solid-state compounds, such as $\text{Ba}_3(\text{PO}_4)_2$, SrB_4O_7 , $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ and BaMgSiO_4 doped with Eu^{3+} [10–12]. In our system, there are the existences of ZnO_4 tetrahedra, but there are no trails of Eu^{2+} emission in the emission spectra. This result is deviated from the above

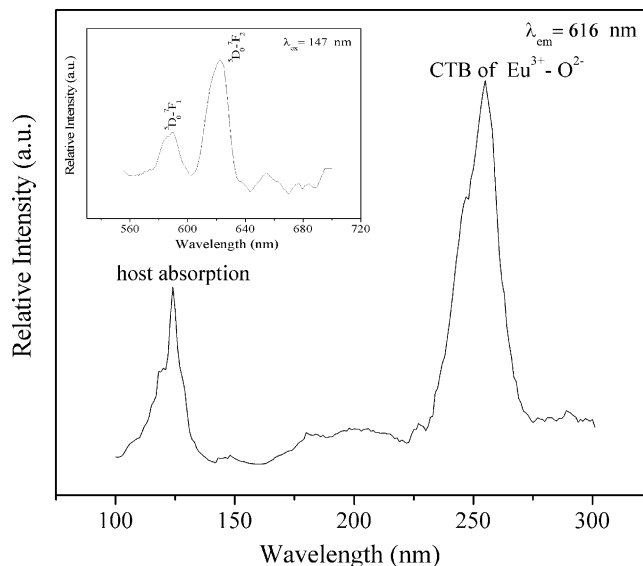


Fig. 5. Excitation spectrum of $\text{SrZnO}_2:5 \text{ mol\% } \text{Eu}^{3+}$.

conclusion, so the reduction rule of $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ needs to be modified and the mechanism of this reduction needs further investigations.

The VUV excitation spectrum of $\text{SrZnO}_2:5 \text{ mol\% } \text{Eu}^{3+}$ is recorded by monitoring the emission at 616 nm, as shown in Fig. 5. There are two bands in these spectra. One is located at VUV spectra range, around 110–130 nm with a sharp feature, and another broad band located at UV range, around 230–280 nm. The VUV band is weaker than the UV one. The VUV excitation band around 110–130 nm could be assigned to host absorption. The broad band in the region from 230 to 280 nm is attributed to CT band of $\text{Eu}^{3+} - \text{O}^{2-}$. Emission spectrum of $\text{SrZnO}_2:5 \text{ mol\% } \text{Eu}^{3+}$ ($\lambda_{\text{ex}} = 147 \text{ nm}$) is given in the inset of Fig. 5. The emission spectrum is similar to that under 254 nm excitation, but the shape of emission peaks exhibit broad band without splitting, which is because this phosphor has the inefficient absorption under 147 nm excitation, so large slit was applied in the testing. The characteristic luminescence is still due to transition of electric dipole transition ${}^5D_0 \rightarrow {}^7F_2$ of Eu^{3+} . Under 147 nm excitation, $\text{SrZnO}_2:5 \text{ mol\% } \text{Eu}^{3+}$ exhibits relatively weak red emission, and calculating the color coordinates gives $x = 0.601$, $y = 0.398$.

4. Conclusions

$\text{SrZnO}_2:\text{Eu}^{3+}$ phosphors with different Eu^{3+} concentration were prepared by solid-state reaction at 1000 °C for 2 h. The broadening of UV excitation spectra indicates that with the increasing of Eu^{3+} , Eu^{3+} could occupy two types of sites: one is the sites of Sr^{2+} and the other is the sites of Zn^{2+} in the structure of SrZnO_2 . The band at about 110–130 nm were observed in VUV region and assigned to the host absorption. The phosphors exhibit red emitting both under UV and VUV excitation. The reduction of $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ was not observed in this compound though it

belongs to un-equivalent substitution between Eu^{3+} and Sr^{2+} (Zn^{2+}).

Acknowledgments

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