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Photoluminescence properties of Eu^{3+}-activated $Y_{1.50}Sc_{0.50}O_3$ phosphors

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In this research, Eu^{3+} activated and Dy^{3+}-co-doped Y_2O_3 based phosphors have been synthesized by solid-state reaction method under open atmosphere. The host lattice is composed of 0.25 moles of Sc_2O_3 which is added to phosphor composition. Thus, Sc^{3+} substitution of Y^{3+} ions is implemented to form $Y_{1.40}Sc_{0.50}O_3$ host lattice. The thermal analysis (DTA/TG) have been carried out from 50 °C to 1400 °C for preliminary examination of thermal behavior of phosphors during heat treatments. After the heating process, the phase formations are characterized by X-ray diffraction resulted as Y_2O_3 single phase cubic structure. The effects of Eu^{3+} and Dy^{3+} dopant ions on the photoluminescence and phase formation properties of the hosts are investigated and determined as Dy^{3+}-co-doped phoshor has the reduced excitation/emission intensities as well as decay lifetimes.

Keywords: Dysprosium ion (Dy^{3+}), Europium ion (Eu^{3+}), Photoluminescence, Scandium ion (Sc^{3+}), Solid-state reaction method, Yttrium oxide (Y_2O_3)

Inorganic type phophorescent materials which are recognized by their chemical and thermal stability as well as their high quantum efficiency, have attracted an interest of researchers for a long time because of their well-known structures and are noted as an alternative to sulfide based phosphors[1,2]. Since the ionic radii of Y^{3+} (0.9–1.075 Å) is similar as with most of the rare earth ions, yttrium oxide (Y_2O_3) host lattice is considered as the ideal structure for doping. Also, Y_2O_3 has good thermal stability up to 2200 °C. Its melting point is about 2500 °C. Y_2O_3 along with CaO, MgO and BN are considered as candidate materials for insulator coating[3].

It is well-understood that rare-earth-doped Y_2O_3 phosphors have excellent luminescent properties namely narrow emission spectrum, long luminescent life times, the color-tunable UC luminescence properties. These phosphors are suitable for fluorescent lamp, solar cell, optical communication, display device, etc. applications. The europium (Eu^{2+} or Eu^{3+}) ions are used as the significant dopant/activator for lost of host lattices provide obtaining blue to red color region emissions depending on synthesizing atmosphere because the synthesizing atmosphere affects the Eu-ions valence. Moreover, the Eu^{2+}-ions give green color emission in some host lattices ($SrAl_2O_4$, $BaAl_2O_4$, etc.) and Eu^{3+}-ions give red color emissions in some hosts (Y_2O_3,), thus the host structure is significative factor in obtaining emission to different wavelengths. Furthermore, it was thought that the emission properties of doped Y_2O_3 could be improved by co-doping with a certain trace amount of Ln^{3+}-ions, for example, by means of Dy co-doping providing in considerable increased emission life time as well as intensity[4-6]. In this work, the Y_2O_3 based host lattice was synthesized successfully by solid state reaction method in open atmosphere. While creating this host lattice, Sc^{3+} ions were added instead of Y^{3+} in the host lattice, or in other words Sc^{3+} ions are substituted for Y^{3+} ions. The indexed structure, Y_2O_3, was still same after substitution of Sc^{3+} because the ionic radii of Sc^{3+} (0.745 Å) is smaller than Y^{3+} ions (1.011 Å). The electronic structure of Sc^{3+} ion is similar, and Sc is often included in that ion. Because the radius of Sc^{3+} is more close to Eu^{3+} and Dy^{3+} than Y^{3+}, therefore adding of Sc^{3+} to Y_2O_3 lattice may improve the dispersity of Eu^{3+} and Dy^{3+} in $Y_{1.50}Sc_{0.50}O_3$. Based on this information given above it is acceptable to think that doping Sc^{3+} to the Y_2O_3 host may enhance the photoluminescence intensity[7]. Then, the effect of Eu^{3+} doping and Dy^{3+} co-doping on the photoluminescent properties including the excitation and emission spectrum of host material were well investigated.

