

Preparation and luminescent properties of europium-activated YInGe₂O₇ phosphors

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Abstract

A novel red emitting phosphor YInGe₂O₇:Eu³⁺ has been synthesized using a vibrating milled solid-state reaction with metal oxides and the characterization and optical properties were investigated. The X-ray diffraction profiles showed that all of the peaks are attributed to the monoclinic YInGe₂O₇ phase as the Eu³⁺ ions doped, and the second phase of Eu₂Ge₂O₇ was observed in the XRD pattern when the Eu³⁺ concentration was 100 mol%. In the PL studies, excitation at 464 nm in terms of Eu³⁺ concentrations in (Y_{1-x}Eu_x)InGe₂O₇ powders shows that the (Y_{1-x}Eu_x)InGe₂O₇ phosphors display reddish luminescence at about 611 nm belonging to ⁵D₀ → ⁷F₂ electric dipole transition, and the time-resolved ⁵D₀ → ⁷F₂ transition presents a single exponential decay behavior. The saturation of emission intensity excited by intra-4f transitions occurs at a concentration of $x = 0.5$, indicating that the concentration quenching is active when the $x > 0.5$.

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1. Introduction

Oxide phosphors have recently gained much attention for applications such as screens in plasma display panels and field emission displays and for white color light emitting diodes because of the higher chemical stability of oxide phosphors relative to that of sulfide phosphors. Many studies have been conducted for developing new oxide phosphors in powder form suitable for full-color emissive displays [1–5]. Over the last decade, many oxide based phosphors were synthesized to improve luminescent performance, including color purity, emission intensity and quantum efficiency. Many efforts have been made to discover host materials as well as activators with high performance for phosphor applications [6,7].

Yttrium indium germanate (YInGe₂O₇) has the thortveitite structure with symmetry described by the space group *C2/m* (No. 12). This crystallizes in the monoclinic system, with cell

parameters $a = 6.8286 \text{ \AA}$, $b = 8.8836 \text{ \AA}$, $c = 4.9045 \text{ \AA}$. The In³⁺ and Y³⁺ cations occupy the same octahedral site forming a hexagonal arrangement on the *ab* planes [8]. In their turn, the hexagonal arrangements of InO₆/YO₆ octahedral layers are held together by sheets of isolated diorthogroups composed of a double tetrahedral sharing a common vertex. It is suggested that the YInGe₂O₇ possesses excellent optical properties. Rare earth ions have been extensively employed as activators for various phosphors. The Eu³⁺-doped compound emitting bright red light has been extensively used as phosphors in many fields [9–12], and the material shows typical f–f transitions of europium ions. For trivalent europium ions, a given optical center in different host lattice will exhibit different optical properties due to the changes of the surroundings of the center. The references concerning the role of the rare earth Eu³⁺ ion doped in YInGe₂O₇ have not yet been studied. In this investigation, YInGe₂O₇ is chosen to be a host material, and YInGe₂O₇ sample doped with different Eu³⁺ concentrations phosphors have been prepared by vibrating milled solid-state reaction process at 1200 °C in air, and the characterization and luminescent properties have also been examined.

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2. Experimental procedures

2.1. The preparation of samples

The Eu^{3+} -doped YInGe_2O_7 sample were prepared by vibrating milled solid-state reaction using Y_2O_3 , In_2O_3 , GeO_2 , and Eu_2O_3 powders. Starting materials with the purity of 99.99% were supplied from Aldrich Chemical Company, and Alfa Aesar. After being mechanically activated by grinding in a high energy vibro-mill for 15 min with zirconia balls in a polyethylene jar, the mixtures were calcined at 1200°C in air for 10 h.

2.2. Characterization

The effects of Eu^{3+} doping and thermal treatment on the structure were carefully studied by X-ray powder diffractometry (XRD, Rigaku Dmax-33 X-ray diffractometer) using $\text{Cu K}\alpha$ radiation with a source power of 30 kV and a current of 20 mA to identify the possible phases formed after heat treatment. Optical absorption spectra were measured at room temperature using a Hitachi U-3010 UV visible spectrophotometer. Both excitation and luminescence spectra of these phosphors were recorded on a Hitachi F-4500 fluorescence spectrophotometer using a 150 W xenon arc lamp as the excitation source at room temperature.

