Preparation and characterisation of yttrium based luminescence phosphors

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High sensitive Y2O3:Eu3+, Gd2O3:Eu3+, (Y,Gd)2O3:Eu3+, YAG (Y2Al2O12):Eu3+ and (Y,Gd1-x)BO3:Eu3+ luminescence display phosphors have been made by pyrolysis route followed by sintering at a relatively low temperature of 1000°C. The photoluminescent (PL) efficiencies of all the five phosphors under UV excitation are found to be comparable to that of commercial (Y,Gd1-x)BO3:Eu3+ (LG make). The PL efficiency as well as 395 nm (4f-4f) to 260 nm (charge transfer) excitation intensity ratio in Y2O3:Eu3+ was found to vary in a complex way with Eu concentration. YAG:Eu3+ could serve as a cheaper substitute to Y2O3:Eu3+ red phosphor used currently in compact fluorescent lamps. While the PL efficiency of Y2O3:Eu3+ remains fairly constant with excitation temperature in the region 25-250°C, the PL efficiency of (Y,Gd1-x)BO3:Eu3+ gets reduced by more than 30% when the excitation temperature increased from 25 to 250°C.

Keywords: Lamp and display phosphors, Y2O3:Eu3+, (Y,Gd1-x)O3:Eu3+, YAG:Eu3+, (Y,Gd1-x)BO3:Eu3+, Thermal quenching, Luminescence phosphors

1 Introduction

The phosphor Y2O3:Eu3+ discovered several years ago is still considered as the best red oxide phosphor because of its high luminescence efficiency, atmospheric stability, reduced degradation under applied voltages and the lack of hazardous constituents as opposed to sulphide phosphors. It is widely used in compact fluorescent lamps (CFL) and other display applications. It constitutes roughly 70% of the phosphor content in CFL. Nayak et al. synthesized Y2O3:Eu3+ by conventional solid state combustion reaction of a mixture of oxalates form of yttrium and europium at 1350°C. Introduction of trace quantities of Al3+ and B3+ ions (added in oxide form) in Y2O3 host enhanced sensitivity due to changes in the field strength of the host. Recent interest concentrated on nanomaterials. Y2O3:Yb3+, Er3+ hollow microspheres have been synthesized via urea co-precipitation using carbon spheres as templates. It showed intense red (up-conversion) emission under 980 nm IR excitation. Silica coated Y2O3:Eu3+ nano particles have been prepared by solid state reaction at 800°C. Flower shaped Y2O3:Eu3+ nanostructures were synthesized by hydrothermal method and subsequent calcinations at 600°C. With increasing annealing temperature from 300° to 1000°C, the intensity of excitation and emission spectra of Y2O3:Eu3+ nanorods is increased nearly three times. The fine structure of both excitation and emission spectra has also changed. Reverse micellar systems were used for the preparation of Y2O3:Eu3+ phosphor nanoparticles (4-8 nm in size). Eu-doped Y2O3 nanospheres and nanorods were prepared by solvothermal reaction under supercritical conditions followed by calcinations. The results showed that the size and shape can be controlled using organic solvents and surfactants as well as by controlling the reaction time and temperature. The as-synthesized nanosphere and nanorods typically have a diameter less than 10 nm. Energy transfer and non-radiative decay between excited states of Eu3+ in Y2O3 have been extensively studied. Effect of different flux materials (BaF2, CaF2, AlF3, NH4F, NH4Cl and H2BO3) on the morphology and luminescence efficiency of Y2O3:Eu3+ have been well studied. In this study which employed solid state reaction, the firing was carried out at 1450°C for 3 h duration in air and the BaF2 flux (melting point 1355°C) was found to give the best results. Adding a flux not only increases the reaction rate but also aids in the formation of well crystallized particles of appropriate size and low melting flux materials are known to reduce the processing temperature, which can lead to reduction in the production cost. Quasi-spherical Y2O3:Eu3+ red phosphor with particle size of 2-3 nm have been prepared by firing the mixture of precursor
and complex molten salts (Na$_2$CO$_3$+S+NaCl) at 1200°C for 2 h. Its luminescent intensity was 30% higher than that of the same phosphor prepared by the same procedure but without molten salts and was 5% higher than that of commercial Y$_2$O$_3$:Eu$^{3+}$ red phosphor$^{11}$.

