Photoluminescence of Eu$^{3+}$, Dy$^{3+}$ and Sm$^{3+}$ codoped Y$_2$O$_3$ nano phosphors

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Abstract

Y$_2$O$_3$ x Eu$^{3+}$(x=0.5,1.0,1.5 mol%), 0.5mol% Sm$^{3+}$, 1.0mol% Dy$^{3+}$ phosphor fired at 1200°C were synthesized via solid state reaction method. The dependence of photoluminescence spectra of Y$_2$O$_3$ phosphor on doping ‘Eu’ concentration under near-ultraviolet (nUV) and visible excitations has been investigated. The excitation spectrum of RE$^{3+}$ ions doped Y$_2$O$_3$ phosphors monitored under 613nm wavelength was characterized by a broad band ranging from 200-550nm with sharp emission peaks at 395nm, 467 and 535nm in the nUV and visible region along with CT band peak at 260nm. The emission spectra of RE$^{3+}$ ions doped Y$_2$O$_3$ phosphors under excitations at 467nm (blue)and 535nm exhibited peaks at 583nm, 589nm, 595nm, 601nm, 632nm and a very high intense red peak at 613nm, assigned to the $^5D_0$$rightarrow$ $^7F_2$ electric dipole transition of Eu$^{3+}$ ion. The phosphor shows weak photoluminescence emission under 395nm excitation wavelength. The CIE co-ordinates of Y$_2$O$_3$: RE$^{3+}$ phosphor are x = 0.674 and y = 0.325 indicates red colour. This is promising phosphor to produce white light under blue (467nm) excitation.

1. Introduction

In recent years, light-emitting diodes have emerged as a prominent class of lighting devices and the study of red, green, blue (RGB) tri colour phosphors suitable for near-ultraviolet (nUV) or red, green (RG) two colour phosphors suitable for blue excitation has been attracting more attention for fabricating white LEDs. For generation of white light emission, three different approaches are developed. These are blue LED with yellow phosphors; an ultraviolet (UV) LED with red, green and blue phosphors; and a device that combines red, green and blue LEDs. The advantage of the blue LED with yellow phosphors is its higher efficacy compared to the other two approaches. Therefore, today’s white LEDs are commonly made by a combination of III-nitride based blue LEDs and a coating of yellow phosphors such as cerium-doped yttrium aluminium garnets [1-2], which are becoming less available since they contain rare-earth metals. The cubic phase YZO is a good host material for rare earth ions. Eu$^{3+}$-doped Y$_2$O$_3$ is a promising redemitting phosphor [3,4], and its photoluminescence (PL) characteristics have been reported for various optical applications. Yttrium oxide (Y$_2$O$_3$) has been investigated widely as a host material for rare-earth (RE) ion doping in optical applications [5-7] on account of its excellent chemical stability, broad transparency range (0.2 to 8 μm) with a band gap of 5eV, high refractive index, and low phonon energy. Furthermore, the similarities in the chemical properties and ionic radius of RE ions and Y$_2$O$_3$ make it an attractive choice as a host material [8]. The color tunability of Yttria-based phosphors can be achieved by codoping the host material with some specific rare-earth elements. Therefore, research into Y$_2$O$_3$ codoped with other different RE activators is important because the color-tunable properties can be used in a wide range of applications. Although many studies have examined the optical properties of RE ion-doped Y$_2$O$_3$ phosphors, only a few have investigated the codoping of two or more different ions in the same yttria host material [9]. Y$_2$O$_3$:Eu$^{3+}$ phosphor, one of the most promising oxides-based red phosphors, was studying for a long time because of its efficient luminescence under ultraviolet (UV) and cathode-ray excitation. Y$_2$O$_3$:Eu$^{3+}$ with micrometer size grains were used as the red component in three chromatic lamps and projection color television. Numerous studies were focused on synthesis and optical properties of
Y$_2$O$_3$;Eu$^{3+}$ phosphors [10-16]. Like many oxide-based materials, rare-earth-doped Y$_2$O$_3$ has a high resilience to ionizing radiation. Synthesis of rare-earth-doped Y$_2$O$_3$ based phosphors has been accomplished through a variety of techniques including homogeneous precipitation, solid state reaction method, chemical vapour synthesis, combustion synthesis, and the sol–gel method [17-23]. The wide variety of dopants that can be incorporated allows the material to be tuned to emit in the blue (Tm$^{3+}$), green (Tb$^{3+}$), or red (Eu$^{3+}$) regions of the electromagnetic spectrum [24]. Eu$^{3+}$ exhibits an atomic-like transition in red region at 612 nm.

