Novel molybdenum based pyrochlore type red phosphors, NaGd$_1-x$SnMoO$_7$:xEu$^{3+}$ under near UV and blue excitation


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1. Introduction

Inorganic luminescent materials have wide applications in many optoelectronic devices such as displays, sensors, light emitting diodes etc. An extensive research is going on in the field of white light generation from phosphor converted white light emitting diodes (pc-WLEDs) owing to their wide applications and advantages such as high luminous efficacy, low power consumption, long lifetime, high color rendering index (CRI), environmental friendliness etc [1,2]. With the emerging global energy crisis, W-LEDs has received much attention as a low-energy, robust, long-lifetime, and compact alternative to traditional incandescent and fluorescent lamps [3,4]. Phosphor converted W-LEDs can be made using various combinations of near UV/blue LED chips and host of Eu$^{3+}$ doped phosphors. Among the primary color phosphors, the red emitting phosphors are requisite to develop high color rendering index (CRI) sources suitable for the replacement of domestic lighting lamps. Currently the available red phosphors are Y$_2$O$_3$:Eu$^{3+}$ and CaS:Eu$^{3+}$ which have some serious drawbacks in terms of low absorption efficiency in the range 370–465 nm and poor thermal and chemical stability under near UV radiation. Also the efficiency and lifetime of currently used sulfide based red phosphor materials are less than that of green and blue phosphors [5]. Hence to solve these problems research is focused on stable materials that have broad and intense charge transfer (C-T) absorption bands in the near UV and are therefore capable of efficiently capturing the emission from a GaN-based LED over a range of wavelengths. According to these requirements a large number of red phosphors have been developed in different host lattices, among which molybdates and tungstates have received considerable attention because of their high stability and outstanding properties. In this regard many Eu$^{3+}$ doped molybdate based powellite type red phosphors were reported and they exhibited wide absorption of near-UV light at about 360 nm due to the charge transfer transition from O to Mo within the MoO$_6$ groups. In addition the energy transfer from MoO$_6$ groups to Eu$^{3+}$ ions is efficient in these systems [6]. Recently there has been a growing interest on the optical properties of pyrochlore based phosphors because of their high chemical and physical stability. Pyrochlore compounds with a general formula A$_2$B$_2$O$_7$ allows a wide variety of cation substitutions at the A and B sites (3$^+$ and 4$^+$, 2$^+$ and 5$^+$ and 1$^+$ and 6$^+$ or combinations of these). Quaternary pyrochlores with combination of 3$^+$ and 4$^+$ and 1$^+$ and 6$^+$ can exhibit interesting properties due to the presence of multivalent ions and distortions in the structure [7]. We have reported many quaternary pyrochlores in the combination of 3$^+$ and 4$^+$ and 2$^+$ and 5$^+$ cations for their photoluminescence and electrical properties [8,9]. As cited above molybdate based compounds are of great interest as host lattices, we have attempted to prepare novel molybdenum based quaternary pyrochlore type red phosphors, NaGd$_1-x$SnMoO$_7$ with europium doping. So far the luminescence properties of the molybdate based pyrochlores are not reported to the best of our knowledge. The developed phosphors exhibit intense red emission due to forced electric dipole transition, $^5$D$_0$$^7$F$_2$ under near UV and blue excitation with high asymmetric ratio and good CIE color coordinates close to National Television System Committee (NTSC) standards. The effect of Eu$^{3+}$ doping concentration to find the concentration quenching is also

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http://dx.doi.org/10.1016/j.jlumin.2017.05.029
Received 4 February 2017; Received in revised form 11 May 2017; Accepted 12 May 2017
Available online 12 May 2017
investigated and some of these results on novel molybdate based pyrochlores are presented in this paper.

2. Experimental

2.1. Materials and methods

Compositions based on NaGd$_2$SnMoO$_7$:xEu$^{3+}$ (x = 0.05, 0.10, 0.15, 0.20, 0.25 and 0.30) were prepared by the solid state reaction using Na$_2$CO$_3$, Gd$_2$O$_3$, SnO$_2$, MoO$_3$ and Eu$_2$O$_3$ (Sigma-Aldrich, 99.99% purity) as starting materials. The chemicals were weighed in stoichiometric ratio and homogenized by wet mixing with acetone in an agate mortar until fine slurry was obtained. The slurry was dried by placing it in an air oven at a temperature of 100°C. The mixing and drying was repeated thrice to obtain a homogenous mixture. The homogeneous mixture was then calcined in an alumina plate in an electric furnace at 1300°C for 6 h. The temperature of the furnace is programmed with an initial heating rate of 10°C/min up to 900°C followed by a heating rate of 5°C/min to attain 1300°C.

2.2. Characterisation

The crystalline structure of the calcined powders were characterized by means of X-ray powder diffraction (XRD) using a Ni-filtered Cu-K$_\alpha$ radiation with a PANalytical X’pert Pro diffractometer operated at 45 kV and 30 mA. Data were collected from 10° to 90° 20 range with a step size of 0.016°. Particle morphological analysis of the powder was performed by means of a scanning electron microscope (CARL ZEISS EVO 18) with an acceleration voltage of 20 kV. The photoluminescence excitation and emission spectra of the prepared samples were obtained using a Spex-Fluorolog DM3000F spectrofluorimeter with a 450 W xenon flash lamp as the exciting source. Luminescence lifetime of the phosphors was recorded by the phosphorimeter attached to Fluorolog*3 spectrofluorimeter.

