

Luminescence properties of $\text{Eu}^{3+} : \text{RE}_2\text{O}_3$ [RE = Gd, Y, La] nanocrystallines prepared by solvothermal reaction method

Jong Won Chung^a, Hyun Kyoung Yang^a, Byung Kee Moon^a, Byung Chun Choi^a, Jung Hyun Jeong^{a,*} and Kwang Ho Kim^{b,*}

^aDepartment of Physics, Pukyong National University, Busan 608-737, Korea

^bSchool of Materials Science and Engineering, Busan National University, Busan 609-735, Korea

Eu^{3+} -doped RE_2O_3 (RE = Gd, Y and La) phosphors were prepared by solvothermal reaction method and their crystalline structure, phase transformation and surface morphologies were investigated by using X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM). The obtained $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ phosphors are nanocrystalline-sized. The luminescence properties of Eu^{3+} ions in different host materials, namely, Gd_2O_3 , Y_2O_3 and La_2O_3 have been investigated. PACS number: 32.50.+d, 78.55.-m, 81.40.Tv.

Key words: Gd_2O_3 ; Eu^{3+} , Y_2O_3 ; Eu^{3+} , La_2O_3 ; Eu^{3+} , Nanophosphors, Solvothermal

Introduction

Luminescent powders play an important role as functional materials in high-resolution devices such as field emission displays (FEDs) [1], plasma display panels (PDPs) [2] and cathode-ray tubes (CRT) [3]. Trivalent Rare-earth oxides [RE_2O_3 (RE = Y, Gd, La)] are the promising host material for efficient luminescent phosphors [4]. In the field of luminescence, phosphors based on gadolinium compounds also play an important roles because the Gd^{3+} ion ($^4\text{F}_7$, ^8S) has its lowest excited levels at a relatively high energy, which is due to the stability of the half filled shell ground state [5]. On the other side, nanosize particles have been extensively studied and have become a research focus in terms of both their fundamental and technological importance [6]. This is particularly true in the case of luminescent materials because of a quantum confinement effect which leads to novel optoelectronic properties. Emission lifetime, luminescence quantum efficiency and concentration quenching have been found to depend strongly on the particle size in the nanometer-sized range [7, 8] and high efficiencies and ultrafast recombination times have been observed in nanometer-sized nanocrystals [9]. Previous studies reported on the preparation of nano-sized phosphor materials using a solid-state reaction [10, 11], co-precipitation methods [12, 13], sol-gel method [10, 14-18], spray pyrolysis, chemical vapor deposition (CVD) [19], and solvothermal reaction methods. Among them, solvothermal reaction method is

one of the most prominent processes for controlling the particle size, morphology and distribution of phosphor particles, resulting in efficient luminescent properties.

This paper reports the synthesis of nano-size $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ [RE = Gd, Y, and La] phosphors by using a simple and economical solvothermal reaction method. The structural and luminescence properties of these phosphors were studied.

Experiments

The $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ ($\text{Eu}^{3+} = 0.03$ mol, RE = Gd, Y and La) phosphors were synthesized using a solvothermal reaction method. $\text{Gd}(\text{NO}_3)_3$, $\text{Y}(\text{NO}_3)_3$, $\text{La}(\text{NO}_3)_3$ and $\text{Eu}(\text{NO}_3)_3$ were used as starting materials and dissolved in 2-PrOH. The final mixture was transferred into a teflon-bowl stainless steel autoclave with a capacity of 40 ml and then sealed. The autoclave was maintained at 230 °C for 10 h with magnetically stirred, and then cooled naturally to room temperature. The samples were dried at 50 °C for 24 h and sintered at 1200 °C for 5 h in air.

The obtained powders were analyzed by X-ray diffraction (XRD, Philips X'pert/MPD) patterns using $\text{Cu K}\alpha$ ($\lambda = 0.15405$ nm) radiation. The crystalline morphology and size of the obtained samples were observed by a field emission-scanning electron microscopy (FE-SEM, JSM-6700F, JEOL). The PL spectra were measured at room temperature using a luminescent spectrophotometer (PTI, Laser Strobe, TM4) with a 75W Xe-lamp as the excitation source.