In the present study, rare earth ions co-doped Y$_2$O$_3$ phosphors have been studied for many applications due to its high stability, emission range and intensity. Y$_2$O$_3$;x Eu$^{3+}$ (x=0.5,1.0,1.5 mol%), 0.5mol% Sm$^{3+}$, 1.0mol% Dy$^{3+}$ phosphors were prepared by the conventional solid state reaction method in air atmosphere for 3 hours at 1200°C. The optical properties of the synthesized particles were explored by photoluminescence spectroscopy. Y$_2$O$_3$ particles with different concentrations of codoped Eu$^{3+}$, Sm$^{3+}$ and Dy$^{3+}$ was investigated, and the luminescence intensity of these particles was found to be strongly dependent on the activator concentration. Photoluminescence studies and CIE co-ordinates of RE$^{3+}$ ions doped Y$_2$O$_3$ under 465nm and 535nm excitations will be discussed.

2. Experimental methods

Y$_2$O$_3$: x Eu$^{3+}$ (x=0.5,1.0,1.5 mol%), 0.5mol% Sm$^{3+}$, 1.0mol% Dy$^{3+}$ phosphors were synthesized by the conventional solid state reaction method.The starting materials were yttrium oxide (Y$_2$O$_3$) assay(99.9%) as raw material was taken for the host and samarium oxide (Sm$_2$O$_3$), dysprosium oxide (Dy$_2$O$_3$), europium oxide (Eu$_2$O$_3$), with purity 99.9% were taken as activators.They were weighed in appropriate compositions. Keeping the co-dopants Sm and Dy concentrations at constant and varied the Eu concentration in each sample as 0.1, 0.5, 1.5mol%.The composite powders were grounded in an agate mortar and pestle about an hour and then placed in an alumina crucible with the lid closed. After the powders had been sintered at 1200°C for 3 hr in a muffle furnace with a heating rate of 5°C/min and then cooled to room temperature. All the samples were again ground into fine powder using an agate mortar and pestle about an hour.

The emission and the excitation spectra of the synthesized powders were characterized with a spectrofluorophotometer (Shimadzu RF 5301 PC) with xenon lamp as excitation source. Emission and excitation spectra were recorded using a spectral slit width of 1.5nm. All the spectra were recorded at room temperature. The Commission International de l’Eclairage (CIE) co-ordinates were calculated by the photometric method using the spectral energy distribution. The chromatic coordinates (x, y) of prepared materials were calculated with colour calculator version 2, software from Radiant Imaging [25].

3 Results and Discussions

3.1 Photoluminescence Study

A series of Y$_2$O$_3$:xEu$^{3+}$ (x=0.5,1.0,1.5 mol%), 0.5mol% Sm$^{3+}$, 1.0mol% Dy$^{3+}$ phosphors heated at 1200°C were prepared and the effect of Eu$^{3+}$ concentration on the emission intensity was investigated. Fig.1 exhibits the PL excitation spectra of Y$_2$O$_3$: x Eu$^{3+}$, 0.5mol% Sm$^{3+}$, 1.0mol% Dy$^{3+}$ phosphors. The excitation spectrum monitored under 613nm wavelength, show the broadband ranging from 200-550nm divided in to two regions, (1) the intense broad band centered at 260nm is attributed to the charge transfer (CT) transition between ligand (O$^{2-}$) to metal (Eu$^{3+}$) ion, (2) the intense broad band range from 380 to 550nm, the sample shows the characteristic intra configuration 4f–4f transitions of the Eu$^{3+}$ ion is split into three levels, which are located in UV and visible regions, attributed to $^5$D$_{0}$$rightarrow$ $^7$F$_{l}$ transition at 395nm and $^5$D$_{0}$$rightarrow$D$_{2}$ transition at 467nm and $^5$D$_{0}$$rightarrow$D$_{1}$ transition at 535nm. The excitation intensity is of the order of 535nm > 467nm > 395nm. It is also observed that the intensity is increases as the Eu concentration increases in the Y$_2$O$_3$: RE$^{3+}$ phosphor. The 467nm is well matched with the blue LED chip in the visible region which is useful for LED applications for white light generation.

