Investigation of Thermal Stability of Red Emitting SrGd21-xEu2O3 Phosphors for Lighting and Display Applications

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Novel red-emitting SrGd21−xEu2O3 samples were prepared via combustion method. Structural and optical characteristics were examined with the help of XRD, FTIR, FESEM and photoluminescence (PL) studies. FESEM images reveal agglomerated rod-like morphology. The intense red emission corresponding to \( \text{Eu}^{3+} \) transitions under UV-excitation 276 nm and higher thermal stability up to 250 °C of SrGd21−xEu2O3 reveals its applicability in lighting and display devices.

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1. INTRODUCTION

Nowadays, rare-earth (RE) doped binary oxides having general formula \( \text{ARE}_2\text{O}_4 \) (where, \( \text{A} = \text{Sr}, \text{RE} = \text{Gd} \)) materials are receiving the attention of scientific communities because these materials show high density (7.3 gm/cm²), good charge stability and high physical and chemical robustness [1-14]. Furthermore, the same valence state and similar ionic radii of \( \text{Gd}^{3+} \) provides an easier way for incorporation of luminescent centers such as \( \text{Eu}^{3+}, \text{Dy}^{3+}, \text{Th}^{3+} \) etc. Above mentioned characteristics of these host reveals its extensive applications towards the development of display devices such as field-emission displays (FED), plasma display panels (PDP) and white light-emitting diodes (W-LED) [1-3].

In this context, \( \text{Eu}^{3+} \) doped SrGdO3 has chosen as a host lattice synthesized by combustion method and \( \text{Eu}^{3+} \) ions used as a dopant in order to yield strong red emissions. The structural and optical properties of prepared phosphors are measured by XRD, FESEM, and PL characterizations. The XRD results revealed the appearance of orthorhombic SrGdO3 phase with space group Pnam (62). The photoluminescence (PL) excitation and emission spectra show the characteristic emission peaks of \( \text{Eu}^{3+} \) due to its presence in the host-lattice. The most intense peaks of \( \text{Eu}^{3+} \) were obtained at 615 nm and 595 nm which correspond to \( \text{D}_0^0 \rightarrow \text{F}_2 \) and \( \text{F}_1 \) transition, respectively. Photometric characterization and thermal stability of phosphors were determined by temperature dependent PL and Arrhenius fit. The present samples show all the characteristics of a suitable phosphor material for display and lighting application.

2. EXPERIMENTAL

High purity \([\text{Sr(NO_3)_2}], [\text{Gd(NO_3)_3}], \) and \([\text{Eu(NO_3)_3}]\) is taken \(1.2_{(1-x)}2.2_x\) molar ratio in a beaker. Urea \([\text{H}_2\text{NCONH}_2]\) is used as a fuel and its amount is calculated using total oxidizing and reducing values. All these chemicals are taken in a beaker and mixed in deionised water.

An aqueous concentrated paste containing a calculated amount of metal nitrates and urea in preheated furnace maintained at 500 °C, white foamy solid obtained by combustion process. The solid obtained was again fired at 1200 °C for 5 h to increase the brightness and crystallinity.

The crystalline structure of prepared materials, morphology of particles and their optical properties were examined by XRD, FTIR, FE-SEM and photoluminescence studies (PL). The X-ray diffraction (XRD) patterns of the phosphors prepared at various temperatures were recorded on Bruker-D8 Focus X-ray powder diffractometer with Cu \( \text{K}_\alpha = 1.5406 \) Å. The morphology of prepared phosphors was examined by the field-emission scanning electron microscope (FESEM Supra-55, Germany) images.

The room-temperature photoluminescence (PL) excitation, emission spectra and life time measurement were recorded on Horiba FL3-21 fluorescence spectrophotometer. The temperature-dependent PL was performed with Cary Eclipse Fluorescence spectrophotometer comprising of a Xenon lamp as an excitation source and a temperature-controlled square-shaped brass block. The temperature of the brass block is controlled and maintained by a proportional-integral-derivative (PID) controller and a \( K \)-type thermocouple.

3. RESULTS AND DISCUSSIONS

The XRD patterns of prepared at 1200 °C show the orthorhombic phase with space group Pnam (Fig. 1). However, an insignificance presence of impurity phase cubic \( \text{Gd}_2\text{O}_3 \) having JCPDS No. 076-0155 is also observed. The lattice parameters of the unit cell are \( a = 10.955 \) Å, \( b = 12.009 \) Å and \( c = 3.4603 \) Å which are in correspondence with the JCPDS database for \( \text{SrGd}_2\text{O}_3 \) (JCPDS No. 052-1744).