Results and discussion

The crystalline and the surface morphology of phosphors are well known to have a strong effect on the

*Corresponding author:

Tel : +82 51 629 5564; +82 51 510 2391

Fax: +82 51 629 5549; +82 51 510 3660

E-mail: jhjeong@pknu.ac.kr; kwhokim@pusan.ac.kr

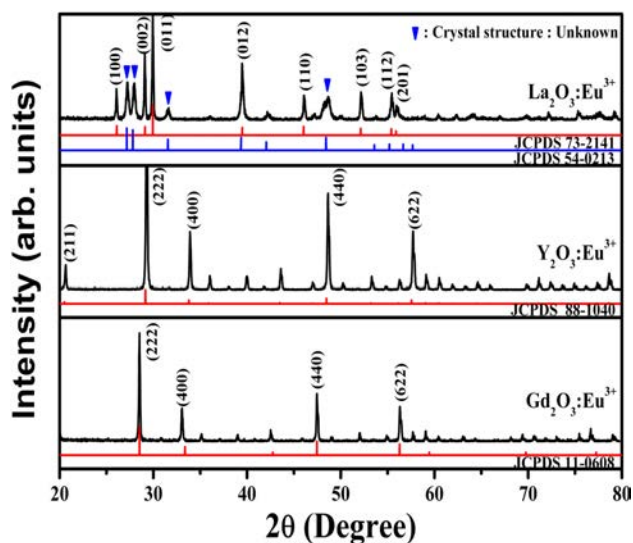


Fig. 1. XRD patterns of $\text{RE}_2\text{O}_3 : \text{Eu}^{3+}$ ($\text{RE} = \text{Gd}, \text{Y}$ and La) nanopowders.

PL intensity [20]. Fig. 1 shows the XRD patterns of $\text{RE}_2\text{O}_3 : \text{Eu}^{3+}$ phosphors sintered at 1200°C along with standard JCPDS data. Four main peaks were observed in the XRD patterns of $\text{Gd}_2\text{O}_3 : \text{Eu}^{3+}$ and $\text{Y}_2\text{O}_3 : \text{Eu}^{3+}$ phosphors. All the observed peaks were assigned to the cubic structure of Gd_2O_3 (JCPDS card 11-0608) and Y_2O_3 (JCPDS card 88-1040). However, $\text{La}_2\text{O}_3 : \text{Eu}^{3+}$ phosphor showed hexagonal structure which is found in good agreement with the JCPDS card 73-2141.

Fig. 2 shows FE-SEM images of the $\text{RE}_2\text{O}_3 : \text{Eu}^{3+}$ powders. The samples showed different morphologies. It can be seen that all the samples mainly showed the spherical like similar morphology. The average particle size of $\text{Gd}_2\text{O}_3 : \text{Eu}^{3+}$ nanopowders is larger than that of

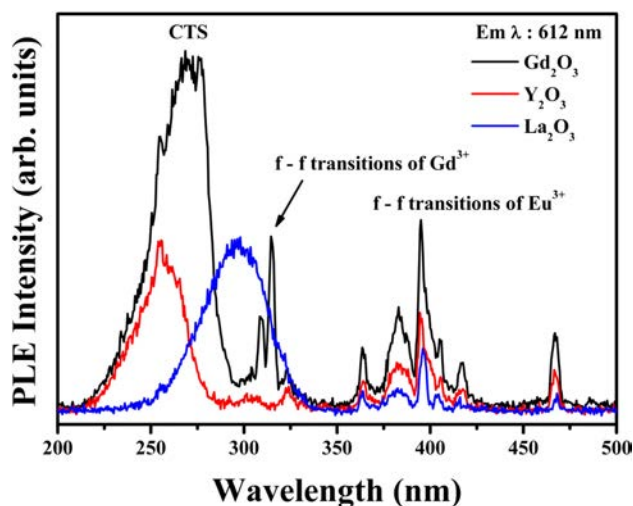


Fig. 3. Photoluminescence excitation spectra of $\text{RE}_2\text{O}_3 : \text{Eu}^{3+}$ phosphors.

