Research Article

Synthesis and Optical Characterization of Europium Doped MY$_2$O$_4$ (M = Mg, Ca, and Sr) Nanophosphors for Solid State Lightening Applications

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Trivalent europium doped yttriate nanophosphors were synthesized by rapid facile gel combustion technique. The photoluminescence (PL) properties of these Eu$^{3+}$ activated MY$_2$O$_4$ (M = Mg, Ca, and Sr) nanophosphors showed red luminescence and exhibited excellent emission properties in their respective regions of color coordinates. Based on the excitation wavelengths multiple emission peaks were obtained. The main peak in the emission spectra was ascribed to $^5$D$_0$ $\rightarrow$ $^7$F$_2$ transition of Eu$^{3+}$ ion. The structural and morphological studies were performed by the measurements of X-ray diffraction profiles, scanning electron microscope (SEM) images, and transmission electron microscope (TEM) micrographs. Furthermore, the effects of additional heating on the different host lattices of these phosphors were also studied.

1. Introduction

Rare earth doped oxide materials have excellent chemical as well as thermal stability along with outstanding luminescent efficiency and their colour purity; consequently these are used for the various applications of display devices [1, 2]. The field emission display (FED) is a developing technology in recent years which has the potential to provide display of high brightness, high contrast ratio, and low power consumption [3–5]. Phosphor materials have been playing an important role in the development of these advanced lightening and display technologies [6–8]. The 4f electrons of rare earth ions are responsible for optical and electronic properties to these oxide lattices. Hence, these materials have been used in the field of optical transmission, biochemical probes, and medical diagnosis and have been used for numerous applications [9].

The RE$^{3+}$ doped phosphors originate as suitable materials as these show highly intense emission of light. The selected lattice should be having two or more sites for the integration of RE$^{3+}$ and these sites are also less distant for assisting fast energy transfer between ions. Hence, the obtained phosphors will be highly intense with long decay times even with low doping concentration of rare earth ion. Hence, above both conditions are suitable with these MRE$_2$O$_4$ (M = Ca, Sr, and Ba; RE = Y, Gd, Lu, Sc, and In) lattices. Consequently, Eu$^{3+}$ doped MRE$_2$O$_4$ luminescent materials are more significant than Eu$^{3+}$ doped RE$_2$O$_4$ phosphors. In recent times, MRE$_2$O$_4$ oxide lattices have been searched as potential lattices for the synthesis of rare earth activated phosphors [10]. The SrY$_2$O$_4$ lattice resembles CaFe$_2$O$_4$ related structures which consists of one strontium site of bicapped trigonal prismatic and two yttrium sites. One site for yttrium is almost perfect octahedral site, and the other is significantly distorted one, and both sites occupy without the inversion symmetry [11]. All the powder samples of MY$_{2(1-z)}$O$_4$:Eu$_z$ series show bright red emission and Eu$^{3+}$ ions substitute the Y$^{3+}$ ions available in two nonequivalent sites providing the splitting of $^5$D$_0$ $\rightarrow$ $^7$F$_0$ and $^5$D$_0$ $\rightarrow$ $^7$F$_1$ transitions [11, 12].

Generally, phosphor materials are synthesized by various techniques, that is, solid state reaction [11, 13, 14], sol-gel [15–19], soft-chemical [20], precipitation [21], solvothermal...
Figure 1: Prepared europium doped nanophosphor materials (3 mol% Eu$^{3+}$). Without UV excitation source (a) MgY$_2$O$_4$:Eu$^{3+}$, (b) CaY$_2$O$_4$:Eu$^{3+}$, and (c) SrY$_2$O$_4$:Eu$^{3+}$. With UV excitation (360 nm) (d) MgY$_2$O$_4$:Eu$^{3+}$, (e) CaY$_2$O$_4$:Eu$^{3+}$, and (f) SrY$_2$O$_4$:Eu$^{3+}$.

