Structural and luminescent characteristic of Sm$^{3+}$ doped magnesium sulfide borate orange-red phosphor for white LED

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INTRODUCTION

A light-emitting diodes (LEDs) have many significant such as energy saving, high luminous efficiency, environmental protection and maintenance when compared with the incandescent and fluorescent lamps (Kumar et al., 2013). In few years, remarkable advancement can be seen in the improvement of white LED utilizing GaN and in addition InGaN chip. Obviously, three ways to produce white LEDs: (i) a blue LED is combined with a yellow YAG:Ce phosphor, (ii) mixing red, green, and blue emissions from three LEDs and (iii) exciting red/green/blue tricolour phosphors with a near-UV LED (370–410 nm) (Liao et al., 2012). The third one (iii) is more convenient way to obtain white LEDs due to the advantages, generated white colour by phosphors, that is, high tolerance to UV chips’ colour variation, intense luminescence efficiency as well as chemical stability. However, there exist disadvantages in this mix, viz., white emitting color changes with input power, low color rendering index due to two color mixing and low reproducibility due to strong dependence of white color quality on input power. To solve these proble

Graphical abstract

Polycrystalline compositions based on MgO, SO$_3$ and B$_2$O$_3$ have both scientific and technological importance because of their useful applications. Doping with rare earth elements not only due to a rearrangement in the structure, but also to variation in the luminescence properties. Magnesium sulfide borate doped samarium oxide (MgSBO$_3$:Sm$^{3+}$) phosphors were prepared by solid state reaction and their structural and luminescence characteristic were studied and reported. IR and Raman spectral studies have been made to explore the presence of functional groups and various structural units in the prepared Polycrystalline. The formation of SO$_3$, BO$_3$, B-O-B and S-O-B structural units have been investigated. The emission and excitation properties were studied. And the results show that the emission and excitation spectra of these phosphors can be excited by ultraviolet (UV) 341, 370 and 403 nm light, and emit green, yellow and red light with intense peak at 601 nm, which are nicely in accordance with the widely applied near- UV LED chip. The emission spectral intensity of Sm$^{3+}$ ions in the tilled phosphors increases up to 1 mol% of Sm$^{3+}$ ions and then decreases for 1.5 mol%. These results indicate that MgSBO$_3$:Sm$^{3+}$phosphor could be a potential suitable orange-red emitting phosphor candidate for white LEDs with excitation of a –403 nm near UV LED chip.

Keywords: MgSBO$_3$:Sm$^{3+}$, phosphor, luminescence, structural, orange–red LEDs, IR and raman

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compound is a good type of promising host material for rare-earth ions doped phosphor. However, there are no detailed reports on the luminescence properties of MgSO$_4$:Sm$^{3+}$ under near UV excitation and its potential application in near UV LEDs. In this work, Sm$^{3+}$ doped MgSO$_4$ was synthesized by a solid-state reaction for the first time, structural and luminescence characteristics were investigated. The results showed that MgSO$_4$:Sm$^{3+}$ may potentially be a good candidate as red phosphor for near UV LEDs.

**EXPERIMENTAL**

**Materials**

The starting materials were the analytic H$_2$BO$_3$, MgO, H$_2$SO$_4$ and Sm$_2$O$_3$ (99.99% in mass), were used as beginning materials for preparing polycrystals having the compositions 10MgO–40SO$_4$–(50–x)B$_2$O$_3$–xSm$_2$O$_3$ mol% (0.1≤ x ≤1.0). The Powder samples of MgSO$_4$:Sm$^{3+}$ samples were prepared by the conventional solid state reaction method. After the individual materials, had been mixed in the requisite proportions sufficiently, the powders were calcined at 800°C for 4 hours. The obtained products were MSBO$_4$:Sm$^{3+}$ phosphors. The structure was checked by powder X-ray diffraction (XRD) D/max–rA, CuK$_\alpha$, 40 kV, 100 mA, IR measurements are carried out using Perkin-Elmer Spectrum and Raman measurement is perform by a Raman XploRA plus spectrometer. The emission and excitation spectra were measured by a Shimadzu RF-540 ultraviolet spectrophotometer. All the photoluminescence properties of the phosphors were measured at room temperature.