3. Results and discussions

3.1. Structure

Fig. 1 shows the X-ray powder diffraction pattern of YInGe_2O_7 doped with various Eu^{3+} concentrations calcined at 1200°C in air for 10 h. All of the peaks are attributed to the monoclinic YInGe_2O_7 phase. The full width of half maximum (fwhm) of these peaks seems to increase and the crystallinity of $\text{YInGe}_2\text{O}_7:\text{Eu}^{3+}$ becomes worse with the increase in Eu^{3+} concentration. The second phase of $\text{Eu}_2\text{Ge}_2\text{O}_7$ was observed in the XRD pattern when the Eu^{3+} concentration was 100 mol%. The trivalent europium ions (0.947 \AA) [13] are introduced to substitute the trivalent yttrium ions (0.9 \AA) [13] in $(\text{Y, Eu})\text{InGe}_2\text{O}_7$ system. The variations are almost the same for Eu^{3+} and Y^{3+} ion radius, so they can form a solid solution easily. This indicated that the grain sizes do not change significantly with the increase

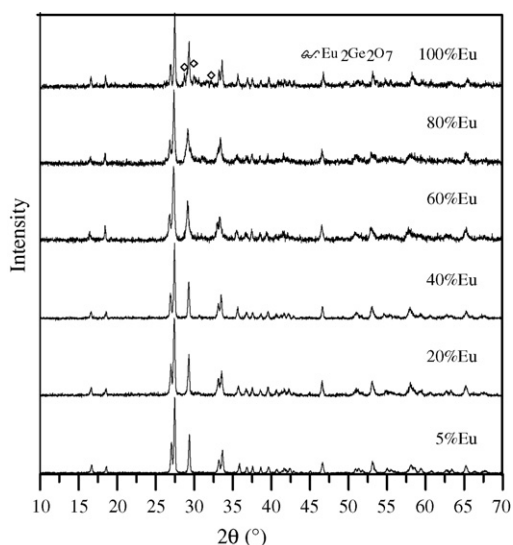


Fig. 1. The X-ray diffraction patterns of the YInGe_2O_7 doped with different Eu^{3+} concentrations calcined at 1200°C in air for 10 h.

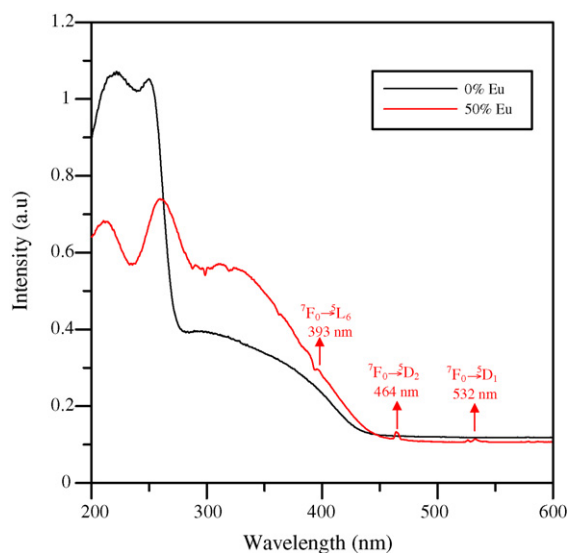


Fig. 2. Absorption spectra of undoped and 50 mol% Eu -doped YInGe_2O_7 powders calcined at 1200°C in air for 10 h.

in Eu^{3+} concentration. Additionally, there are no charge compensation issues for the Eu^{3+} ion substituting the Y^{3+} ion in YInGe_2O_7 lattice, as both have the same valence.

3.2. Optical properties

3.2.1. Absorption spectrum

Fig. 2 is the optical absorption spectrum for pure YInGe_2O_7 doped with 50 mol% Eu^{3+} concentrations which were measured at room temperature. The series of sharp absorption bands between 200 and 290 nm correspond to the charge transfer between the In^{3+} and O^{2-} ions of the InO_6 anionic group in the host lattice. The absorption behavior between 290 and 450 nm is caused by the GeO_4 anion. After europium was added to YInGe_2O_7 , the compounds exhibited a charge transfer state (CTS) between 250 and 350 nm, caused by the electron transferred from the oxygen 2p orbital to the empty 4f orbital of europium, which may be described as ligand-to- Eu^{3+} charge-transfer transitions (LMCT) [14]. The weak peaks in the range from 350 to 580 nm are associated with the typical f-f transitions of the Eu^{3+} ions that appeared at 393, 464 and 532 nm, which were attributed to the transition from the ${}^7\text{F}_0$ ground state to the charge transfer state corresponding to ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$, ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ and ${}^7\text{F}_0 \rightarrow {}^5\text{D}_1$, respectively. Additionally, the absorption intensity of CTS is stronger than that of intra-4f transitions.