[22] spray pyrolysis [23], and combustion [24, 25]. All these methods require high temperature and time consuming heating process which produces large aggregates and these must be grinded to obtain the finer particles. The grinding process damages the phosphor surfaces, resulting in loss of emission intensity. Among all the above techniques the combustion process has attracted enormous attention due to less reaction time, comparatively low reaction temperature (600$^\circ$C), and resulting of more homogeneous products of fine size.

Here, in our work, we used rapid facile gel combustion method for the synthesis of MY$_2$O$_4$:Eu$^{3+}$ (M = Mg, Ca, and Sr) nanomaterials. The prepared materials are further characterized by X-ray diffraction profiles (XRD), scanning electron microscope (SEM) images, transmission electron microscope (TEM) micrographs, and photoluminescence (PL) spectra. The prepared phosphor particles are obtained in the nanorange having high luminescence efficiency.

2. Experimental

2.1. Synthesis of Nanophosphors. The europium doped MY$_2$O$_4$ nanomaterials were prepared by the rapid facile

<table>
<thead>
<tr>
<th>Starting raw materials (metal nitrates)</th>
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<tbody>
<tr>
<td>Double distilled water stirring for 10 minutes</td>
</tr>
<tr>
<td>Homogeneous mixture</td>
</tr>
<tr>
<td>Heating at hot plate for 10 minutes</td>
</tr>
<tr>
<td>A semisolid gel paste is obtained</td>
</tr>
<tr>
<td>Addition of fuel and few drops of water</td>
</tr>
<tr>
<td>Mixture of nitrates and fuel</td>
</tr>
<tr>
<td>Insertion of the mixture into furnace at 600$^\circ$C for half an hour</td>
</tr>
<tr>
<td>Fluffy white coloured powder is obtained</td>
</tr>
</tbody>
</table>

Figure 2: Schematic flow diagram for the rapid facile gel combustion synthesis of MY$_2$O$_4$:Eu$^{3+}$ (M = Mg, Ca, and Sr) nanophosphors.
gel combustion procedure. High purity (99.9% purity) \( M(\text{NO}_3)_2 \cdot x\text{H}_2\text{O} \) (where \( M \) may be magnesium, calcium, or strontium), yttrium nitrate hexahydrate \([\text{Y(NO}_3)_3 \cdot 6\text{H}_2\text{O}]\), europium nitrate hexahydrate \([\text{Eu(NO}_3)_3 \cdot 6\text{H}_2\text{O}]\), and hexamethylenetetramine (HMT) \([\text{C}_6\text{H}_{12}\text{N}_4]\) as fuel were used as raw materials to synthesize \( \text{Eu}^{3+} \) doped nanocrystals with a general formula \( \text{MY}_{(2-z)}\text{O}_4\cdot \text{Eu}_z^3+ \) (where \( z \) is 0.03). \([\text{Y(NO}_3)_3 \cdot 6\text{H}_2\text{O}]\) 1.97 mol (2.515 gm), \( M(\text{NO}_3)_2 \cdot x\text{H}_2\text{O} \) 1 mol (where \( M = \text{Sr}/\text{Ca}/\text{Mg} \)). When Sr used then weight was taken 0.787 gm/when Mg used then weight was taken 0.855 gm), \( \text{Eu}^{3+} \) 0.03 mole (0.045 gm) and calculated HMT (1.402 gm) was used along with small quantity of double distilled water, were heated on a preheated hot plate maintained at 100°C which produced an aqueous concentrated white semisolid paste within a few minutes. Amount of hexamethylenetetramine fuel was calculated using total oxidizing and reducing valences of materials. The fuel was mixed into previously prepared nitrate mixture. After a smooth mixing the mixture was then transferred to a preheated furnace at 600°C. On rapid heating the mixture evaporated and ignited, with evolution of a large amount of gasses, to yield yttriate phosphor materials. Entire process was completed within a few minutes. To study the effect of heating the phosphors were reheated in the muffle furnace at 800 and 1100°C for one hour. The images of prepared phosphor materials without and with UV excitation are shown in Figure 1. The schematic complete procedure used for the preparation of these nanomaterials is also shown in Figure 2. The chemical reaction that took place in the combustion of the reactants is represented as follows:

\[
\begin{align*}
M(\text{NO}_3)_2 \cdot x\text{H}_2\text{O} + z\text{Eu(NO}_3)_3 \cdot 6\text{H}_2\text{O} + (2 - z) [\text{Y(NO}_3)_3 \cdot 6\text{H}_2\text{O}] \\
+ C_6\text{H}_{12}\text{N}_4 \text{ (HMT as fuel)}
\rightarrow \text{MY}_{(2-z)}\text{Eu}_z \text{O}_4 \text{ (s) + gaseous products + water}
\end{align*}
\]