However, in view of the high cost of Y$_2$O$_3$, a cheaper alternate to it is desired. Phosphors that have high conductivity and good luminescence efficiency in high voltage range are required for field emissive displays (FEDs). Therefore, one of the constituent of the phosphor material has to be a metal such as Zn, Gd etc. Y$_2$O$_3$ and Gd$_2$O$_3$ have the same cubic structure and a very small difference in lattice constant and hence, Y can be easily substituted by Gd. Y$_2$-xGd$_x$O$_3$:Eu$^{3+}$ thin films on Al$_2$O$_3$ substrate were found to be encouraging for the FED applications$^{12}$. However, Gd substitutions usually lead to an increased thermal quenching in yttrium based phosphors$^{13}$. Synthesis of these compounds using solid state diffusion reaction routes, despite the use of flux materials, require a much higher sintering temperature (>1000°C). Y$_2$Al$_5$O$_{12}$:Eu$^{3+}$ (popularly known as YAG or garnet) is used$^{14}$ in FED. YAG:Eu$^{3+}$ could also serve as a cheaper substitute to Y$_2$O$_3$:Eu$^{3+}$ red phosphor used in compact fluorescent lamps.

In this study, all the above phosphors were synthesized at a relatively low sintering temperature of 1000°C in air following pyrolysis carried out at 600°C in air and a comparative study of optical fluorescence of these phosphors under UV excitation is made.

2 Experimental Details

Y$_2$O$_3$:Eu$^{3+}$, (Y$_x$Gd$_{1-x}$)O$_3$:Eu$^{3+}$ and YAG:Eu$^{3+}$ phosphors were made with pyrolysis route using Y$_2$O$_3$, Gd$_2$O$_3$, Al$_2$O$_3$, Eu$_2$O$_3$ and suitable flux materials as well as stabilizing agents as ingredients. The recipe of (Y$_x$Gd$_{1-x}$)BO$_3$:Eu$^{3+}$ and its luminescence properties are discussed elsewhere$^{17}$. Chemical decomposition by the action of heat is known as pyrolysis. While in combustion, the reaction products catch fire, in pyrolysis the decomposition results in smoke and not fire. The spot temperatures reached during pyrolysis are quite high (>>1000°C), or else the phosphor synthesis would not have been possible. After wet mixing the constituent powders, pyrolysis was carried out in air at 600°C for 1 h to remove efficiently volatile constituents. Temperatures lower than 600°C resulted in lower PL efficiency. After this heat treatment, the powder samples were mildly ground and kept in alumina crucibles before sintering at 1000°C in air in a muffle furnace which helps in crystallization of samples. The samples were fast cooled by withdrawing the crucibles from the furnace at the end of sintering duration and kept on a metal sheet kept outside. Two different routes were tried successfully in the synthesis of Y$_2$O$_3$:Eu$^{3+}$. In one route, Li$_2$CO$_3$ was used as the flux agent and NH$_4$NO$_3$ was used as the oxidizer. NH$_4$NO$_3$ melts at 170°C and dissociate at 210°C. Li$_2$CO$_3$ melts at 723°C but decomposes at 1310°C. Since spot temperatures reached during pyrolysis are quite high we believe decomposition of Li$_2$CO$_3$ takes place during pyrolysis and Li gets incorporated in the Y$_2$O$_3$ lattice. In another route, urea (CH$_4$N$_2$O) and NH$_4$NO$_3$ were used as fuel (F) and oxidizer (O), respectively. The O/F ratio was kept at unity. Equimolar concentrations of both these chemicals were used for pyrolysis. After wet mixing the starting materials in a porcelain crucible, initial heating was carried out at 600°C for 1 h in a muffle furnace with adequate ventilation so that the gaseous products released during pyrolysis escape and the pyrolysis process is complete. Subsequently, after uniform mixing, the samples were sintered at 1000°C for 1 h in air. Route 2 (urea and NH$_4$NO$_3$ recipe) was adopted for the preparation of YAG:Eu$^{3+}$ phosphor. But the flux materials used in this case during pyrolysis were MgCl$_2$ (melting point = 714°C) and BaF$_2$ instead of monovalent chemical compounds.

PL emission spectra and intensities were compared with that of the commercial (Y, Gd)BO$_3$:Eu$^{3+}$ phosphor with the assistance of Fluorolog Jobin Yvon-Spez spectrofluorimeter described earlier$^{17}$. Thermal quenching behaviour of YAG:Eu and Y$_2$O$_3$:Eu$^{3+}$ has been studied using the experimental set-up described earlier$^{13}$. XRD data of the phosphor powder samples were recorded with a German make STOE X-ray diffractometer with Cu Ka radiation ($\lambda$ = 0.15406 nm).