Materials and Methods

xEu^{3+} (x= 0.1 mol%) and xEu^{3+}, yDy^{3+} (x= 0.1 and y= 0.01 mol%) doped $Y_{1.40}Sc_{0.50}O_3$ phosphors were prepared by the solid state reaction technique. High purity Yttrium(III) oxide (Y_2O_3, 99.99%, Acros Organics), Scandium(III) oxide (Sc_2O_3, 99.9%, abcr chemicals), Europium(III) oxide (Eu_2O_3, 99.9%, Aldrich) and Dysprosium(III) oxide (Dy_2O_3, ≥99.99%, Aldrich) chemicals were used for phosphor compositions. The raw materials were stoichiometrically calculated and well-mixed in the agate mortar to get obtain fine and homogenous mixed particles. Before heat treatments, the compositions thermal behaviors at a heating rate of 10 °C/min from room temperature to 1400 °C were analyzed by differential thermal analysis (DTA) and thermogravimetric (TG) instrument (SII Nanotechnology SII6000 Exstar TG/DTA 6300). Then, the heat treatments were carried out in pure alumina crucibles in a muffle furnace (Protherm MOS180/4) at open atmosphere, then cooled down to the room temperature. Here, we studied and sintered $Y_{1.40}Sc_{0.50}O_3$ host based phosphor under open atmosphere because Eu^{3+} activated Y_2O_3 phosphors are dominate red color emitting materials in commercial applications on fluorescent or LED lighting and display, due to their good luminescent characteristics, suitable atmospheric stability, and lack of hazardous composition opposed to sulfide phosphors. The sintered bulk samples ground to powder form for the characterization process. Powder form of each sample's phase formation investigations were done with Bruker AXS D8 Advance model X-ray diffractometer (XRD), which run at 40 kV and 30 mA (Cu-Kα radiation) in a step-scan mode (0.02°/2θ). The surface morphology and elemental analysis (EDX) were achieved by a scanning electron microscope (SEM). Finally, the photoluminescence (PL) properties including the excitation and emission spectra and the decay curves as well as life times of the samples were analyzed by a fluorometer (Photon Technology International (PTI), Quanta Master TM 30).

Results and Discussion

Thermal analysis

The thermal analysis results (DTA/TG) of $Y_{1.40}Eu_{0.10}Sc_{0.50}O_3$ and $Y_{1.40}Eu_{0.10}Dy_{0.01}Sc_{0.50}O_3$ compositions which were obtained ranges from 50 °C to1400 °C are given in Figs 1-2. The DTA/TG results of all samples show that there is not any mass change or endo/exo-thermic reaction up to 1400 °C despite the hosts were doped with various oxides. SinceY_2O_3 has good thermal stability up to 2200 °C, the host lattice, along with CaO, MgO and BN are considered as candidate materials for insulator coating. Its melting point[8] is about 2500 °C.

X-ray diffraction (XRD) analysis

After thermal behavior analysis, each material was subjected to a pre-heat treatment process, namely at 800 °C for 6 h. After the heat treatment (at 1000 °C for 6 h) for structure formation was performed, the XRD analyses were carried out for each sample. The Fig. 3 illustrates the comparative XRD patterns of $Y_{1.40}Eu_{0.10}Sc_{0.50}O_3$ and $Y_{1.40}Eu_{0.10}Dy_{0.01}Sc_{0.50}O_{3.}$ Fig. 3 proved that all the samples were indexed by cubic Y_2O_3 (JPCDS cards #00-043-1028). There was no major change in peak positions though the doping or co-doping of host material, so the indexed single phase, Y_2O_3, is valid for all samples according to XRD patterns while the host structure is $Y_{1.50}Sc_{0.50}O_3$. Additionally, the result clearly implies that the dopant and co-dopant ions are well substituted into the Sc^{3+} ions in the lattice. This clearly implies that the dopant