(1)

Here, \( M = \text{Ca}, \text{Mg}, \text{and Sr}; x = \text{number of water molecules available according to the nature of metal nitrate.} \)

2.2. Instrumentation. The phase purity was determined by taking the XRD patterns using a Rigaku Ultima IV X-ray
diffractometer with Cu Ka radiation \( (\lambda = 1.54178 \, \text{Å}) \) at a scanning rate of 10° min\(^{-1}\) in 2\( \theta \) range from 10 to 70°. The morphology of the phosphors was characterized by scanning electron microscopy (SEM) (JEOI JSM-6400 microscope). Transmission electron microscopy images were taken using FEI Tecnai with a field emission gun operating at 200 kV. The photoluminescence (PL) measurements were recorded with a Fluorimeter SPEX Fluorolog 1680 (USA) equipped with the SPEX 1934 D phosphorimeter having Xenon lamp as excitation source.

3. Results and Discussion

3.1. X-Ray Diffraction Study. XRD patterns of MY\(_2\)O\(_4\):Eu\(^{3+}\) phosphors are presented in Figures 3–5. All the diffraction peaks of CaY\(_2\)O\(_4\) (Figure 4) matched with JCPDS card number 19-0265 [26], while diffraction patterns available in Figure 5 can be indexed with pure orthorhombic structure of SrY\(_2\)O\(_4\) (JCPDS card number 32-1272). Furthermore, information about the details of lattice construction of MgY\(_2\)O\(_4\) and CaY\(_2\)O\(_4\) lattices is not available till now. The orthorhombic lattice structure of SrY\(_2\)O\(_4\) is consisted of Y\(_2\)O\(_4\) framework of double octahedra and M ions occupying bicapped trigonal prismatic site within the framework. Sr atom is coordinated by eight oxygen atoms and Y atom is coordinated with six oxygen atoms. The average crystallite size was estimated from the FWHM of the diffraction peaks using Scherrer equation:

\[
D = \frac{0.89\lambda}{\beta \cos \theta}
\]

where \( D \) is the crystallite diameter (nm), \( \lambda \) is X-ray wavelength (0.15405 nm), \( \theta \) is the diffraction angle, and \( \beta \) is the full width at half maximum (FWHM, in radian) peak.

The results of XRD patterns are summarized in Table 2, which are found in good agreement with the particle sizes available in TEM images. The sharpness in XRD patterns is recorded when these materials are reheated at higher temperatures, which indicates that with the increase of annealing temperature the crystallinity is also improved. Calculated particle sizes of as prepared phosphors are ~15 nm in average but as on further heating at higher temperatures crystallinity increased. Hence, particle sizes also increased and reached up to 50 nm as shown in Table 2.

3.2. Morphology Study. The morphology of these materials was analyzed using the scanning electron micrographs and transmission electron micrographs which are presented in Figures 6(a), 6(b), 6(c), 7(a), 7(b), and 7(c), respectively. SEM micrographs of these phosphors indicated the narrow size distribution of agglomeration and spherical shape particles as shown in Figures 6(a), 6(b), and 6(c). From these SEM images, it is clear that the tip of every particle had circular morphology of aggregated particles. SEM micrographs precisely cannot measure the particle size but TEM images can give good precision of crystal sizes in agreement with crystals sizes as calculated from XRD with the help of Scherrer equation. In TEM micrographs, the particle size of MY\(_2\)O\(_4\) materials varied in the range of 10–25 nm. The powders synthesized by gel combustion method were observed to be more homogeneous and smaller in particle size.

