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Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

The enhancement of luminescence in Co-doped cubic Eu_2O_3 using Li^+ and Al^{3+} ions

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ARTICLE INFO

Article history:

Received 24 November 2010

Received in revised form

21 May 2011

Accepted 9 June 2011

Available online 20 June 2011

Keywords:

Cubic Eu_2O_3

Co-doping

Enhancement

Luminescence

XPS

Raman

ABSTRACT

The co-doping of Li^+ and Al^{3+} ions drastically enhances the luminescence of cubic Eu_2O_3 . The integrated emission intensity of $^5\text{D}_0 \rightarrow ^7\text{F}_j$ bands ($J=1-4$) at 580–710 nm increases by a factor of about 6.7 in the co-doped Eu_2O_3 compared to the un-doped Eu_2O_3 . In order to confirm that the co-doped ions were actually incorporated into the host lattice, the structural characteristics were studied using Raman spectroscopy, XPS, XRD, photoluminescence lifetime, and an SEM. These analyses consistently indicate a certain structural evolution in their results with an increase in the co-doping concentration. Variations in the crystal structure, the crystal morphology, and the intensity variation of the Raman modes at 465 and 483 cm^{-1} are presented as the evidences showing the incorporation of the co-doped ions into the host. The luminescence enhancement is discussed in terms of concentration quenching, reduction of defect sites, and the modification of the local symmetry of the Eu^{3+} ions, especially in the inversion symmetry sites.

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1. Introduction

Trivalent Eu ions have been utilized in many practical applications, such as lighting fixtures, emissive displays, and LEDs. Numerous optical spectroscopic and luminescence studies have been focused on the Eu^{3+} ions. Nevertheless, only a few studies [1–3] have been done regarding the luminescence properties of bulk Eu_2O_3 . The reason for the scarcity of Eu_2O_3 studies is mainly ascribed to the very low luminescent intensity of Eu_2O_3 regardless of its crystal structure.

From a practical application aspect, pure Eu_2O_3 itself cannot be used due to its high material cost. However, it is still an interesting subject to find a method to improve the luminescent intensity of Eu_2O_3 , which has very low intensity in its pure form. The understanding of how to enhance the luminescence intensity of Eu_2O_3 can be utilized for the development of brighter and higher color quality phosphors.

The enhancement of the luminescent efficiency and the improvement of the color purity are the most important issues in phosphor materials. The factors necessary for improving the luminescent intensity of most phosphors are yet to be fully understood. The

important parameters reported hitherto regard multi-ion doping, the defect levels, the electronic states, and the crystallinity [4,5].

In cubic Eu_2O_3 , the origin of the low luminescent intensity is found in the concentration quenching, which takes place as a consequence of the excitation energy transfer to a killer or quenching sites. Structural defects produced during the manufacturing process and chemical trace impurities introduced from raw materials can be the quenching centers [6]. Even with a very low trap concentration, excited energy can be transferred to the traps easily via the exchange interaction between the Eu^{3+} ions ($< 5 \text{ \AA}$) and dipole–dipole interaction ($> 5 \text{ \AA}$). In Eu_2O_3 the excited energy can migrate more rapidly than in other phosphors through the two interaction pathways and so it has a very low luminescent emission.

In addition, when the Eu^{3+} ions occupy the centrosymmetric sites in the cubic Eu_2O_3 , only the magnetic–dipole transition ($\sim 595 \text{ nm}$, $^5\text{D}_0 \rightarrow ^7\text{F}_1$) is allowed. These have a very low transition probability. When the Eu^{3+} ions are situated at the noncentrosymmetric sites, both the prominent electric dipole transition ($\sim 613 \text{ nm}$, $^5\text{D}_0 \rightarrow ^7\text{F}_2$) and the magnetic–dipole transition are allowed [7]. Hence the local symmetry of Eu^{3+} ions is very important for the luminescence efficiency in Eu_2O_3 .