3 Results and Discussion

3.1 Synthesis routes and luminescence efficiency

The two recipes (one with Li$_2$CO$_3$ and the other with urea) for making Y$_2$O$_3$:Eu$^{3+}$ PL phosphor are described in Table 1. Typical quantities of raw materials used are also given. Both recipes involve a pre-firing (pyrolysis) at 600°C, 30 min in air followed by mixing and refiring at 1000°C for 1 h in air. In both cases, the ammonia and other gases released during pyrolysis were let out during pre-firing. Table 2
Table 1 — Two Simple Recipes for making high sensitive Y$_2$O$_3$.Eu$^{3+}$ PL phosphor. Typical quantities of raw materials used are given. Both recipes involve a pre-firing at 600°C, 30 min in air followed by grinding and re-firing at 1000°C for 1h in air. In both cases the ammonia and other gases released during pyrolysis were let out during.

<table>
<thead>
<tr>
<th>Recipe 1 (Li route)</th>
<th>Recipe 2 (urea route)</th>
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<tbody>
<tr>
<td>$\text{Y}_2\text{O}_3$ 0.724 g</td>
<td>$\text{Y}_2\text{O}_3$ 0.098 g</td>
</tr>
<tr>
<td>$\text{Eu}_2\text{O}_3$ 0.022 g</td>
<td>$\text{Eu}_2\text{O}_3$ 0.009 g</td>
</tr>
<tr>
<td>$\text{Li}_2\text{CO}_3$ 0.169 g</td>
<td>$\text{NH}_4\text{NO}_3$ 1.623 g</td>
</tr>
<tr>
<td>$\text{NH}_4\text{NO}_3$ 2.392 g</td>
<td>Urea – 1.242 g</td>
</tr>
</tbody>
</table>

Relative PL efficiency – 1.00

| \(\lambda_{\text{exi}} = 254 \text{ nm}, \lambda_{\text{emi}} = 611 \text{ nm} \) | \(\lambda_{\text{exi}} = 254 \text{ nm}, \lambda_{\text{emi}} = 611 \text{ nm} \) |

Table 2 — Effect of Li$_2$CO$_3$ and NH$_4$NO$_3$ on the PL efficiency of Y$_2$O$_3$.Eu$^{3+}$ (2.4 mol%)

| Sample with Li$_2$CO$_3$ and NH$_4$NO$_3$ | 1.00 |
| Sample without Li$_2$CO$_3$ | 0.50 |
| Sample without NH$_4$NO$_3$ | no fluorescence |

presents the effect of Li$_2$CO$_3$ and NH$_4$NO$_3$ on the PL efficiency of Y$_2$O$_3$.Eu$^{3+}$ in the former recipe. While Li$_2$CO$_3$ assists in increasing the fluorescence efficiency, NH$_4$NO$_3$ was found to be very essential in producing the luminescence. This shows that the dissociation of NH$_4$NO$_3$ and the heat released during this exothermic reaction is absolutely essential for the formation Y$_2$O$_3$ crystalline phase and the incorporation of Eu$^{3+}$ activator in it. The dissociation of NH$_4$NO$_3$ at a low temperature (210°C) seems to promote the dissociation of Li$_2$CO$_3$ and incorporation of Li in Y$_2$O$_3$ host lattice which results in the observed enhancement in luminescence. In other words, in the absence of NH$_4$NO$_3$, Y$_2$O$_3$.Eu$^{3+}$ phase is not formed and Li$_2$CO$_3$ does not decompose during pyrolysis at 600°C.

The PL excitation and emission spectra of Y$_2$O$_3$.Eu$^{3+}$ made by Li$_2$CO$_3$ and urea routes are compared in Fig. 1. The charge transfer (CT) band near 254 nm and 4f-4f excitation peaks near 394 nm are seen in both cases. The CT band is assigned to the O$^5$-Eu$^{3+}$ CT state, which corresponds to the electronic transition from the 2p orbital of O$^2-$ to the 4f orbital of Eu$^{3+}$. The Eu$^{3+}$ emission spectra consisted of peaks at 593 nm (5D$_0$ $\rightarrow$ 7F$_1$), 613 nm (5D$_0$ $\rightarrow$ 7F$_2$), 642 nm (5D$_0$ $\rightarrow$ 7F$_3$) and 680 nm (5D$_0$ $\rightarrow$ 7F$_4$) with 613 nm dipole transition being the brightest. Both samples gave nearly the same fluorescence efficiency at 611 nm under 254 nm excitation. However, the 4f-4f excitation bands near 394 nm are relatively more intense in the Y$_2$O$_3$.Eu$^{3+}$ sample made with Li$_2$CO$_3$.