3.3. Photoluminescence Properties. Sites occupied by Eu\(^{3+}\) ions in MY\(_2\)O\(_4\) host lattice are a very interesting feature. Different arguments were given by different authors for the occupation of sites by Eu\(^{3+}\) ions. As energetically it is not easy for Eu\(^{3+}\) to substitute M\(^{2+}\) due to different valence states; but the size of Y\(^{3+}\) (1.04 Å) is also comparable to that of Eu\(^{3+}\) (1.08 Å). So due to having almost similar size and valence state there are maximum probabilities for the substitution of Y\(^{3+}\) ions by Eu\(^{3+}\) ions than the Sr\(^{2+}\) (1.18 Å), Ca\(^{2+}\) (1.14 Å) ions, but least chances for the substitution of Mg\(^{2+}\) (0.86 Å) due to very small size than Eu\(^{3+}\) [27].

Figures 8–11 show the photoluminescence excitation spectra (inset) of MY\(_2\)O\(_4\):Eu\(^{3+}\) phosphors by monitoring the emission wavelength at 612 nm. Broad bands in PLE spectra appeared due to charge transfer (high energy) and sharp
peaks (lower energy) are obtained due to f-f transitions of Eu$^{3+}$ ion. The charge transfer band ($\lambda_{\text{max}} = 267$ nm) is due to the charge transfer between the completely filled 2p orbital of O$^{2-}$ ion and the partially filled 4f orbital of Eu$^{3+}$ ion and its position depends strongly on the host lattice. The sharp excitation peaks of Eu$^{3+}$ ions are ascribed to the electronic transitions ($^7F_0 \rightarrow ^5D_2$) at 362 nm, ($^7F_0 \rightarrow ^5G_{4}$) at 382 nm, and ($^7F_0 \rightarrow ^5L_4$) at 395 nm. The emission spectrum monitored at 267 nm radiation has strongest peak at about 612 nm. The discrete emission lines lying between 580–630 nm are observed due to transitions from excited $^5D_0$ to $^7F_J$ ($J = 0–3$) levels of Eu$^{3+}$ ions. The origin of these transitions (electric dipole or magnetic dipole) from excited state to the ground state depends upon the location of Eu$^{3+}$ ions in SrY$_2$O$_4$ lattice and the type of transition is determined by selection rule [28]. The most intense peak at 612 nm corresponds to the hypersensitive transition between $^5D_0$ and $^7F_2$ levels due to forced electric dipole transition [29, 30]. The weak emission in the vicinity of 580 to 600 nm is ascribed to the magnetic dipole transition of $^5D_0$ and $^7F_{0,1}$ levels. Here, dopant ions in the host lattice occupied mainly the low symmetric site due to which the $^5D_0 \rightarrow ^7F_2$ transition is strongly enhanced, while $^5D_0 \rightarrow ^7F_{0,1}$ is reduced significantly [31]. A weak intense band is also obtained due to $^5D_0 \rightarrow ^7F_4$ transition.

The effect of sintering temperature on photoluminescent intensity is also investigated. Figures 8–10 show effect of reheating on these phosphors. The results showed that emission intensity increased with increase of sintering temperature as well as its time duration. Yttriate phosphors are synthesized at 600°C and then each sample is divided into three parts: one is as prepared; second is recalcined at 800°C; and third is also recalcined at 1100°C for 1h. As sintering temperature increases from 600–1100°C, the luminescence intensity increases and is found to be maximum at 1100°C. The effect of change of alkali earth metal ions in this oxide lattice is also shown in Figure 11. SrY$_2$O$_4$:Eu$^{3+}$ nanophosphor is having maximum luminescence intensity, while MgY$_2$O$_4$:Eu$^{3+}$ material has lowest luminescence intensity.