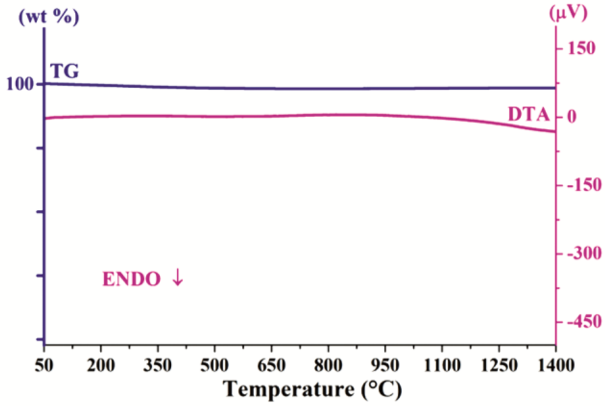

Fig. 1 — DTA/TG curves of $Y_{1.40}Eu_{0.10}Sc_{0.50}O_3$ phosphor

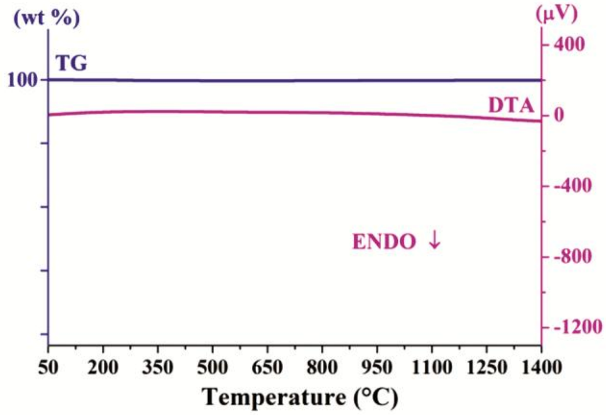

Fig. 2 — DTA/TG curves of $Y_{1.40}Eu_{0.10}Dy_{0.01}Sc_{0.50}O_3$ phosphor

and co-dopant ions are well substituted into the Sc^{3+} ions in the lattice. Thus, with doping of Eu^{3+} and co-doping of Dy^{3+} ions no shift was observed in the diffraction peaks. All samples well-crystallized in the cubic structure so the lattice parameters are a=b=c=9.845 Å, α=90°, β= 90° and γ= 90°.

SEM-EDX Analysis

Figs 4 and 5 show typical SEM images and EDX results of prepared and powdered $Y_{1.40}Eu_{0.10}Sc_{0.50}O_3$ and $Y_{1.40}Eu_{0.10}Dy_{0.01}Sc_{0.50}O_3$ phosphors in the cubic phase. As it is clear from all the SEM images that all samples have been agglomerated from very small particles. The particle distributions measured directly from all SEM images were approximately between 0.18–0.31 µm and 0.18–0.39 µm ranges for $Y_{1.40}Eu_{0.10}Sc_{0.50}O_3$ and $Y_{1.40}Eu_{0.10}Dy_{0.01}Sc_{0.50}O_3$ phosphors, respectively. Furthermore, it was confirmed that all prepared samples with the micron size particles exhibit relatively irregular morphology and have the same morphological characteristics. When the EDX results are examined, the dopant and co-dopant materials added in low quantities gave peak at low intensities as expected.

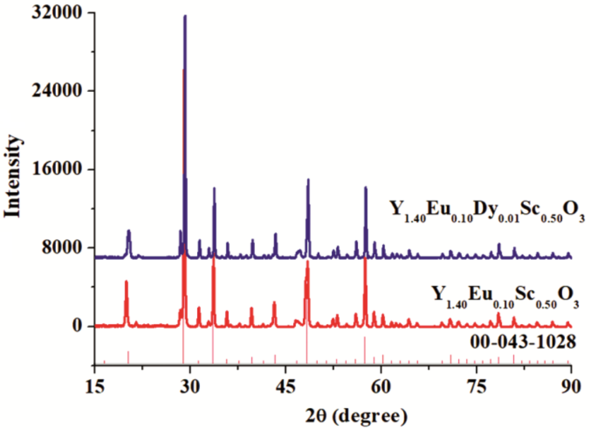

Fig. 3 — The comparative XRD patterns of $Y_{1.40}Eu_{0.10}Sc_{0.50}O_3$ and $Y_{1.40}Eu_{0.10}Dy_{0.01}Sc_{0.50}O_3$

