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RESEARCH ARTICLE

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

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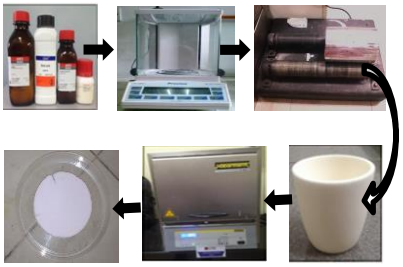
Graphical abstract



Abstract

Polycrystalline compositions based on MgO, SO_3 and B_2O_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_4, BO_4, 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 titled 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

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 an amount of phosphor. To solve these problems, LED phosphors has been employing such as green, yellow and red, which are excited by ultraviolet (UV) (Mao *et al.*, 2014). However, the commercially applicable red phosphor of $MgSBO_3$:Eu^{3+} is lower efficient under near UV light excitation wavelength within 300 to 400 nm region, and its decomposition products are harmful to the environment (Dalhatu *et al.*, 2016). Therefore, it is an urgent to investigate new red-emitting phosphors that can be efficiently excited by the near UV LED range 350 to 410 nm chips. The rare earth are good activators, especially Sm^{3+} is an essential activator for many different inorganic lattices to yield orange–red emission due to its $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $^4G_{/2} \rightarrow {}^6H_{7/2,}$ $^4G_{5/2} \rightarrow {}^6H_{9/2}$ and $^4G_{52} \rightarrow {}^6H_{11/2}$ transitions.

Luminescent properties of phosphors are strongly dependent on the crystal structure of the host lattice and the kind of activator. To our knowledge, alkaline earth borate is considered as potential host matrices for phosphors because of its excellent thermal stabilization, stable crystal structure, cheap raw material (H_3BO_3) and excellent optical properties (Li *et al.*, 2010). The luminescence properties of samarium as a doped have been reported by many researchers. For example, $LaInO_3$: RE^{3+} (RE = Sm, Pr and Tb) phosphor have application for field emission displays (Liu and Lin, 2009). The $Bi_2ZnB_2O_7$ doped Sm^{3+} phosphor considered as a luminescence for solid state lightning (Palaspagar *et al.*, 2015). $ZnGa_2O_4$:Mn^{2+} and $LaGaO_3$:Ln^{3+} (Ln= Eu, Tb, Dy, Tm, Sm) phosphors is a candidate for applications in field of white LED (Mao *et al.*, 2014). There are some reports currently about phosphor for white LEDs (Zhang *et al.*, 2012; Li *et al.*, 2009). The IR and Raman spectroscopy are an important tool for study of structural features of a material. The borate network. Borate are known to have important properties which include low melting point, good thermal stability, good solubility of rare-earth ions (Guan *et al.*, 2013). Borate constitute an interesting system, which the network building unit can be either borate triangles (BO_3) with non-bridging atoms or borate tetrahedral (BO_4) with all bridging oxygen atoms. Borate glass can easily be melted, owning smaller mass compare to others glass network former, thermal stable and chemical durable (Dalhatu *et al.*, 2016). Previous reports show that the $MgSBO_3$

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 $MgSBO_3:Sm^{3+}$ under near UV excitation and its potential application in near UV LEDs. in the this work, Sm^{3+} doped $MgSBO_3$ was synthesized by a solid-state reaction for the first time, structural and luminescence characteristics were investigated. The results showed that $MgSBO_3:Sm^{3+}$ may potentially be a good candidate as red phosphor for near UV LEDs.

EXPERIMENTAL

Materials

The starting materials were the analytic H_3BO_3, MgO, H_2SO_4 and Sm_2O_3 (99.99% in mass). were used as beginning materials for preparing polycrystals having the compositions$10MgO–40SO_4–(50-x)B_2O_3–xSm_2O_3$ mol% ($0.1\leq x \leq 1.0$). The Powder samples of $MgSBO_3:Sm^{3+}$ 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 $MSBO_3:Sm^{3+}$ phosphors. The structure was checked by powder X-ray diffraction (XRD) D/max–rA, CuKα, 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 $MgSBO_3:Sm^{3+}$ 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 $MgSO_3B_3$ and $MgSO_3B_3$-1Sm_2O_3 mol%. All diffraction peak positions correspond to that of the triclinic phase of $MgSO_3B_3$ and the diffraction peaks matched well with the standard data (JCPDS no. 01-072-1068). 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 $MgSO_3B_3$(Dalhatu *et al.*, 2016).