Commission Internationale de l’Eclairage (CIE) in 1931 invented a set of three colour matching functions [$x(\lambda)$, $y(\lambda)$, and $z(\lambda)$] subsequent to red, green, and blue for a 2-degree observer to generate the full range of monochromatic colours. By the use of colour matching functions, light stimuli having any spectral power distribution could be specified for colour by the three ($X$, $Y$, and $Z$) values. Table 1 lists the CIE colour coordinates derived from the emission spectra of MY$_2$O$_4$:Eu$^{3+}$ nanophosphors prepared at various sintering temperatures. The colour coordinates of MY$_2$O$_4$:Eu$^{3+}$ (M = Mg, Ca, and Sr) calcined at 1100°C were marked on the CIE chromaticity diagram which are shown in Figure 12.
4. Conclusions

The series of red-orange light emitting phosphors, that is, \( \text{MY}_2\text{O}_4 \) (M used for Mg, Ca, and Sr), was successfully synthesized using a rapid facile gel combustion process using hexamethylenetetramine as an organic fuel. The XRD patterns confirmed the cubic structure of \( \text{MgY}_2\text{O}_4:\text{Eu}^{3+} \) as well as \( \text{CaY}_2\text{O}_4:\text{Eu}^{3+} \) phosphor and orthorhombic structure of \( \text{SrY}_2\text{O}_4:\text{Eu}^{3+} \). Crystal sizes obtained from TEM images of phosphors were found in nanorange and were found in good agreement with the sizes calculated from XRD patterns. Photoluminescence spectra of all these phosphors \( \text{MY}_2\text{O}_4:\text{Eu}^{3+} \)

Table 1: Showing the color coordinates of synthesized \( \text{MY}_2\text{O}_4:\text{Eu}^{3+} \) nanophosphors.

<table>
<thead>
<tr>
<th>Phosphor compound</th>
<th>Colour coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{MgY}_2\text{O}_4:\text{Eu}^{3+} )</td>
<td>( x = 0.5099 ), ( y = 0.3747 )</td>
</tr>
<tr>
<td>( \text{CaY}_2\text{O}_4:\text{Eu}^{3+} )</td>
<td>( x = 0.5198 ), ( y = 0.3556 )</td>
</tr>
<tr>
<td>( \text{SrY}_2\text{O}_4:\text{Eu}^{3+} )</td>
<td>( x = 0.5342 ), ( y = 0.3025 )</td>
</tr>
</tbody>
</table>

were provided emission at 612 nm. Emission intensity of \( \text{SrY}_2\text{O}_4:\text{Eu}^{3+} \) nanophosphor was found maximum than the other prepared materials of this series. On increasing calcination temperature, the luminescence intensity of these materials was also enhanced. XRD patterns showed the presence of single phase components at 600°C; on further calcination at higher temperature, crystallinity of phosphors was also increased. These prepared phosphors are having efficient light emitting properties that could be suitably used for various solid state lighting applications.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.
Table 2: Showing the calculated size of particles and structure of prepared MY$_2$O$_4$:Eu$^{3+}$ nanophosphors.

<table>
<thead>
<tr>
<th>Phosphor compound</th>
<th>29</th>
<th>Crystal size (nm)</th>
<th>Matched JCPDS file number</th>
<th>Crystalline structure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>All temperatures</td>
<td>600°C</td>
<td>800°C</td>
<td>1100°C</td>
</tr>
<tr>
<td>MgY$_2$O$_4$:Eu$^{3+}$</td>
<td>30.6</td>
<td>25.64</td>
<td>41.03</td>
<td>52.36</td>
</tr>
<tr>
<td>CaY$_2$O$_4$:Eu$^{3+}$</td>
<td>29.04</td>
<td>12.62</td>
<td>16.74</td>
<td>28.37</td>
</tr>
<tr>
<td>SrY$_2$O$_4$:Eu$^{3+}$</td>
<td>29.04</td>
<td>7.67</td>
<td>19.35</td>
<td>32.38</td>
</tr>
</tbody>
</table>

**Figure 12:** Chromaticity diagram of prepared MY$_2$O$_4$:Eu$^{3+}$ nanophosphors calcined at 1100°C. (a) MgY$_2$O$_4$:Eu$^{3+}$, (b) CaY$_2$O$_4$:Eu$^{3+}$, and (c) SrY$_2$O$_4$:Eu$^{3+}$.

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**References**


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