The substitution of aliovalent ions in the phosphors is known to modify the crystal symmetry of the host lattice and/or introduce defects, such as vacancies [8,9]. When the host lattice ions are replaced by either aliovalent ions or isovalent ions with different

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ionic sizes, the local symmetry of the activators is modified. Even when the host crystal symmetry remains the same after substitution, the local crystal environment of the activator Eu^{3+} can be modified to a lower symmetry, e.g., to a non-centered symmetry from a centered symmetry due to the ion size difference as well as the defects such as oxygen vacancies [8,9]. This can cause the luminescent intensity to be increased.

In thin film phosphors $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ ($\text{RE}=\text{Y}, \text{Gd}$), Li-doping was suggested to improve luminescence efficiency [10,11]. In these reports the enhanced luminescence was ascribed to the improved crystallinity and increased surface roughness of the thin films. In addition, the local crystal environment of Eu^{3+} was considered as an important parameter for the luminescence efficiency.

In this study the cubic Eu_2O_3 (SG Ia-3) was selected for verifying the mechanism of luminescence enhancement with the doping in the sesquioxides. In cubic Eu_2O_3 the Eu^{3+} ions occupy two different symmetry sites, i.e., centrosymmetry (S_6) and non-centrosymmetry (C_2). The centrosymmetric sites can be locally modified to a noncentrosymmetric nature by co-doping. When the prohibited electric dipole transition ($\sim 613 \text{ nm}$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$) at the centrosymmetric sites is allowed, then the luminescence efficiency of the cubic Eu_2O_3 would be improved.

We doped Li^+ and Al^{3+} into cubic Eu_2O_3 in order to modify the local crystal symmetry of the Eu^{3+} ions and characterized the luminescence properties and the structural characteristics, such as photoluminescence (PL) lifetime, the valence charge state, the crystal structure, the lattice vibration mode, and the crystal morphology. These parameters are discussed as they relate to the luminescence enhancement of the bulk Eu_2O_3 co-doped with Li^+ and Al^{3+} .

2. Experiment

The phosphor samples were prepared using a solid state reaction method. Commercially available reagents, Eu_2O_3 (99.9% STREM Co.), Li_2CO_3 , and nano-sized Al_2O_3 (AKP-50, Sumitomo), were used for the raw materials. The raw Eu_2O_3 powder possessed a cubic crystal structure. Three types of samples were prepared: co-doped with Li^+ and Al^{3+} , mono-doped with either Li^+ or Al^{3+} , and non-doped. For the Li^+ and Al^{3+} co-doping, a low melting compound of Li_5AlO_4 (JCPDS #70-0432) was prepared in advance as the doping material and mixed into the Eu_2O_3 powder. The chemical formula of the co-doped sample was $\text{Eu}_2\text{O}_3:\text{xLi}_5\text{AlO}_4$ ($\text{x}=0\text{--}0.25, 4.0$).

The mono-doped samples were prepared by mixing the Eu_2O_3 powder with either Al_2O_3 or Li_2CO_3 . The raw materials were mixed thoroughly using a mortar with added ethyl alcohol and then calcined in air at 600°C for 5 h. The calcined powders were reground and re-fired at 900°C in air for 5 h. The fired samples were cooled in the furnace. The photoluminescence spectra were obtained using a vacuum ultraviolet PL measurement system (PS-PLUI-XWP1400, PSI) at room temperature. The evolution of the crystal morphology was observed using a FE-SEM. The X-ray data for the Rietveld refinements were taken using the theta–2theta scan method with a step size of 0.02° and a count time of 5 s. The crystal structural parameters were analyzed by the Fullprof software using the X-ray data.

Raman measurements were made with a backscattering geometry using a JY LabRam HR fitted with a liquid-nitrogen cooled CCD detector. The spectra were collected under ambient conditions using the 514.5 nm line of an argon-ion laser. The laser power on the sample was kept at 50.5 mW . The XPS measurements were carried out by an AXIS NOVA (Kratos) X-ray Photoelectron Spectrometer at the Korea Research Institute of Chemical Technology. The Al $K\alpha$ line (1486.6 eV) was used for the analysis.

The spectra were recorded using a high resolution analyzer utilizing 20 eV pass energy.