The luminescence emission of phosphor materials depends strongly on the synthetic route, size of the phosphor materials, and concentration of dopant ions. The emission intensity is strongly depends on phosphor crystallinity therefore the phosphors were calcinated at 1200°C. A series of Y$_2$O$_3$: x Eu$^{3+}$ (x=0.5,1.0,1.5 mol%), 0.5mol% Sm$^{3+}$, 1.0mol% Dy$^{3+}$ phosphors heated at 1200°C were prepared and the effect of Eu$^{3+}$ concentration on the emission intensity was investigated.

Fig.2(a) & (b) shows the emission spectra under 467 and 535nm excitation wavelengths respectively. The shape of the emission spectra and emission peak wavelength is independent of the excitation wavelengths. No emission line was observed under 260nm excitation wavelength of CT band.

Upon excitation at 467nm, the emission spectrum of Y$_2$O$_3$: x Eu$^{3+}$, 0.5mol% Sm$^{3+}$, 1.0mol% Dy$^{3+}$ phosphors emits a broad band range from 575-625nm with four peaks at 583, 589, 595, 601, 632nm and a very strong intense peak at 613nm (red) with the full width at half maximum (5nm) as shown in fig.2(a). The Stokes shift is 353nm (2.738eV), determined from the difference between the first excitation maximum (260nm) and the emission maximum (613nm). The $^5$D$_{0}$$rightarrow$F$_{2}$ electric dipole transition of Eu$^{3+}$, which is responsible for red emission, strongly depends on the
Table 1 Transitions at different emission peaks

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>Peak Wavelength (nm)</th>
<th>RE ion</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>535</td>
<td>Eu</td>
<td>$^5D_0 \rightarrow F_7$</td>
</tr>
<tr>
<td>2</td>
<td>539</td>
<td>Eu</td>
<td>$^5D_0 \rightarrow F_7$</td>
</tr>
<tr>
<td>3</td>
<td>556</td>
<td>Sm</td>
<td>$^4G_{5/2} \rightarrow ^4H_{5/2}$</td>
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<tr>
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<td>583</td>
<td>Eu</td>
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</tr>
<tr>
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<td>589</td>
<td>Eu</td>
<td>$^5D_0 \rightarrow F_7$</td>
</tr>
<tr>
<td>6</td>
<td>595</td>
<td>Eu</td>
<td>$^5D_0 \rightarrow F_7$</td>
</tr>
<tr>
<td>7</td>
<td>601</td>
<td>Sm</td>
<td>$^4G_{5/2} \rightarrow ^4H_{5/2}$</td>
</tr>
<tr>
<td>8</td>
<td>613</td>
<td>Eu</td>
<td>$^5D_0 \rightarrow F_7$</td>
</tr>
<tr>
<td>9</td>
<td>632</td>
<td>Eu</td>
<td>$^5D_0 \rightarrow F_7$</td>
</tr>
</tbody>
</table>

Figure 2(a) Emission spectrum of Y$_2$O$_3$: RE$^{3+}$ phosphor under 467nm excitation wavelength

Figure 2(b) Emission spectrum of Y$_2$O$_3$:RE$^{3+}$ phosphor under 535nm excitation wavelength

Figure 2(c) Energy level diagram of Y$_2$O$_3$:Eu$^{3+}$ with possible electric dipole transitions within energy levels of Eu$^{3+}$ ions.