the other samples. Due to the increased particle size, the density of grain boundaries in the $\text{Gd}_2\text{O}_3 : \text{Eu}^{3+}$ powders is smaller than that of the other powders. Therefore, the $\text{Gd}_2\text{O}_3 : \text{Eu}^{3+}$ powder with fewer grain boundaries is expected to exhibit better PL properties.

Fig. 3 shows the comparisons of the room temperature photoluminescence excitation (PLE) of $\text{RE}_2\text{O}_3 : \text{Eu}^{3+}$ nanopowders for different host materials. The $\text{Gd}_2\text{O}_3 : \text{Eu}^{3+}$ nanopowders showed a wide band between 220 and 290 nm with a peak at about 264 nm, and that of $\text{Y}_2\text{O}_3 : \text{Eu}^{3+}$ nanopowders showed a wide band between 220 and 270 nm with a peak at about 250 nm. In case of the $\text{La}_2\text{O}_3 : \text{Eu}^{3+}$ nanopowders, the PLE spectra showed a wide band between 240 and 340 nm with a peak at 290 nm. These bands are due to the excitation

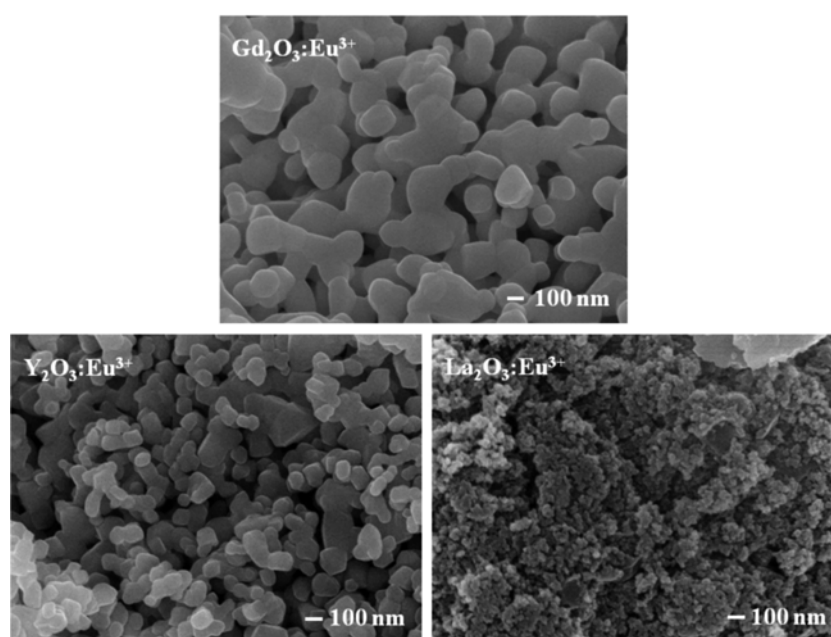


Fig. 2. FE-SEM images of $\text{RE}_2\text{O}_3 : \text{Eu}^{3+}$ ($\text{RE} = \text{Gd}, \text{Y}$ and La) phosphors.