3.2.2. Excitation and emission spectrum

For rare earth Eu^{3+} ions, the electron transition caused by excitation can be classified into two types: (1) charge transfer transition, CTS; (2) intra-4f transition [15]. The excitation spectra of the red emission at 611 nm of $\text{YInGe}_2\text{O}_7:\text{Eu}^{3+}$ phosphors obtained in the spectral region from 200 to 550 nm are shown in Fig. 3. The spectrum of $\text{YInGe}_2\text{O}_7:\text{Eu}^{3+}$ exhibits a wide band in the UV region centered at about 260 nm, and several groups of sharp lines between 300 and 550 nm. The weak wide absorption band originates from the ${}^7\text{F}_0$ ground state transitions to the

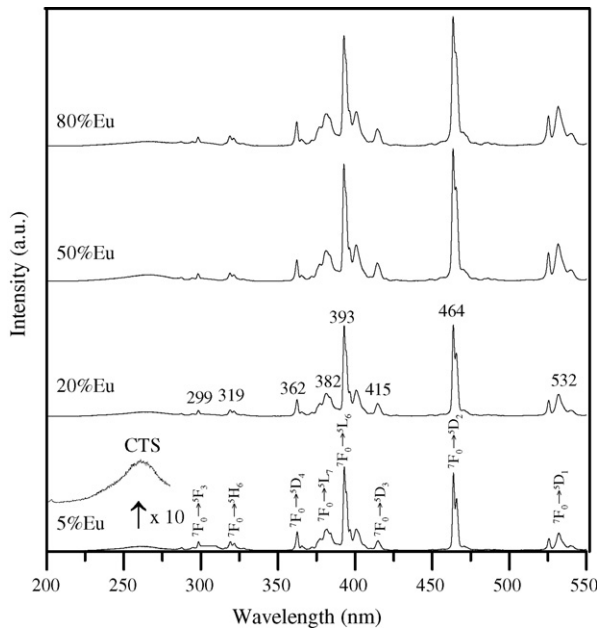


Fig. 3. Photoluminescence excitation spectra of YInGe_2O_7 doped with various Eu^{3+} concentrations calcined at 1200°C in air for 10 h ($\lambda_{\text{em}} = 611$ nm).

CTS band due to the europium–oxygen interactions, which may be ascribed to an electron transfer from an oxygen 2p orbital to an empty 4f orbital of europium. The sharp excitation peaks between 300 and 550 nm correspond to the Eu^{3+} intra-4f transitions. The intensities of CTS transitions are less than that of intra-4f transition for YInGe_2O_7 doped with Eu^{3+} ions. The CTS intensities seem to decrease, but the intensities of intra-4f transition increase along with the Eu^{3+} ions concentrations. Furthermore, as seen in Fig. 3, the strongest peak is located at 464 nm corresponding to the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ transition, which is opposite to the observation in the absorption spectrum. It demonstrates that the optimum emission performance was provided by the excitation at intra-4f energy levels at the high Eu^{3+} concentration. Because 464 nm is the strongest absorption peak for excitation, the 464 nm was chosen to be the excitation wavelength to observe the emission behavior for $\text{YInGe}_2\text{O}_7:\text{Eu}^{3+}$ phosphors. Fig. 4 is the photoluminescence emission spectra ($\lambda_{\text{ex}} = 464$ nm) for (a) $\text{YInGe}_2\text{O}_7:5$ mol% Eu and (b) the ${}^5\text{D}_1 \rightarrow {}^7\text{F}_0$ transition relative intensity of $\text{YInGe}_2\text{O}_7:x$ mol% Eu phosphors calcined at 1200°C in air for 10 h. In Fig. 4(a), the emission wavelengths are all in the red light region, which corresponds to 578 nm (${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$), 587 nm (${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$), 611 nm (${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$), 649 nm (${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$), and 700 nm (${}^5\text{D}_0 \rightarrow {}^7\text{F}_5$) for intra 4f⁶ transition.

According to the studies by Judd [16] and Ofelt [17], due to the absence of a center of symmetry, the 4f orbitals mix with the opposite parity orbitals resulting in the appearance of electric-dipole transitions (${}^5\text{D}_0 \rightarrow {}^7\text{F}_J, J=2n$) [18,19]. The emission wavelength of 611 nm for ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition is an electric-dipole allowed transition, and its intensity is hypersensitive to the variation of the local structure environment of the Eu^{3+} ions. While ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ emission is a magnetic-dipole allowed transition, its intensity hardly changes with the local structure symmetry of the Eu^{3+} ions [15]. Besides, the appearance of