It can be seen in Fig. 1 that all the samples having different \( \text{Eu}^{3+} \) contents show same XRD profile and there is absence of impurity phases associated to europium. XRD results reveal that \( \text{Eu}^{3+} \) doping does not alter the basic crystal structure of the host lattice and properly incorporated in the host lattice.

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In order to find out the crystallite size of Eu³⁺ activated SrGd₂O₄ samples, Debye-Scherrer method and Hall-Williamson relations are adopted. The average crystallite sizes of Eu³⁺ doped SrGd₂O₄ powder samples were calculated by the Debye Scherrer method which is given by the formula:

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

where, $\beta$ is full width at half maxima (FWHM) and $D$ is the crystallite size.

In order to verify the crystallite sizes obtained from Debye-Scherrer method, the crystallite sizes were also calculated from Hall-Williamson relation, which is given by the equation:

$$\frac{\beta \cos \theta}{\lambda} = \frac{1}{D} + \frac{\varepsilon \sin \theta}{\lambda}$$

where $\varepsilon$ is the micro-strain present in the sample.

Fig. 2 shows the Hall–Williamson plot of the XRD graphs for Eu³⁺ doped SrGd₂O₄. The crystallite sizes and the calculated micro-strain are shown in Table 1. The crystallite sizes of all the samples are found to be in the range of 15 - 65 nm. Table 1 shows a systematic reduction in the crystallite size of the SrGd₂O₄:Eu³⁺ samples with an increase in the doping concentrations (1-8 mol%), which suggest that the incorporation of Eu³⁺ ions suppresses the growth of the crystals.

FTIR studies were performed in the range 400 - 4000 cm⁻¹ of prepared samples to examine the detailed structure of the bonding environment. Fig. 3 shows the FTIR spectrum of Eu³⁺ doped SrGd₂O₄ samples. The important structural entities associated with the vibrations of Gd-O and Sr-O bonds are seen in the range of 540 to 592 cm⁻¹, respectively [3, 4]. The broad transmission minima at 1458 cm⁻¹ can be attributed to -CH₃ bending mode. However, two relatively low intense peaks, situated at 859 and 1380 cm⁻¹, are designated to be the stretching and bending modes of C-H bond, respectively. It is worth to mention that the presence of residual contents such as C = N, C-H and O-H vibrations has a negative effect on the photoluminescence.

Table 1 – Crystallite size distribution and microstrain of Eu³⁺ doped SrGd₂O₄ phosphors

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Debye-Scherrer</th>
<th>Hall-Williamson</th>
<th>Microstrain</th>
<th>ε (10⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrGd₂O₄:Eu³⁺</td>
<td>10-55</td>
<td>50</td>
<td>20</td>
<td>12</td>
</tr>
<tr>
<td>1 mol%</td>
<td>15-55</td>
<td>44.5</td>
<td>18.6</td>
<td>12</td>
</tr>
<tr>
<td>2 mol%</td>
<td>15-55</td>
<td>40.8</td>
<td>18</td>
<td>12</td>
</tr>
<tr>
<td>4 mol%</td>
<td>15-55</td>
<td>36.4</td>
<td>12</td>
<td>10.5</td>
</tr>
<tr>
<td>6 mol%</td>
<td>15-55</td>
<td>32.0</td>
<td>10.5</td>
<td></td>
</tr>
<tr>
<td>8 mol%</td>
<td>15-55</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Fig. 4 shows the field emission scanning electron microscope (FESEM) images of Eu³⁺ doped SrGd₂O₄ samples prepared at 1200 °C. It is remarkable that all the samples are exhibiting agglomerated rod-shaped morphology having sizes with an average length of about 0.3-3 μm. All the samples show similar morphology which indicates that the doping of Eu³⁺ ions do not affect the morphology of samples.

Additionally, it is noteworthy that many pores and voids are also present in these FESEM images. The presence of pores and voids is owing to the fact that, in the combustion process the reaction takes place in a very short duration of time with the evolution of a lot of gases that generally generates nanosized materials.
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levels respectively (Fig. 5b). The strongest emission band at 615 nm and the weakest one at 627 nm are attributed to the electric dipole transition $^5D_0 \rightarrow ^7F_2$, which is hypersensitive in the host structure symmetry.