Photoluminescence properties

The PL studies of all samples have effective results with PL spectra and intensities. Figs 6 and 7 give the PL spectra including excitation and emission wavelengths and intensities of $Y_{1.40}Eu_{0.10}Sc_{0.50}O_3$ phosphor and $Y_{1.40}Eu_{0.10}Dy_{0.01}Sc_{0.50}O_3$ phosphor, respectively. The PL results given in Figs 8 and 9 are similar because of these two doped phosphors are activated with Eu^{3+}-ions as luminescent center. The results indicate at prominent emission band attributed to $^5D_0 \rightarrow {}^7F_2$ (610/611 nm), transitions of Eu^{3+} ion. The other emission at about 700 and 702 nm were related to $^5D_0 \rightarrow {}^7F_4$ transitions of Eu^{3+}. Obviously,

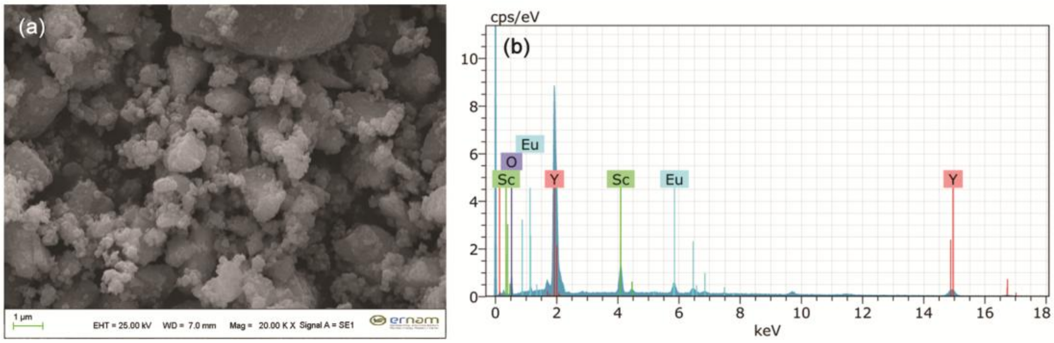

Fig. 4 — (a) SEM image and (b) EDX spectrum of $Y_{1.40}Eu_{0.10}Sc_{0.50}O_3$ phosphor

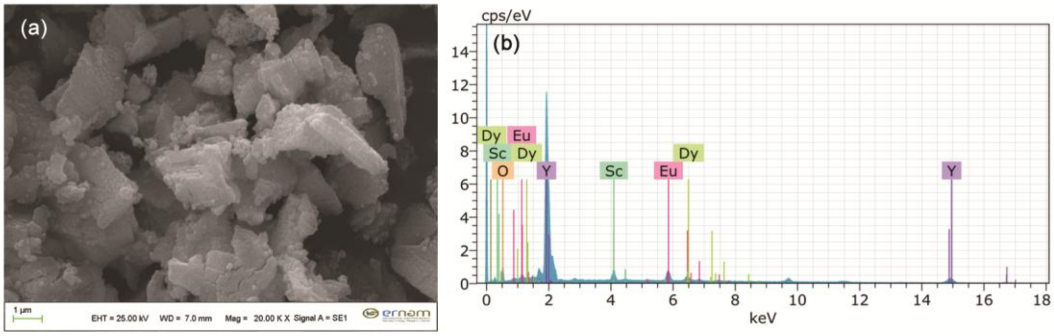

Fig. 5 — (a) SEM image and (b) EDX spectrum of $Y_{1.40}Eu_{0.10}Dy_{0.01}Sc_{0.50}O_3$ phosphor