**RESULTS AND DISCUSSION**

**Structure of MgSO$_4$:Sm$^{3+}$ phosphor**

The X-ray diffraction analysis was carried out to investigate the crystalline phase of the magnesium sulfoborate doped Sm$^{3+}$. Fig.1 shows the XRD pattern for MgSO$_4$B and MgSO$_4$B–1Sm$_2$O$_3$ mol% All diffraction peak positions correspond to that of the triclinic phase of MgSO$_4$B and the diffraction peaks matched well with the standard data (JCPDS no. 01-0721068). No Sm$^{3+}$ ion phase was detected, proving only act as a dopant and not changing overall host lattice which confirm the formation of a single-phase MgSO$_4$B (Dalhatu et al., 2016).

![Fig. 1 XRD pattern for MgSO$_4$B and MgSO$_4$B–1Sm$_2$O$_3$ mol% phosphor.](image)

The IR spectra of 10MgO+40SO$_4$+(50–y) B$_2$O$_3$+ySm$_2$O$_3$ with y from 0.1 to 1.0 mol % are shown in Fig. 2. As the concentration of doped Sm$^{3+}$ increased up to 1.0 mol %, the vibration modes are still similar without changing much in term of position and shape. The bending mode of δ(SO$_4^2$) of (BO$_3$) is located at around 432–473 cm$^{-1}$ appeared in all the spectra (Vyatchina et al., 2009). The band observed at about 548-560 cm$^{-1}$ appeared in all spectra which is due to bending mode of δ(SO$_4^2$) and δ(BO$_3$) (Daub et al., 2013). The bending vibration of SO$_4^2$ which is located at around 613-630 cm$^{-1}$ is observed in the spectra when the content of Sm$_2$O$_3$ is from 0.3 to 1.0 mol % (Vyatchina et al., 2009). The band at around 701-715 cm$^{-1}$ appeared in all spectra is due to bending of B-O-B linkages in borate network (Ganguli and Rao, 1999). The intensity of the band is increased as the content of Sm$_2$O$_3$ decreased. The vibration combination of BO$_3$ and BO$_3$ group is shifted to the high wavenumber was observed in all the spectra which is located around 870-880 cm$^{-1}$ (Vyatchina et al., 2009), the intensity of the band is increased as the content of Sm$_2$O$_3$ increased. The intensity of the band is increased with increased the content of Sm$^{3+}$. The asymmetric stretching vibration (S-O-B) is splitting into two small bands at 924 cm$^{-1}$ and 986 cm$^{-1}$ (Daub et al., 2014). The splitting of the band indicates that the vibration of S-O-B is stronger with Sm$_2$O$_3$ content. The band at round 1040-1078 cm$^{-1}$ appeared in all spectra which is due to B-O bond symmetric stretching vibration of the tetrahedral BO$_4$ units (Rada et al., 2010). Asymmetric vibration (S-O) of the SO$_4$ tetrahedral is located around 1204-1207 cm$^{-1}$ appeared in all the spectra (Daub et al., 2013). The bands around 1340-1350 cm$^{-1}$ and 1444-1447 cm$^{-1}$ appeared in all spectra which is due to boroxol rings and B-O bond asymmetric stretching vibration of the trigonal BO$_4$ units respectively (Rada et al., 2010).

![Fig. 2 IR spectra for magnesium sulfoborate doped with 0.1 ≤ y ≤ 0 mol% of Sm$^{3+}$ phosphor.](image)