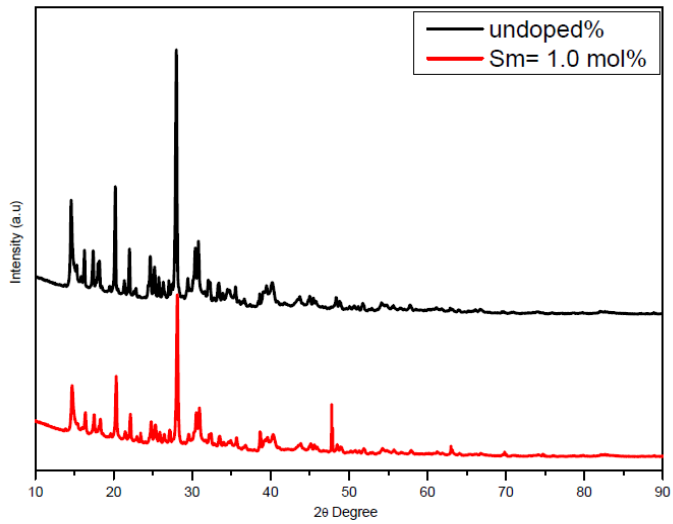


Fig. 1 XRD pattern for $MgSO_3B_3$ and $MgSO_3B_3$-1Sm_2O_3 mol% phosphor.

The IR spectra of $10MgO+40SO_3+(50-y)\ B_2O_3+ySm_2O_3$ 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 $\delta(SO_4)^{2-}$, $(BO_3)^-$ 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 $\delta(SO_4)$ and $\delta(BO_4)$ (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_2O_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_2O_3 decreased. The vibration combination of BO_3 and BO_4 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 increases as the content of Sm_2O_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_2O_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_3 units respectively (Rada *et al.*, 2010).

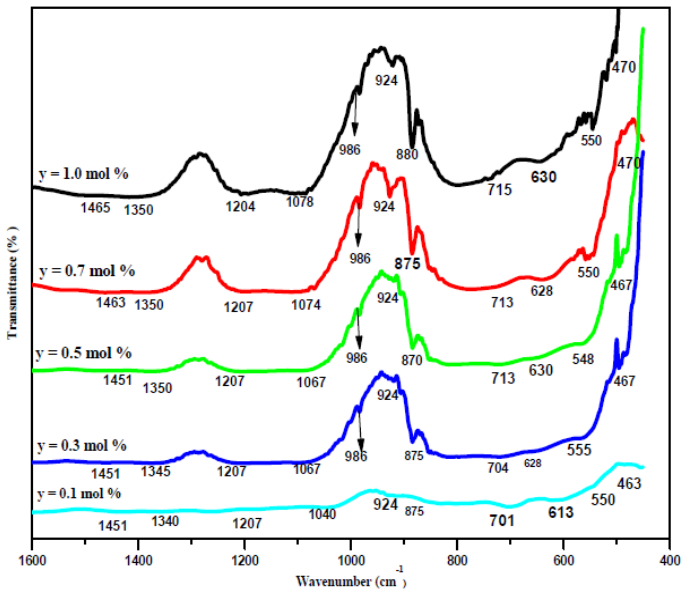


Fig. 2 IR spectra for magnesium sulfoborate doped with $0.1 \leq y \leq 0$ mol% of Sm^{3+} phosphor.