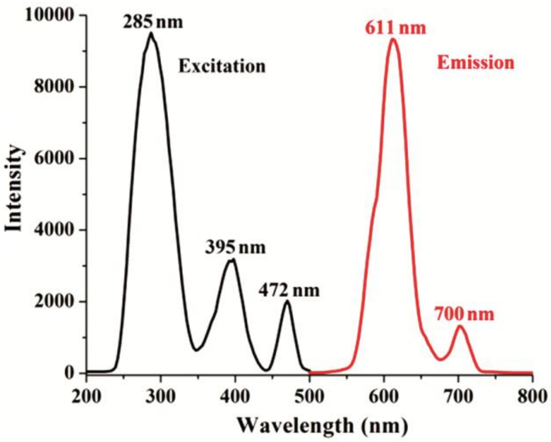

Fig. 6 — The PL spectra of $Y_{1.40}Eu_{0.10}Sc_{0.50}\ O_3$ phosphor

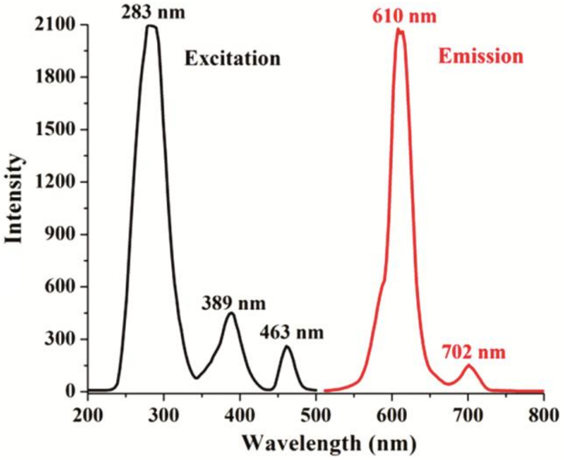

Fig. 7 — The PL spectra of $Y_{1.40}Eu_{0.10}Dy_{0.01}Sc_{0.50}O_3$ phosphor

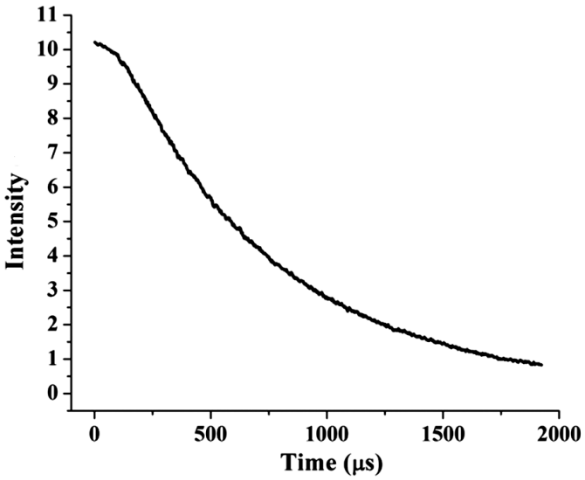

Fig. 8 — Luminescence decay from the $^5D_0$ level of Eu^{3+} in $Y_{1.40}Eu_{0.10}Sc_{0.50}\ O_3$ phosphor by monitoring the $^5D_0 \rightarrow {}^7F_2$ transition at ~611 nm

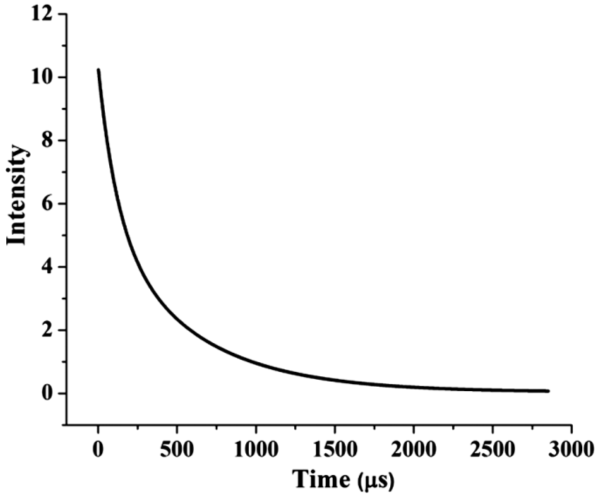

Fig. 9 — Luminescence decay from the $^5D_0$ level of Eu^{3+} in $Y_{1.40}Eu_{0.10}Dy_{0.01}Sc_{0.50}O_3$ phosphor by monitoring the $^5D_0 \rightarrow {}^7F_2$ transition at ~610 nm