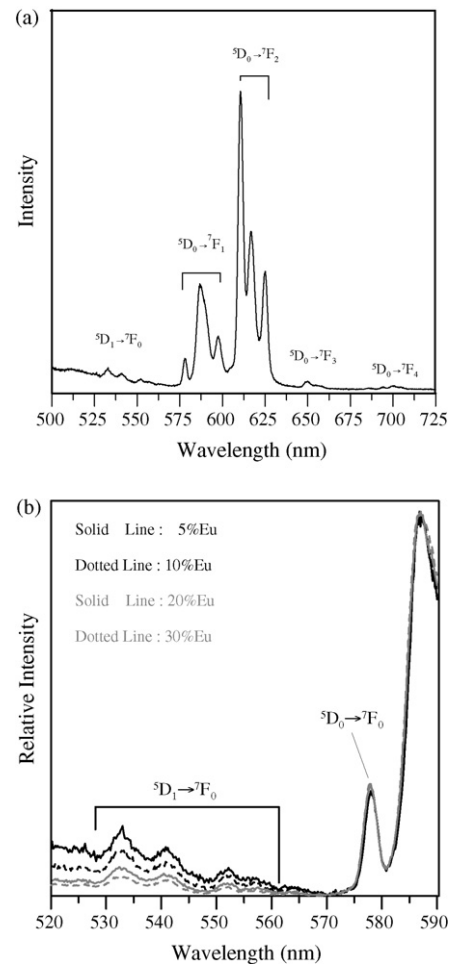
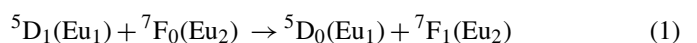


Fig. 4. Photoluminescence emission spectra ($\lambda_{\text{ex}} = 464$ nm) for (a) $\text{YInGe}_2\text{O}_7:5$ mol% Eu and (b) the relative intensity of ${}^5\text{D}_1 \rightarrow {}^7\text{F}_0$ transition for $(\text{Y}_{1-x}\text{Eu}_x)\text{InGe}_2\text{O}_7$ phosphors calcined at 1200°C in air for 10 h.

${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ transition is due to the J – J mixing by the crystal field effects [20]. The ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transitions appear to have the maximum intensity value in emission spectra. For the YInGe_2O_7 structure, the In^{3+} and Y^{3+} cations occupy the same octahedral site forming a hexagonal arrangement on the ab planes [8]. The hexagonal arrangements of InO_6/YO_6 octahedral layers are held together by sheets of isolated diorthogroups composed of a double tetrahedral sharing a common vertex and every two GeO_5 hexahedrons form the Ge_2O_9 structure via an oxygen ion sharing which introduces the YO_6 octahedral layer disorder and causes the non-symmetric center of lattice due to internal stress. It is guessed that the Eu^{3+} ions occupy such lattices for the non-symmetric center to cause the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transitions to appear at a maximum value.

In general, it is difficult to find the ${}^5\text{D}_{1,2} \rightarrow {}^7\text{F}_J$ ($J = 1, 2, 3, 4$) transition for Eu^{3+} ion doped phosphors, because the transition transfers the energy via a relaxation process to form a cross-relaxation process [15,21,22]. The following cross-relaxation may occur:



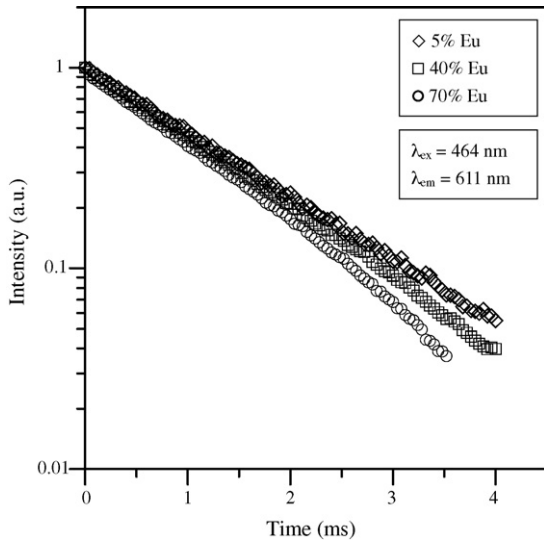


Fig. 5. The decay curve of YInGe₂O₇ doped with different concentrations of Eu³⁺ ion under excitation at 464 nm. The signals were detected at 611 nm.

When the Eu³⁺ ion concentration is high enough, the higher level transition will disappear gradually and only the ⁵D₀ → ⁷F₁ transition will remain. In Fig. 4(b), it is obvious that the ⁵D₁ → ⁷F₀ transition decreases gradually with the increasing Eu³⁺ concentration.