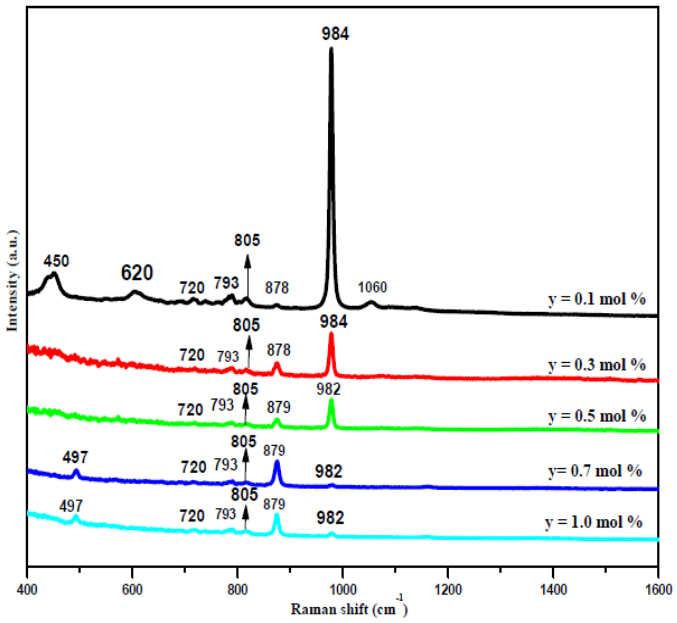


Fig. 3 Raman spectra for magnesium sulfoborate doped with $0.1 \leq y \leq 1.0$ mol % of Sm^{3+} phosphor.

The Raman spectra of $10MgO+40SO_3+(50-y)B_2O_3+ySm_2O_3$ with $0.1 \leq y \leq 1.0$ mol % are shown in Fig. 3. The mode of SO_4^{2-} group which is around 450 cm^{-1} is observed in the Raman spectra when the content of Sm_2O_3 is 0.1mol % (Daub *et al.*, 2014). This is due large amount of SO_3 and small amont of B_2O_3. While band at 497 cm^{-1} is observed in the spectra when the content of Sm_2O_3 is 0.7 and 1.0 mol % which is due to the non-ring BO_4^- (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 Sm_2O_3 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 Sm_2O_3 increased. This is due to large amount of SO_3 B_2O_3. The intense peak among all the peak was observed at band 984 cm^{-1} is due to the Symmetric stretching vibration of the SO_4 ion (Vyatchina *et al.*, 2005). The intensity of SO_4 ion is increased as the content of Sm_2O_3 decreases with SO_3 content at 40 mol %. This shows that at small content of Sm_2O_3 the vibration of SO_4 ion is stronger. The band at 1060 cm^{-1} is observed in the spectra when content of Sm_2O_3 is o.1 mol % which is due the mixture from vibration of BO_4 and SO_4 (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 1 IR and Raman for magnesium sulfoborate doped Sm^{3+} phosphor.

IR	Raman	Reported values	Assignments
463–470	450–497	440-470 (Vyatchina *et al.*, 2009)	Bending $\delta(SO_4)^{2-}$, $(BO_3)^-$.
548–555	-	500-600 (Daub *et al.*, 2013)	bending $\delta(SO_4)$ and $\delta(BO_4)$.
613–630	620	610-630 (Vyatchina *et al.*, 2009)	Bending $\delta(SO_4)^{2-}$
701–715	720	720-790 (Vyatchina *et al.*, 2009)	Bending of B-O-B linkages
-	793–805	804 (Yiannopoulos *et al.*, 2001)	boroxol rings
870–986	879–984	850-1060 (Daub *et al.*, 2014)	Asym. stretching vibr. (S-O-B)
-	1011	1010 (Ganguli and Rao, 1999)	Symm. Stret. Vib. of SO_4^{2-}
1046–1074	1060	900-1100 (Rada *et al.*, 2010)	Symm.stret. vibr. of BO4 units
1204–1207	-	1200 (Daub *et al.*, 2013)	V_{as}(S-O) vibration of the SO_4
1340	-	1350 (Rada *et al.*, 2010)	boroxol rings
1451	-	1420-1550 (Rada *et al.*, 2010)	Asymmetric stret. Vibr. of BO_3 units