the emission spectrum is dominated by the red region ($^5D_0 \rightarrow {}^7F_2$, 610 nm) transition of the Eu^{3+}, which is an electric-dipole allowed transition and is hypersensitive to the environment[6,9,10]. The major excitation peak of samples centered at range of 285 nm was associated with the charge-transfer state (CTS) band which is proved that the typical Eu^{3+}-activated phosphors show strong CTS transition band excitation around 200–300 nm. Furthermore, the CTS is related to an electron transferred from the oxygen 2p orbital to the empty 4f orbital of europium, which may be ascribed as ligand-to-Eu^{3+} charge-transfer transitions (LMCT). Furthermore, the excitation peaks generally between 300-500 nm can be assigned to typical intra-4f transitions of the Eu^{3+} ion[9]. Also, no more emission was not observed related to the co-dopant Dy^{3+} in $Y_{1.40}Eu_{0.10}Dy_{0.01}Sc_{0.50}O_3$ phosphor, indicating that the doped Dy^{3+} ion do not show any significant emission under those excitations.

Decay time curves of all samples recorded at 611 nm and 610 nm emissions, respectively after excitations are shown in Figs 8 and 9. The decay process of all samples is composed of medium decay ($Y_{1.40}Eu_{0.10}Dy_{0.01}Sc_{0.50}O_3$ phosphor) and subsequent of slow decay ($Y_{1.40}Eu_{0.10}Sc_{0.50}\ O_3$ phosphor). The decay curves of materials are fitted as representatives, which are presented in figures. The decay curves are well fitted with the following double exponential functions:

$$y=I= A_1*\exp(-x/t1) + A_2*\exp(-x/t2) + y_0$$

Table 1 — Results for fitted decay curve of samples

Samples	Decay Lifetimes (μs)		
	τ_1	τ_2	$\tau_{average}$
$Y_{1.40}Eu_{0.10}Sc_{0.50}O_3$	684.275	684.275	684.275
$Y_{1.40}Eu_{0.10}Dy_{0.01}Sc_{0.50}O_3$	529.878	105.181	317.529

where x is the time (t), I_0 (y_0) and y (I) is the luminescence intensity at initial time and t, respectively. A_1 and A_2 are constants. t_1 (τ_1) and t_2 (τ_2) are the decay time for the exponential components, respectively[11]. Results for fitted decay curve of samples are given in Table 1.

As clearly seen in decay curves and lifetimes' (μs) $\tau_{average}$ of $Y_{1.40}Eu_{0.10}Sc_{0.50}O_3$ and $Y_{1.40}Eu_{0.10}Dy_{0.01}Sc_{0.50}O_3$ phosphors clearly prove that Dy^{3+} co-doped phosphor reduced the lifetime by half as well as it is shown in reduced PL intensities. This result is related with the luminescence intensity of the $^5D_0 \rightarrow {}^7F_2$ (~611 nm, hypersensitive to the environment) transition which is decreased significantly with co-dopant (Dy^{3+}) concentration in this host.

Conclusions

The phosphors in this research were prepared by solid-state reaction method under open atmosphere by obtaining $Y_{1.40}Sc_{0.50}O_3$ host lattice. By 0.5 moles of Sc^{3+}-ions were added to the system substitution of Y^{3+}-ions, $Y_{1.40}Sc_{0.50}O_3$ host lattice was achieved. XRD measurements verified the samples as Y_2O_3, the single phase, cubic structure with high crystallinity. SEM observations indicated the particle size distributions are between 0.17–0.39 μm for samples and the EDX spectra confirmed the presence of doping of Eu and Dy in the phosphors. The PL analysis exhibited that the Eu^{3+}-activated phosphors based on same activator/co-activator couples exhibit excitations and red emissions due to Eu^{3+}-ions because of its f-f transitions. The point is Dy^{3+}-co-doped phoshor has the reduced excitation/emission intensities as well as decay lifetimes. Thus, Dy^{3+}may cause the quenching effect for the photoluminescence intensity and lifetime of Y_2O_3:Eu^{3+} phosphors.

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