3.2.3. Decay curve and decay time

In many rare earth element activated phosphors, it is reported that there are more than one kind of site for activators to occupy [23,24], including both surface sites and lattice sites. The decay behavior of emission could be used to identify how many emission mechanisms are employed in the luminescence process. The decay curve of ⁵D₀ → ⁷F₂ transition under the excitation at 464 nm of (Y_{1-x}Eu_x)InGe₂O₇ powders is shown in Fig. 5. The time decreases as Eu³⁺ concentration increasing, and the curve demonstrates almost perfect single-exponential decay, revealing that the presence of the Eu³⁺ environment is unique in accordance with the crystal structure and the decay mechanism of the ⁵D₀ → ⁷F₂ transition is a single decay component between Eu³⁺ ions only.

The luminescence intensities of phosphor materials are always dependent on the doping concentrations. The emission intensity and decay time of ⁵D₀ → ⁷F₂ transition with different Eu³⁺ concentrations under the excitation at 464 nm is shown in Fig. 6. In the current study, the concentration quenching effect was also observed. The emission intensity of ⁵D₀ → ⁷F₂ transition increases with increasing Eu³⁺ concentration in the lower Eu³⁺ concentration region until the saturated PL intensity is reached and then diminishes. The probability of an energy transfer among Eu³⁺ ions increases when the Eu³⁺ concentration increases [25]. It reached a maximum when the Eu³⁺ concentration was 50 mol% and decreased with the increasing Eu³⁺ concentration, which indicated that the concentration quenching is active when $x > 0.5$.

Moreover, the decay time for (Y_{1-x}Eu_x)InGe₂O₇ phosphors under the excitation at 464 nm indicated that the time decreases

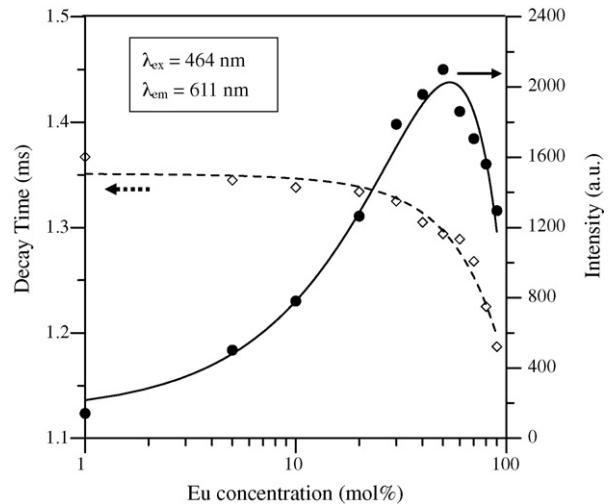


Fig. 6. The emission intensity and decay time of Eu³⁺ as a function of doping concentration under excitation at 464 nm. The signals were detected at 611 nm.

from 1.37 to 1.185 ms as Eu³⁺ concentration increases from 0 to 90 mol%. According to a previous study [26], the lifetime τ of a term is related to the radiative and nonradiative transition rates ($k_{\text{radiative}}$, $k_{\text{nonradiative}}$) by

$$\tau = \frac{1}{k_{\text{nonradiative}} + k_{\text{radiative}}} \quad (2)$$

The ⁵D₀ → ⁷F₂ transition considered is a hypersensitive forced electric dipole transition which is sensitive to changes in the crystal field. The decreasing lifetime must be caused by the increasing nonradiative transition, because the crystallinity of the YInGe₂O₇ host decreases with the increasing Eu³⁺ concentration. This might be caused by the formation of the second phase, and this conclusion is agreement with the observation by XRD analysis.

4. Conclusions

A new red emitting Eu³⁺ ion doped YInGe₂O₇ phosphor was synthesized by vibrating milled solid-state reaction and its luminescence properties have been investigated. The second phase of Eu₂Ge₂O₇ was observed in the XRD pattern when the Eu³⁺ concentration was 100 mol%. The phosphor shows a reddish emission at 611 nm under excitation at 464 nm, which belongs to the electric dipole transition (⁵D₀ → ⁷F₂) of Eu³⁺ ions. The time-resolved ⁵D₀ → ⁷F₂ transition presents a single exponential decay equation under excitation at 464 nm, because most Eu³⁺ ions just occupy the distorted octahedral sites in the (Y_{1-x}Eu_x)InGe₂O₇. The optimum concentration of Eu³⁺ ions showing the maximum photoluminescence intensity was 50 mol%, and quenching occurred for higher concentrations.

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