Fig. 1 — PL excitation (a and c; $\lambda_{\text{emi}} = 611$ nm) and emission (b and d; $\lambda_{\text{exi}} = 254$ nm) spectra of Y$_2$O$_3$.Eu$^{3+}$ made by Li$_2$CO$_3$ (a, b) and urea (c, d) routes.

Table 2 — Effect of Li$_2$CO$_3$ and NH$_4$NO$_3$ on the PL efficiency of Y$_2$O$_3$.Eu$^{3+}$ (2.4 mol%)

<table>
<thead>
<tr>
<th>Y$_2$O$_3$.Eu$^{3+}$</th>
<th>Relative PL efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample with Li$_2$CO$_3$ and NH$_4$NO$_3$</td>
<td>1.00</td>
</tr>
<tr>
<td>Sample without Li$_2$CO$_3$</td>
<td>0.50</td>
</tr>
<tr>
<td>Sample without NH$_4$NO$_3$</td>
<td>no fluorescence</td>
</tr>
</tbody>
</table>

3.2 XRD

Figure 2 shows the XRD spectrum of Y$_2$O$_3$.Eu$^{3+}$, YAG:Eu$^{3+}$ and (Y, Gd)BO$_3$.Eu$^{3+}$. All the major diffraction peaks match well, respectively with those of Y$_2$O$_3$ (JCPDS standard NO:25-1200), Y$_2$Al$_2$O$_3$ (JCPDS standard NO:33-0040) and YBO$_3$:Eu$^{3+}$ (JCPDS 16-0277).

3.3 Y$_2$O$_3$.Eu$^{3+}$, Gd$_2$O$_3$.Eu$^{3+}$ and (Y$_{0.5}$Gd$_{0.5}$)$_2$O$_3$.Eu$^{3+}$

Table 3 presents that the PL efficiency of Gd$_2$O$_3$.Eu$^{3+}$ is 23% less than that of Y$_2$O$_3$.Eu$^{3+}$. The
luminescence efficiency $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ prepared elsewhere recently by solution combustion technique was found to be only 50% of that of the commercial $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ sample\textsuperscript{19}. ($\text{Y}_0.7\text{Gd}_0.3\text{O}_3:\text{Eu}^{3+}$, however, showed a slightly higher luminescence efficiency compared to $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ under 254 nm excitation (Table 4). Fig. 3 shows that the PL spectral shape of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ and ($\text{Y}_0.7\text{Gd}_0.3\text{O}_3:\text{Eu}^{3+}$ are identical. The PL efficiencies under UV excitation of all the three phosphors synthesized in this work are found to be comparable to that of commercial ($\text{Y}, \text{Gd})\text{BO}_3:\text{Eu}^{3+}$ (LG make).

### 3.4 $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ and $\text{Y}_3\text{Al}_2\text{O}_{12}:\text{Eu}^{3+}$

Figure 4 compares the PL excitation and emission spectra of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ and $\text{Y}_3\text{Al}_2\text{O}_{12}:\text{Eu}^{3+}$. Table 5 compares their PL efficiencies. Both the spectra as well as the emission efficiencies of the two samples are comparable. This preliminary result shows that YAG:$\text{Eu}^{3+}$ could serve as a cheaper substitute to $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ red CFL phosphor. More detailed studies on YAG:$\text{Eu}^{3+}$ are in progress. Other co-dopants which will bring down the cost of the red CFL phosphor are being studied.

### 3.5 Eu concentration

Table 6 shows the PL efficiency as well as 395 nm (4f-4f) to 260 nm (CT) excitation intensity ratio in $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$. The PL emission intensity increases with increasing Eu concentration from 0.7 to 3.4 mol%. At a higher Eu concentration (6.1 mol%), the PL intensity decreases due to concentration quenching.