Emission and excitation spectra of $MgSBO_3:Sm^{3+}$ phosphor

The excitation of $10MgO+40SO_4+(50-y)$ $B_2O_3+ySm_2O_3$ with $0.1 \leq y \leq 1.0$ 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 of $^6H_{5/2}$ to the excited state $^4D_{3/2}$ (341 nm), $^6P_{7/2}$ (370 nm) and $^6F_{7/2}$ (403 nm) of Sm^{3+} ions respectively (Liu and Lin, 2009; Zhang *et al.*, 2006; Changmin *et al.*, 2007). The peak position and the shape of the excitation spectra do not change as the concentration of Sm^{3+} ions increase. Meanwhile, the intensity of the excitation spectra increases as the concentration of Sm^{3+} ion increases up to 1.0 mol%, beyond is decrease in intensity with increases in concentration of Sm^{3+} ion was observed. Among the transitions, the intense excitation spectra at 403 nm ($^6H_{5/2} \rightarrow {}^6F_{7/2}$) was chosen to measure the emission spectrum of $10MgO+40SO_3+(50-y)$ B_2O_3+y Sm_2O_3 with $0.1 \leq y \leq 1.0$.

Fig. 5 shows the emission spectra of $10MgO+40SO_3+(50-y)B_2O_3+y$ Sm_2O_3 with $0.1 \leq y \leq 1.0$. The emission spectra show four emission bands corresponding to $^4G_{5/2} \rightarrow {}^6H_{5/2}$ (561 nm), $^4G_{5/2} \rightarrow {}^6H_{7/2}$ (601 nm), $^4G_{5/2} \rightarrow {}^6H_{9/2}$ (644 nm), and $^4G_{5/2} \rightarrow {}^6H_{11/2}$ (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 $^4G_{5/2} \rightarrow {}^6H_{7/2}$ is more intense. From Fig. 5, the emission spectral intensity of Sm^{3+} 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 Sm^{3+} ions in these phosphors may be due to nonradiative energy transfer processes among the Sm^{3+} ions (Xiong *et al.*, 2014). These phosphors have a very distinct orange–red luminescence, which is mainly due to the luminescence of the intense $^4G_{5/2} \rightarrow {}^6H_{7/2}$ (601 nm) and $^4G_{5/2} \rightarrow {}^6H_{9/2}$ (644 nm). Therefore, these transitions clearly a capable orange–red emitting phosphor for the LEDs (Palaspagar *et al.*, 2015).

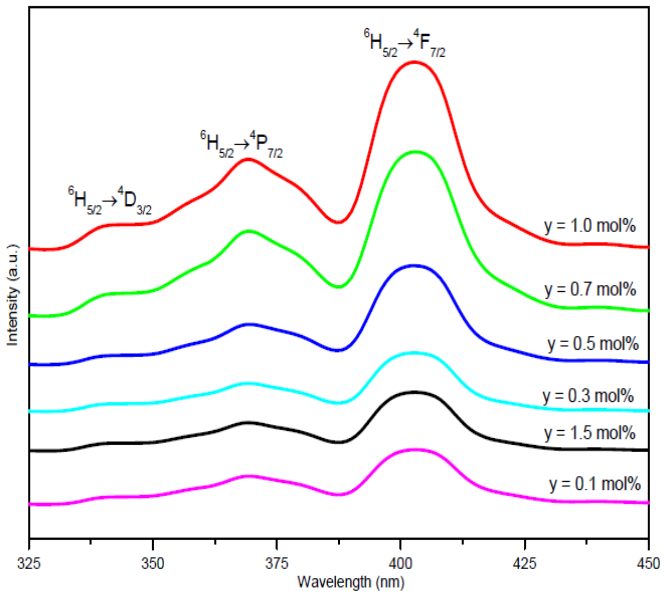


Fig. 4 Excitation spectra for magnesium sulfoborate doped with $0.1 \leq y \leq 1.5$ mol % of Sm^{3+}phosphor.