Generally, the PL intensity of the phosphors relies on the doping concentration. It is expected that with the increase of doping concentrations photoluminescence should increase. However, the PL intensity decreases after 4 mol% Eu ions due to the non-radiative interaction between the ions as the resonant energy transfer becomes stronger rather than by emission of visible light, called concentration quenching (Fig. 5b-c) [2-4].

Fig. 5 – (a) PL excitation spectra, (b) PL emission spectra of SrGd$_{2}$(1-x)Eu$_x$O$_4$ samples, (c) representation of quenching phenomenon, (d) CIE diagram with digital images of phosphors excited with 276 nm UV light

Fig. 5d illustrates the CIE (Commission Internationale de l’Eclairage) chromaticity diagram of SrGd$_2$O$_4$:Eu$^{3+}$ phosphors for different Eu$^{3+}$ concentrations. The colour coordinates (0.66, 0.33) corresponding to the red emission were observed for 4 mol% concentration of Eu$^{3+}$, which is very much nearer to the commercial red phosphor Y$_2$O$_3$:Eu$^{3+}$ (0.67, 0.33) [4]. The following results suggest that SrGd$_2$O$_4$:Eu$^{3+}$ phosphors are suitable for lighting and display applications.

The temperature stability of the phosphors is the key factors when the practical applicability is taken into account. To investigate the effect of temperature on luminescence of the synthesized phosphors, the emission spectra of 4 mol% Eu$^{3+}$ doped SrGd$_2$O$_4$ samples at 276 nm excitation were measured at different temperatures ranging from 300 to 523 K (Fig. 6). Similar spectral profiles are observed for all the samples having different Eu$^{3+}$ contents.

It is clearly visible in Fig. 6 that the emission intensity of the samples was decreased with the increase in the sample temperature. But, the integrated emission intensity of Eu$^{3+}$ ions remained more than 80% at 523 K of those recorded at room temperatures, as shown in Fig. 6.
The activation energy ($\Delta E$) for thermal quenching can be obtained by using Arrhenius fit. The Arrhenius fitting of the emission intensity of SrGd$_2$O$_4$:Eu$^{3+}$ samples were investigated and given in the inset of Fig. 6. The activation energy ($\Delta E$) can be expressed by the following equations [10, 11]:

$$I_\gamma = \frac{I_0}{1 + c \exp \left( \frac{\Delta E}{kT} \right)}$$

where, $I_0$ and $I_\gamma$ are the luminescence intensities at room and testing temperatures respectively, $c$ is a constant and $k$ is the Boltzmann constant ($8.617 \times 10^{-5}$ eV K$^{-1}$).

The fitting of $\ln(I_\gamma/I_0) - 1)$ vs. 1000/T gives the estimation of activation energy ($\Delta E$) for the present phosphor (inset of Fig. 6). It is estimated to be 0.21 eV for the Eu$^{3+}$ doped SrGd$_2$O$_4$ phosphors. The thermal stable behaviour of present phosphor system is found to be more than the commercial red phosphor Y$_2$O$_3$:Eu$^{3+}$ and Y$_2$O$_3$:S:Eu$^{3+}$, respectively [10-14]. The above results validate the suitability of present host for advanced lighting and color display devices.

To clarify the physical mechanism behind temperature quenching, it is important to explain the crossover process (Fig. 7). The crossover process has been widely observed in various Eu$^{3+}$ activated host matrices [22, 23]. The typical configurational coordinate representation of the crossover process from $^5$D$_0$ level to the Eu-O charge transfer band (CTB) is shown in the Fig. 7. In this process, the electron situated at $^5$D$_0$ state can be thermally activated and goes to the CTB through the cross point and then further relaxes through another cross point of CTB to $^7$F$_j$ states, finally tending toward the ground state of Eu$^{3+}$. In this process, the electron absorbs the thermal energy to overcome the potential barrier ($\Delta E$) also called the activation energy [10, 11].

The value of the activation energy mainly relies on the location of the $^5$D$_0$--$^7$F$_j$ CTB, since the position of the $^5$D$_0$ level is almost independent from host matrices. Higher activation energy may arise due to higher location of CTB. It is easy to understand that the higher the activation energy is, the harder the crossover is and the most thermally stable the phosphor is [10, 11]. Moreover, the complex crystal structure of the present phosphor system could also be a reason of high thermal stability of the SrGd$_2$O$_4$ phosphors.

![Fig. 6 - Temperature dependent PL and Arrhenius plot of SrGd$_2$O$_4$:Eu$^{3+}$ samples](image)

![Fig. 7 - Configurational coordinate diagram of thermal quenching mechanism](image)

### REFERENCES