### 3.6 Li concentration

Table 7 compares the PL efficiencies of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, Li$^+$ as a function of Li concentration. Over the Li concentration range 8.3-16.6 mol%, the PL sensitivity remains nearly the same. However, the PL intensity declines at higher Li concentrations (25-290 mol%). The Li$_2$CO$_3$ concentration is mentioned in Table 7 is actually the percentage of the raw materials added during the phosphors synthesis. However, the actual quantity of Li getting into the $\text{Y}_2\text{O}_3$ host is not known. It could perhaps be much lower.

### 3.7 Effect of monovalent co-dopants

Table 8 presents the effect of flux materials (all added as carbonates) on the PL efficiency of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (2.36 mol%) made by Li$_2$CO$_3$ route. The
PL sensitivity of Y₂O₃:Eu³⁺ obtained with other monovalent compounds such as Na₂CO₃ and K₂CO₃ is quite less compared to that with Li₂CO₃. This might be related to the smaller ionic radius of Li⁺ ion (76 pm) when compared to that of Y⁺ (90 pm). Other monovalent dopants such as Na⁺ (102 pm) and K⁺ (138 pm) have a larger ionic radii than that of Y⁺ and hence, their poor solubility in Y₂O₃ host. Additionally, the melting points of Na₂CO₃ and K₂CO₃ are higher than that of Li₂CO₃. It is likely that following decomposition during pyrolysis, the monovalent dopants (Li⁺, Na⁺ and K⁺) get incorporated in the Y₂O₃ lattice as co-dopants. The sensitivity with Na⁺ or K⁺ dopants is lower than that with Li⁺ because of their larger ionic radii and higher melting temperatures. In general, monovalent co-dopants enhances the PL sensitivity of Y₂O₃:Eu³⁺ which is reported to be related to its improved crystallinity as corroborated by other researchers.²⁰ Monovalent dopants substituting divalent or trivalent cations should in principle create anion (O²⁻) vacancies or remove existing cation (Y²⁺) vacancies. Other possible defects in Y₂O₃:Eu include O²-, O₁, Eu²⁺ etc. Charge compensation could be achieved by the creation/removal of anion/cation vacancies.

### 3.8 Divalent dopants

Table 9 shows that all divalent co-dopants (Mg, Ca, Sr and Ba) tried decrease the PL efficiency of Y₂O₃:Eu³⁺ and hence, no further work was carried out in this direction.

#### 3.9 Thermal quenching

Figure 5 shows the thermal quenching data in Y₂O₃:Eu³⁺ (a-λ_exi = 254 nm, λ_emis = 611 nm) and (Y, Gd)BO₃:Eu³⁺ (b-λ_exi = 394 nm, λ_emis = 590 nm).
quenching of \((Y_{x}Gd_{1-x})BO_{3}:Eu^{3+}\) occurs due to two reasons. One is \(YBO_{3}\) is a well known high phonon lattice and increased lattice vibrations at high temperature promote non-radiative transitions. Secondly all Gd based lattices\(^{13}\) [e.g. \((Y, Gd)_{3}Al_{5}O_{12}:Ce^{3+}\)] are known to show a relatively higher thermal quenching as compared to the respective host lattices without Gd [e.g. \(Y_{3}Al_{5}O_{12}:Ce^{3+}\)]. For lighting applications in light emitting diodes, where the operation temperature can be quite high, phosphors exhibiting least thermal quenching are preferred.

4 Conclusions
A simple recipe for three widely used display and lighting phosphors \(Y_{2}O_{3}:Eu^{3+}\), YAG:Eu\(^{3+}\) and \((Y_{x}Gd_{1-x})BO_{3}:Eu^{3+}\) is described. Both \(Y_{2}O_{3}:Eu^{3+}\) and \(Y_{3}Al_{5}O_{12}:Eu^{3+}\) exhibit high color purity coupled with high fluorescence efficiency with the predominant red emission at 611 nm due to \(^{5}D_{0} \rightarrow ^{7}F_{2}\) electric dipole transition for eight coordinated Eu\(^{3+}\) ion. Apart from the poor red colour purity due to its predominant orange emission, \((Y_{x}Gd_{1-x})BO_{3}:Eu^{3+}\) PDP phosphor was found to exhibit a relatively higher thermal quenching. But the high luminescence efficiency makes borate as an excellent host matrix. Therefore, for luminescence applications, other borate host matrix variations such as Ca, Ba, Sr (\(B_{4}O_{7}\)) with Eu dopant are worth trying.

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