The energy level diagram of the Sm^{3+} ion doped magnesium sulfoborate phosphors are shown in Fig. 6 which shows the probable transitions involved in this process. The interaction of $MgSBO_3:Sm^{3+}$ phosphor with exciting wavelengths 403 nm, leads to the transition of Sm^{3+} ions from the ground level $^6H_{5/2}$ to the higher levels $^6F_{7/2}$. The Sm^{3+} ions from the higher states make non-radiative transition up to $^4G_{5/2}$ level after that the transitions are radiative, as the energy gap of $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $^4G_{5/2} \rightarrow {}^6H_{7/2}$, $^4G_{5/2} \rightarrow {}^6H_{9/2}$ and $^4G_{5/2} \rightarrow {}^6H_{11/2}$ transitions states are sufficient to give yellow-orange emission (Bedyal *et al.*, 2014).

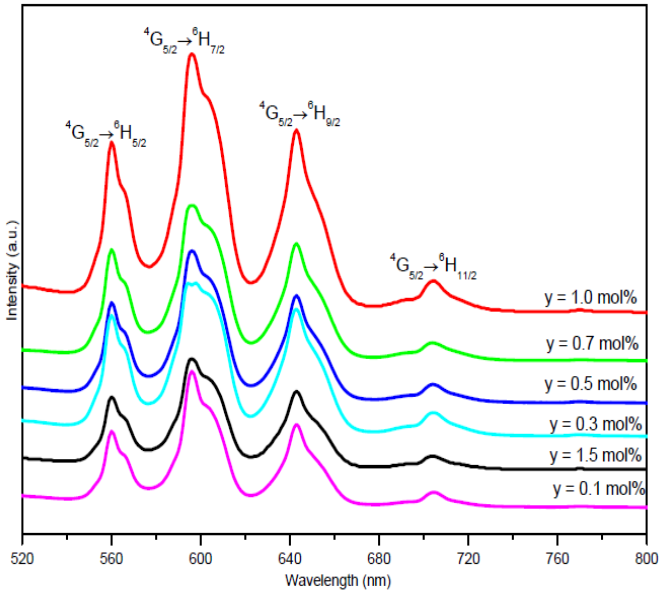


Fig. 5 Emission spectra for magnesium sulfoborate doped with 0.1 ≤ y ≤ 1.5 mol % of Sm^{3+}phosphor.

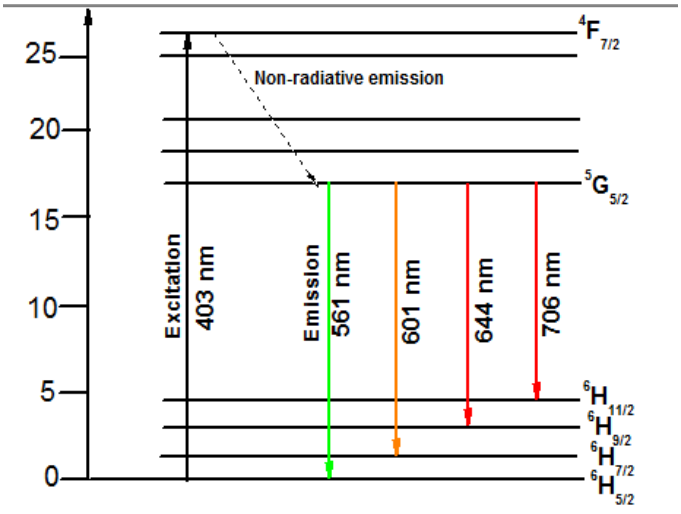


Fig. 6 The energy level diagram for magnesium sulfoborate doped with 0.1 ≤ y ≤ 1.5 mol % of Sm^{3+}phosphor.

CONCLUSION

In conclusions, $MgSBO3:Sm^{3+}$ red phosphor was prepared by solid state reaction method. XRD analysis of the prepared material shows $MgSO_3B_3$ phase. IR and Raman studies confirm the presence of SO_4, BO_4, BO_3, B-O-B and S-O-B structural units. The excitation spectrum indicates that the phosphor can be excited by near-UV, under excitation of 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 $^4G_{5/2} \rightarrow {}^6H_{5/2}$,$^6H_{7/2}$, $^6H_{9/2}$ and $^6H_{11/2}$ transitions of Sm^{3+}, respectively. Therefore, $MgSBO3:Sm^{3+}$ phosphors are promising phosphors for white orange-red LEDs.

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