3. Results and discussion

3.1. Powder X-ray diffraction analysis

Fig. 1 shows the powder XRD patterns of NaGd$_{1-x}$SnMoO$_7$:xEu$^{3+}$ samples. All the peaks can be indexed to a pyrochlore phase (space group Fd3m) which is in good agreement with the standard pattern (JCPDS No.17-0450). The pyrochlore characteristic super lattice peaks correspond to (311), (331), (511) lattice planes are clearly observed in the XRD patterns. In NaGd$_{1-x}$SnMoO$_7$ lattice, A site is shared by Na$^+$, Gd$^{3+}$ and Eu$^{3+}$ ions and is surrounded by eight oxygen atoms forming a cubic polyhedron and Sn$^{4+}$ and Mo$^{6+}$ ions share B sites and are six coordinated forming octahedron. Since the ionic radii of Eu$^{3+}$ (r = 1.066 Å when CN = 8) is close to that of Gd$^{3+}$ (r = 1.07 Å when CN = 8) the Eu$^{3+}$ ion prefers to occupy Gd$^{3+}$ site. In NaGd$_{0.85}$SnMoO$_7$:Eu$^{3+}$ (x = 0.15) the crystal structure correctly. The starting model used for the refinement of the NaGd$_{0.85}$SnMoO$_7$:0.15Eu$^{3+}$ phosphor is shown in Table 1. A pseudo-Voigt profile function was used to fit the XRD pattern. The background polynomial was refined with respect to a flat background and two other coefficients. Other profile functions including Caglioti parameters and the asymmetry parameter along with the structural parameters like lattice constant and the oxygen x-parameter were refined. The refined parameters obtained from the Rietveld analysis and their values corresponding to the best fit are listed in Table 2. The refined R values suggest that the refinement is in good agreement with the space group in all respects. It can be seen that the lattice parameter increases with increase in Eu$^{3+}$ concentration which suggests the replacement of Gd$^{3+}$ (r = 1.053 Å CN = 8) ions by larger Eu$^{3+}$ (r = 1.066 Å CN = 8) ions in the lattice.

Table 1

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<tr>
<th>Atom</th>
<th>Position</th>
<th>Site of occupancy</th>
<th>x</th>
<th>y</th>
<th>z</th>
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<td>0.5</td>
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<tr>
<td>Gd</td>
<td>16d</td>
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<td>0.5</td>
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<tr>
<td>Eu</td>
<td>16d</td>
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<td>0.5</td>
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<tr>
<td>Sn</td>
<td>16c</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Mo</td>
<td>16c</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
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</tr>
<tr>
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Fig. 1. Powder X-ray diffraction patterns of NaGd$_{1-x}$SnMoO$_7$:xEu$^{3+}$ (x = 0, 0.05, 0.10, 0.15, 0.20, 0.25 and 0.30).

Fig. 2. Observed (points), calculated (continuous line) and difference (bottom line) powder X-ray diffraction profiles of NaGd$_{0.85}$SnMoO$_7$:0.15Eu$^{3+}$ phosphors obtained from the Rietveld refinement.
3.2. Morphology

Typical SEM photographs recorded for NaGd\(_{1-x}\)SnMoO\(_7\):xEu\(^{3+}\) phosphor powders were shown in Fig. 3. The micrographs show uniform morphology with typical cuboid type grains having size range from 0.5 to 1 µm. The morphology of the as prepared grains presents a smooth surface which may be advantageous for luminescence applications.

3.3. Photoluminescence Studies

Figs. 4 and 5 shows the excitation and emission spectra of NaGd\(_{1-x}\)SnMoO\(_7\):xEu\(^{3+}\) phosphors. The excitation spectra include both broad band (240–350 nm, peaking around 313 nm) and sharp peaks (beyond 360 nm) of excitation. The broad band in the spectra corresponds to the combined charge transfer bands (CTB) from O\(^2-\)→Eu\(^{3+}\) and O\(^2-\)→Mo\(^{6+}\) and the sharp lines at 393 and 464 nm excitation wavelengths are assigned to intra-configurational 4f–4f transitions of Eu\(^{3+}\) ions in the host lattice (which are emission wavelengths of near UV and blue LED chips), are much stronger than the other transitions of Eu\(^{3+}\) [10]. This implies that molybdate based pyrochlore phosphors can be effectively excited by the radiations in the near UV and blue wavelength regions. It is also observed that absorption peaks of intra configurational 4f transitions of Eu\(^{3+}\) increase with increasing doping concentration of Eu\(^{3+}\), indicating the effective incorporation of Eu\(^{3+}\) in the host lattice. The increase of excitation strengths of 7F\(_0\)→5L\(_6\) and 7F\(_0\)→5D\(_2\) transitions can contribute to enhanced red emission from these phosphors with respect to Eu\(^{3+}\) concentration under both near UV and blue excitations.