For the measurement of PL decay rate, another PL measuring system was used as follows. A pulsed frequency doubled Nd:YAG laser, which operated at 532 nm , was used as an excitation source of PL. The pulsed 532 nm laser was utilized to record the time evolution of PL. The time-averaged power supplied on samples was $\sim 1 \text{ mW}$ from the 532 nm pulsed laser with pulse duration of $\sim 1 \text{ ns}$. The size of the beam focused on samples was $\sim 0.1 \text{ mm}$. PL was collected in a back-scattering configuration and was dispersed by a 50 cm single grating monochromator after passing through a holographic notch filter to remove elastically scattered laser light. Any attempt to correct the spectral response of the equipment was not performed. Time-resolved PL was obtained using a thermoelectrically cooled photo-multiplier tube and the ancillary electronics including a multi-channel scaler. All the measurements were performed at room temperature.

3. Experiment results

3.1. Photoluminescence (PL) characteristic

The PL spectra of the three types of samples, co-doped (Li^+ and Al^{3+}), mono-doped (Li^+ or Al^{3+}), and un-doped, are represented in Fig. 1. In the excitation spectra the broad band with a peak centered at about 285 nm represents the charge transfer state (CTS) band of the $\text{Eu}\text{--}\text{O}$ bonds [7]. The $4f^6 \rightarrow 4f^55d^1$ transition of the Eu^{3+} ions is known to appear at a higher energy level ($> 50 \times 10^3 \text{ cm}^{-1}$) than that found for the CTS level [12,13]. In the excitation spectra found in Fig. 1(a), the sharp lines between 323 and 480 nm correspond to the f–f transitions from the ${}^7\text{F}_0,1$ ground states: ${}^7\text{F}_0,1\text{--}{}^5\text{D}_{2-4}$, ${}^7\text{F}_0,1\text{--}{}^5\text{G}_{2-6}$, ${}^7\text{F}_0,1\text{--}{}^5\text{H}_{4-7}$, and ${}^7\text{F}_0,1\text{--}{}^5\text{L}_{6-7}$ [14]. The intensity level of the f–f transition band is similar to that of the CTS band.

In the emission spectra (Fig. 1(b)) the dominant peak centered at 612 nm is the ED transition (${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$). The small peak at 595 nm is the magnetic-dipole transition (${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$). The undoped- Eu_2O_3 sample shows a very low luminescent intensity. Even after annealing the un-doped- Eu_2O_3 at the elevated temperature range of $1100\text{--}1400^\circ\text{C}$, the PL emission intensity remains very low compared to the co-doped samples as shown in Fig. 2. In this figure the PL emission spectra of the un-doped Eu_2O_3 are compared to the co-doped Eu_2O_3 ($\text{x}=0.13$).

However, the effect of doping on the PL intensity in Eu_2O_3 is quite drastic. Not only the doping concentration but also the type of doping ions critically affects the luminescent intensity, as represented in Fig. 1. In the co-doped sample, $\text{Eu}_2\text{O}_3:\text{xLi}_5\text{AlO}_4$ ($\text{x}=0\text{--}0.25, 4.0$), the luminescent intensity increases drastically and shows a maximum at $\text{x}=0.13$. The integrated emission intensity of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ bands ($j=1\text{--}4$) at $580\text{--}710 \text{ nm}$ increases by a factor of about 6.7 compared to the un-doped Eu_2O_3 . Further increasing the co-dopant $\text{x} > 0.13$ results in the intensity decrease.

When the co-doped samples ($\text{x}=0.03\text{--}0.25$) and the un-doped samples are excited under the same excitation light source, the co-doped ones appear surpassingly bright compared to the un-doped ones even to our naked eyes. The un-doped samples appear dark to our eyes because the relative brightness of the co-doped samples is very high compared to the un-doped ones.

The Al^{3+} mono-doped ($\text{Eu}_2\text{O}_3:0.1\text{Al}^{3+}$) sample shows a lower emission intensity than that of the un-doped one. Contrary to the Al^{3+} mono-doping, the Li^+ mono-doped ($\text{Eu}_2\text{O}_3:0.1\text{Li}^+$) sample has a substantially high luminescent intensity. The luminescent intensity is similar to that of the co-doped one with $\text{x}=0.01$ (xLi_5AlO_4).

The time evolution of the PL for the three samples ($\text{x}=0, 0.01, 0.25$) with 532 nm excitation is shown in Fig. 3(a). We see that

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