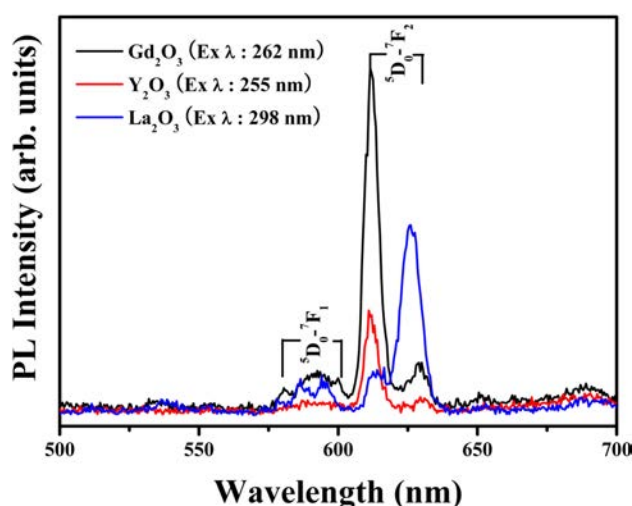


Fig. 4. Photoluminescence emission spectra of $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ phosphors.

process consisted of the charge transfer state (CTS) of Eu^{3+} and f-f transition within $4f^6$ of Eu^{3+} configuration. The peak position of CTS is related to the covalence of the $\text{Eu}^{3+}-\text{O}^{2-}$ bond and the coordination number of Eu^{3+} [21]. Upon excitation with the CTS of Eu^{3+} ions, the strongest emission peak centered at 590 nm is radiated from the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ magnetic dipole (MD) transition. The weak broad peak observed at 314 nm in $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ phosphors is related to Gd^{3+} transitions, which are due to the $\text{Gd}^{3+}-\text{Eu}^{3+}$ energy transfer. The f-f transitions of Eu^{3+} ions have also been observed at 364, 382, 395, 417 and 467 nm for all phosphors.

The emission spectra of $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ nanopowders under UV light excitation are shown in Fig. 4. The excitation wavelengths are 262, 255 and 298 nm for $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$, $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ and $\text{La}_2\text{O}_3:\text{Eu}^{3+}$, respectively. The main emission peak was observed at 612 nm, which corresponds to red emission and is assigned to the electronic dipole transition (ED) of $^5\text{D}_0 \rightarrow ^7\text{F}_2$. The peak is caused by an electron dipole transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$ of Eu^{3+} , which is induced by the lack of inversion symmetry at the Eu^{3+} site. The emission near 590 nm was assigned to the magnetic dipole transition of $^5\text{D}_0 \rightarrow ^7\text{F}_1$, which is insensitive to site symmetry. The other energy transition peaks for Eu^{3+} correspond to $^5\text{D}_0 \rightarrow ^7\text{F}_2$ at 630 nm. The intensity of the transition between different J levels depends on the symmetry of the local environment of the Eu^{3+} activators. According to the selection rules $\Delta J = 0 \pm 1$ and $\Delta S = 0$ MD is allowed and ED is forbidden. However, in this study, Eu^{3+} activators occupy sites without inversion symmetry and parity forbiddance is not strictly maintained [21]. In particular, the $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ particles exhibited strong red emission. The Gd_2O_3 and Y_2O_3 are cubic structure, and La_2O_3 is hexagonal structure. Therefore, Gd_2O_3 and Y_2O_3 have similar luminescence properties. This result demonstrated that a kind of host material and their crystalline structure plays an important role on the

luminescent intensity of $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ phosphors.

Conclusions

In summary, high quality $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ nanopowder phosphors were synthesized using a solvothermal reaction method. The indexed XRD peaks are in good agreement with the results of JCPDS card. The host materials affected not only the particle size but also the photoluminescence behavior of the nanopowders. The $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$, $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ and $\text{La}_2\text{O}_3:\text{Eu}^{3+}$ nanopowders showed different PLE and PL spectra due to the different crystal fields. In the case of nanocrystalline $\text{RE}_2\text{O}_3:\text{Eu}^{3+}$ powder, upon excitation with the CTS of Eu^{3+} ions, the strongest emission peak centered at 615 nm is radiated from the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ electric dipole transition. The $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ nanopowder showed the optimal result. In particular, the crystalline structure and particle size control the internal reflection, which is one of the most important factors determining the photoluminescence intensity of the nanopowders.

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