The emission spectra exhibit dominant hypersensitive forced electric dipole 5D\(_0\)→7F\(_2\) transition at 615 nm indicating the occupancy of

Table 2
Refined parameters obtained from the Rietveld analysis of the NaGd\(_{1-x}\)SnMoO\(_7\):xEu\(^{3+}\) phosphors.

<table>
<thead>
<tr>
<th>Sample</th>
<th>x = 0.05</th>
<th>x = 0.10</th>
<th>x = 0.15</th>
<th>x = 0.20</th>
<th>x = 0.25</th>
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<td>Pyrochlore</td>
<td>Pyrochlore</td>
<td>Pyrochlore</td>
<td>Pyrochlore</td>
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<td>Fd3m</td>
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<td>10.4618(2)</td>
<td>10.4625(2)</td>
<td>10.4634(2)</td>
<td>10.4639(2)</td>
<td>10.4654(2)</td>
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<td>36.7063</td>
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<td>5.1164</td>
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<td>Oxygen x parameter</td>
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<td>0.414(2)</td>
<td>0.420(2)</td>
<td>0.416(2)</td>
<td>0.411(2)</td>
<td>0.413(2)</td>
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<tr>
<td>Caglioti parameters</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>U</td>
<td>0.010(4)</td>
<td>0.010(4)</td>
<td>0.010(5)</td>
<td>0.010(4)</td>
<td>0.016(4)</td>
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<tr>
<td>V</td>
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<td>0.002(3)</td>
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<td>0.003(4)</td>
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<tr>
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<td>0.001(7)</td>
<td>0.002(7)</td>
<td>0.002(8)</td>
<td>0.002(7)</td>
<td>0.003(8)</td>
<td>0.006(8)</td>
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<tr>
<td>Residual parameters</td>
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<td>Rexp (%)</td>
<td>13.79</td>
<td>14.03</td>
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<td>13.68</td>
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<td>Rr (%)</td>
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<td>Rwp (%)</td>
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<td>15.22</td>
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<tr>
<td>GOF</td>
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<td>1.20</td>
<td>1.11</td>
<td>1.17</td>
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<td>1.23</td>
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</table>

Fig. 3. SEM micrographs of NaGd\(_{1-x}\)SnMoO\(_7\):xEu\(^{3+}\) (a) x = 0.05, (b) x = 0.10, (c) x = 0.15, (d) x = 0.20, (e) x = 0.25 and (f) x = 0.30.
Eu$^{3+}$ at a site without inversion symmetry. The allowed magnetic dipole $^5D_0 \rightarrow ^7F_1$ transition at 587 nm have comparable lower intensity compared to that of electric dipole $^5D_0 \rightarrow ^7F_2$ transitions, indicating the occupancy of some Eu$^{3+}$ ions at an inversion symmetry site [11]. The intensity (R/O) ratio (which is also known as asymmetry ratio) is a measure of the degree of distortion from the inversion symmetry of the local environment of the Eu$^{3+}$ ion in the lattice. The R/O value of these phosphors is found to be high and constant in the order of 10 indicating high color purity. Further their fwhm is very small (~6 nm) which is suitable for improving the efficacy of the white light emitting diodes.

Increase in the Eu$^{3+}$ content does not change the shape and peak positions of the emission spectra although the intensity changes. The same emission profile is observed in the case of 464 nm excitation except the decrease in intensity. As the concentration of Eu$^{3+}$ ions increases, the emission intensity of $^5D_0 \rightarrow ^7F_2$ transitions increases up to $x = 0.25$ and a concentration quenching is observed beyond that as the distance between the Eu$^{3+}$ ions becomes smaller which favors the non-radiative pathway by energy transfer among Eu$^{3+}$ [12]. Fig. 6 shows the lifetime decay curves of $^5D_0 \rightarrow ^7F_2$ transition (615 nm) for all the samples under 393 nm excitation and found to be 0.39 ms for 25 mol% Eu$^{3+}$. The CIE (Commission Internationale de l’Eclairage) color coordinates of these phosphors were calculated using the software CIE Calculator and are (0.65, 0.35) matching with that of standard NTSC red phosphors (0.67, 0.33).

4. Conclusions

Novel molybdenum based pyrochlore type red phosphors, NaGd$_{1-x}$SnMoO$_7$:xEu$^{3+}$ ($x = 0.05, 0.10, 0.15, 0.20, 0.25$ and $0.30$) were prepared successfully by the solid state reaction method. The prepared phosphors show strong absorption peaks of intra 4f transitions of Eu$^{3+}$ at near UV (393 nm) and blue region (464 nm), which makes them suitable to be used along with near UV/blue LED chips. These phosphors exhibit narrow red emissions with high color purity and small lifetimes 0.39 ms. The developed phosphors could be potential red candidates for applications in phosphor converted white light emitting diodes.

Acknowledgments

The authors thank Department of Science and Technology (DST) GAP-215739, Govt. of India for the research facilities and financial support.

References