crystal field symmetry around Eu$^{3+}$ ion [7, 8]. Transitions at different emission peaks reported in Table 1. In the PL spectra (Fig. 2a, b) a number of sharp peaks associated with forced electric dipole transition from excited $^5D_0 \rightarrow F_J(J = 1, 2, 3)$ levels of Eu$^{3+}$ activator ions. The deep red peak corresponding to 613nm is attributed to $^5D_0 \rightarrow F_2$ electric dipole transition with FWHM of 5nm, whereas the 589 nm orange emission originates due to magnetic dipole transition $^5D_0 \rightarrow F_1$. Lower symmetry of crystal field near the activator Eu$^{3+}$ ion results in higher ratio of red and orange peak intensity (R/O value) [9-14]. The R/O value strongly depends on local symmetry of activator Eu$^{3+}$ ion. The ratio of the emission intensity of the C$_{3v}$ site to the emission intensity of the C$_2$ site decreases with increasing europium content due to strong energy transfer from semiconductor host to Ln$^{3+}$ ions. One possible reason is that Sm$^{3+}$ ions occupy on the surface rather than lattice sites of semiconductor host due to large ionic size differences between Ln$^{3+}$ and metal ions. Due to the co-dopants in the Y$_2$O$_3$ phosphor the FWHM value is increased up to 45nm.

It was observed that the PL emission intensity of Y$_2$O$_3$:xEu$^{3+}$ (x=0.5, 1.0, 1.5 mol%), 0.5mol% Sm$^{3+}$, 1.0mol% Dy$^{3+}$ under 467 and 535nm excitations, enhances with the increase of Eu$^{3+}$ concentration. From the emission spectrum except the transitions of Eu$^{3+}$ and Sm$^{3+}$, the transitions of Dy$^{3+}$ ions around 480/575/655nm was not found. The presence of Sm$^{3+}$ RE ion transition in the phosphor around 556nm and 601nm was evident but the intensity is very low. The R/O value strongly depends on local symmetry of activator Eu$^{3+}$ ion. The ratio of the emission intensity of the C$_{3v}$ site to the emission intensity of the C$_2$ site decreases with increasing europium content due to strong energy transfer from semiconductor host to Ln$^{3+}$ ions. One possible reason is that Sm$^{3+}$ ions occupy on the surface rather than lattice sites of semiconductor host due to large ionic size differences between Ln$^{3+}$ and metal ions. Due to the co-dopants in the Y$_2$O$_3$ phosphor the FWHM value is increased up to 45nm.

3.2 CIE study

The CIE co-ordinates of (chart -1931) were calculated by the Spectrophotometric method using the spectral energy distribution. Based on the emission spectra, it was possible to see the color of the emission of each sample in the CIE.
4. Conclusions

Y₂O₃ phosphor co-doped with Eu³⁺, Sm³⁺, Dy³⁺ phosphor powders were successfully synthesized by the high temperature solid state reaction method. The prepared phosphor powders emit their characteristic lines. The luminescence color emission could be controlled by the excitation wavelength. Therefore, the emission wavelength and color output of the same Y₂O₃: RE³⁺ phosphor can be adjusted by switching the radiation from 467 to 535nm. The Stoke shift and the FWHM of the emission of Y₂O₃: RE³⁺ phosphor under 467nm excitation is more than Stoke shift under 535nm excitation and observed that the emission intensity is less.

The ⁵D⁰→⁷Fᵢ (J =0, 1, 2, etc.) transitions of Eu³⁺ were recorded in the all of samples. The ratio of the emission intensity of the C₃ site to the emission intensity of the C₂ site decreases with increasing europium content as well as decreasing crystal size due to strong energy transfer from the C₃ to the C₂ site. The Commission International de l’Eclairage [CIE] co-ordinates of Y₂O₃:RE³⁺ phosphor exhibit red colour. Y₂O₃: x Eu³⁺(x=0.5, 1.0, 1.5 mol%), 0.5mol% Sm³⁺, 1.0mol% Dy³⁺ phosphors may be a red component for white light generation in LEDs under blue LED chip (467nm) excitation.

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References

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