![Fig. 3 Raman spectra for magnesium sulfoborate doped with 0.1 ≤ y ≤ 1.0 mol % of Sm$^{3+}$ phosphor.](image)
The Raman spectra of 10MgO+40SO₃+(50-y)B₂O₃+ySm₂O₃ with 0.1 ≤ y ≤ 1.0 mol % are shown in Fig. 3. The mode of SO₄²⁻ group which is around 450 cm⁻¹ is observed in the Raman spectra when the content of Sm₂O₃ is 0.1 mol % (Daub et al., 2014). This is due to large amount of SO₄ and small amount of B₂O₃. While band at 497 cm⁻¹ is observed in the spectra when the content of Sm₂O₃ is 0.7 and 1.0 mol % which is due to the non-ring BO₃ (Youngman and Zwanziger, 1996). A small band at 720 cm⁻¹ appeared in all the spectra which is due to bending vibrations of B-O-B linkages (Vyatchina et al., 2009). As the Sm₂O₃ content increases, one spectacular change in the Raman band is observed, i.e; the splitting of band at 804 into two small bands at 793 cm⁻¹ and 805 cm⁻¹ is due to symmetric vibration of boroxol rings (Yiannopoulos et al., 2001). The Raman band at 873 cm⁻¹ is due to sulfoborate type S-O-B (Ganguli and Rao, 1999). The intensity of S-O-B increased as the content of Sm₂O₃ increased. This is due to large amount of SO₄B₂O₃. The intense peak among all the peak was observed at band 984 cm⁻¹ is due to the symmetric stretching vibration of the SO₄ ion (Vyatchina et al., 2005). The intensity of SO₄ ion is increased as the content of Sm₂O₃ decreases with SO₃ content at 40 mol %. This shows that at small content of Sm₂O₃ the vibration of SO₄ ion is stronger. The band at 1060 cm⁻¹ is observed in the spectra when content of Sm₂O₃ is 0.1 mol % which is due the mixture from vibration of BO₃ and SO₄ (Daub et al., 2014). This indicates that at large amount of boric oxide and sulfate the vibration is intense. Table 1 summarized IR and Raman band assignments and the reported values for dopants crystal samples.

<table>
<thead>
<tr>
<th>IR</th>
<th>Raman</th>
<th>Reported values</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>463–470</td>
<td>450–497</td>
<td>440–470 (Vyatchina et al., 2009)</td>
<td>Bending δ(SO₄)²⁻, (BO₃)⁻.</td>
</tr>
<tr>
<td>548–555</td>
<td>-</td>
<td>500–600 (Daub et al., 2013)</td>
<td>b. δ(SO₄) and δ(BO₃).</td>
</tr>
<tr>
<td>613–630</td>
<td>620</td>
<td>610–630 (Vyatchina et al., 2009)</td>
<td>Bending δ(SO₄)²⁻</td>
</tr>
<tr>
<td>701–715</td>
<td>720</td>
<td>720–790 (Vyatchina et al., 2009)</td>
<td>Bending of B-O-B linkages</td>
</tr>
<tr>
<td>-</td>
<td>793–805</td>
<td>804 (Yiannopoulos et al., 2001)</td>
<td>boroxol rings</td>
</tr>
<tr>
<td>870–986</td>
<td>879–984</td>
<td>850–1060 (Daub et al., 2014)</td>
<td>Asym. stretching vibr. (S-O-B)</td>
</tr>
<tr>
<td>-</td>
<td>1011</td>
<td>1010 (Ganguli and Rao, 1999)</td>
<td>Symm. Stret. Vib. of SO₄</td>
</tr>
<tr>
<td>1046–1074</td>
<td>1060</td>
<td>900–1100 (Rada et al., 2010)</td>
<td>Symm. stret. vibr. of BO₄ units</td>
</tr>
<tr>
<td>1204–1207</td>
<td>-</td>
<td>1200 (Daub et al., 2013)</td>
<td>V₄u(S-O) vibration of the SO₄</td>
</tr>
<tr>
<td>1340</td>
<td>-</td>
<td>1350 (Rada et al., 2010)</td>
<td>boroxol rings</td>
</tr>
<tr>
<td>1451</td>
<td>-</td>
<td>1420–1550 (Rada et al., 2010)</td>
<td>Asymmetric stre. Vib. of BO₃ units</td>
</tr>
</tbody>
</table>

### Emission and excitation spectra of MgSBO₃:Sm³⁺ phosphor

The excitation of 10MgO+40SO₃+(50-y)B₂O₃+ySm₂O₃ with 0.1 ≤ y ≤ 1.0 are presented in Fig. 4. The excitation spectra are obtained by monitoring at emission wavelength of 601 nm in the range of 275–450 nm. A total of three excitation spectra were observed from ground state with 0.1 ≤ y ≤ 1.0. The emission spectra show four transitions corresponding to ⁴G⁵/₂→⁶H₆/₂ (561 nm), ⁴G⁵/₂→⁶H₇/₂ (501 nm), ⁴G⁵/₂→⁶H₈/₂ (601 nm), ⁴G⁵/₂→⁶H₉/₂ (644 nm), and ⁴G⁵/₂→⁶H₁₀/₂ (706 nm) transition (Liao et al., 2012; Liu and Lin, 2009; Changmin et al., 2007). The peak position and the shape of the excitation spectra do not change as the concentration of Sm³⁺ ions increased. Meanwhile, the intensity of the excitation spectra increases as the concentration of Sm³⁺ ions increases up to 1.0 mol%, beyond is decrease in intensity with increase in concentration of Sm³⁺ ion was observed. Among the transitions, the intense excitation spectra at 403 nm (⁴H₂/₉₀ →⁴F₇/₂) was chosen to measure the emission spectrum of 10MgO+40SO₃+(50-y)B₂O₃+ySm₂O₃ with 0.1 ≤ y ≤ 1.0. The emission spectra show four emission bands corresponding to ⁴G⁵/₂→⁴H₆/₂ (561 nm), ⁴G⁵/₂→⁴H₇/₂ (601 nm), ⁴G⁵/₂→⁴H₈/₂ (644 nm), and ⁴G⁵/₂→⁴H₁₀/₂ (706 nm) transition (Liao et al., 2012; Liu and Lin, 2009; Changmin et al., 2007; Xiong et al., 2014). Among the four observed bands, the ⁴G⁵/₂→⁴H₇/₂ is more intense. From Fig. 5, the emission spectral intensity of Sm³⁺ ions in the titled phosphors increases gradually up to 1 mol% of Sm³⁺ ions and then decreases for 1.5 mol%. This concentration quenching observed at 1mol% of Sm³⁺ ions in these phosphors may be due to nonradiative energy transfer processes among the Sm³⁺ ions (Xiong et al., 2014). These phosphors have a very distinct orange–red luminescence, which is mainly due to the luminescence of the intense ⁴G⁵/₂→⁴H₆/₂ (601 nm) and ⁴G⁵/₂→⁴H₇/₂ (644 nm). Therefore, these transitions clearly a capable orange–red emitting phosphor for the LEDs (Palaspagar et al., 2015).
The energy level diagram of the Sm³⁺ ion doped magnesium sulfoborate phosphors are shown in Fig. 6 which shows the probable transitions involved in this process. The interaction of MgSBO₃:Sm³⁺ phosphor with exciting wavelengths 403 nm, leads to the transition of Sm³⁺ ions from the ground level ⁴I₆ to the higher levels ⁴F₉/₂. The Sm³⁺ ions from the higher states make non-radiative transition up to ⁴G₉/₂ level after that the transitions are radiative, as the energy gap of ⁴G₅/₂−⁴H₅/₂, ⁴G₉/₂−⁴H₉/₂, ⁴G₅/₂−⁴H₉/₂ and ⁴G₅/₂−⁴H₁₁/₂ transitions states are sufficient to give yellow-orange emission (Bedyal et al., 2014).

The energy level diagram for magnesium sulfoborate doped with 0.1 ≤ y ≤ 1.5 mol % of Sm³⁺phosphor.

In conclusions, MgSBO₃:Sm³⁺ red phosphor was prepared by solid state reaction method. XRD analysis of the prepared material shows MgSO₄·B₂O₃ phase. IR and Raman studies confirm the presence of SO₄, BO₄, BO₃, B-O-B and S-O-B structural units. The excitation spectrum of MgSBO₃:Sm³⁺ phase. IR and Raman studies confirm the presence of SO₄, BO₄, BO₃, B-O-B and S-O-B structural units. The excitation spectrum of MgSBO₃:Sm³⁺ phosphor with exciting wavelengths 403 nm, the phosphor displayed orange-red luminescence with the emission spectrum bands at 561 (green color), 601 (yellow), 644 (red color) and 706 (red color) nm which are correspond to ⁴G₉/₂→⁴H₉/₂, ⁴H₉/₂ and ⁴H₁₁/₂ transitions of Sm³⁺, respectively. Therefore, MgSBO₃:Sm³⁺ phosphors are promising phosphors for white orange-red LEDs.

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REFERENCES


Li, P., Wang, Z., Yang, Z., Guo, Q. and Li, X. 2009. Emission features of LiBaBO₃: Sm³⁺ red phosphor for white LED. Materials Letters, 63(9), 751-753.

Li, P., Wang, Z., Yang, Z., Guo, Q. and Li, X. 2010. Luminescent characteristics of LiCaBO₃: M (M=Eu³⁺, Sm³⁺, Tb³⁺, Ce³⁺, Dy³⁺) phosphor for white LED. Journal of Luminescence, 130(2), 222-225.


