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SYNTHESIS AND CHARACTERIZATION OF Sm, Li ACTIVATED MgB_4O_7 PHOSPHORS

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Abstract: In the present study, Sm, Li -activated Magnesium borate (MgB_4O_7) phosphors were synthesized by the solid-state reaction method. The crystal structure was determined by X-ray diffraction (XRD), surface morphology by scanning electron microscopy (SEM), and the nature of bonding by Fourier-transform infrared (FTIR) spectroscopy. The X-ray diffraction pattern exhibited the crystal structure of the prepared phosphors along with JCPDS data 31-0787. The photoluminescence excitation spectra of MgB_4O_7: Sm, Li displays a most intense peak at 408 nm corresponding to $^6H_{5/2} \rightarrow {}^4K_{11/2}$ transition, and emission spectra show the two characteristic bands at 578 nm and 602 nm. The strongest emission peak was obtained at 602 nm due to the excitation of Sm^{3+} ions from $^4G_{5/2}$ to $^6H_{7/2}$ transition. Raman spectroscopy determined the vibrational and bonding behavior of prepared samples and no peak shifting was observed in the host matrix after 2 mol concentration.

Keywords: Solid state reaction method, FTIR. Raman spectroscopy

1. INTRODUCTION

Recently, light-emitting devices and luminescence materials have attracted researchers' attention because of their variety of applications like solid-state illumination devices and optoelectronic devices [1 - 4]. Generally, Borates are considered excellent hosts and important luminescent materials due to their greater stability, low synthetic temperatures, and cheap raw material. Boron has only three electrons ($1s^2$ $2s^2$ $2p^1$) in their outermost orbit, hence the ion is unpolarizable. By sharing electrons, boron, and oxygen make the chemical bond between them. Due to diverse structures and the strong covalent B-O bond borates shows high nonlinear optical properties [5]. To get luminescent materials generally, some rare-earth oxides and transition metals are added as activators into the borate compounds. These materials are promising materials not only for the scientific area but also have a widespread application in a commercial area. Many researchers have focused on the borate-based compound since this compound has strong non-linear optical properties due to its lattice, a unique combination of large electronic band gaps, mechanical robustness, and chemical and environmental stability [6]. Therefore, borates have remarkable potential for the production of high-technology materials. In addition to this, many groups investigated that borate-based compounds are found to be promising materials as they have a broad range of spectral responses from infrared (IR) wavelength to visible and UV wavelengths [7-9].

In order to enhance the luminescence properties, borate compounds are doped with various rare earth elements such as (Eu, Dy, Tm, Ce) or alkali metals (Na, Li,) [2, 3, 4, 10-13] and simultaneous co-doping can also be used to improve the luminescent emission and sensitivity of the materials [14]. Magnesium tetraborate (MgB_4O_7) is an attractive host material with a low effective atomic number (Zeff) for photoelectric absorption equal to 8.4 and soft biological tissue [15-16]. MgB_4O_7 activated with various rare earth ions was tried by different groups, which is vital for personal, radiation, and medical dosimetry [3, 17-20]. There are various rare earth ions that can be occupied as activators for various phosphors. Among various rare-earth ions, Sm^{3+} ion is an excellent and efficient activator for producing reddish orange emission due to the transition of $^4G_{5/2} \rightarrow {}^6H_J$ (J = 5/2, 7/2, 9/2, 11/2) state [21-24]. It is investigated by several researchers that samarium-doped phosphors yield strong orange-red emissions with different

excitation wavelengths like 350 [25], 355 [26], and 405 nm [[27]. To obtain an efficient phosphor, various alkali metals such as Na, and Li are co-doped usually as sensitizers, which increases the luminescent properties of materials. In the present study MgB_4O_7:Sm, Li phosphor has been synthesized by the solid-state reaction method. The morphology and structural properties of the synthesized phosphor were determined by X-ray diffraction (XRD) scanning electron microscopy (SEM), Fourier Transform Infrared (FTIR), and Raman spectroscopy which describe the phase, surface structure, vibrational and bonding nature of the samples. The luminescence characteristics of MgB_4O_7:Sm, Li phosphor, and the effect of dopants on the PL are also reported in this work.

2. EXPERIMENTAL DETAILS

Rare earth-doped magnesium tetraborate phosphors were synthesized by solid-state reaction. Himedia chemicals magnesium carbonate ($MgCO_3$), boric acid (H_3Bo_3), samarium oxide (Sm_2O_3), and lithium carbonate (Li_2CO_3) were used as raw materials. Required quantities of all the raw materials along with the required dopant/codopant were mixed homogenously and continuously grounded in an agate mortar for 5 hours. The dopant concentration may be varied from 0.01 to 0.05 mol. After the homogeneous mixing, fine powder was obtained which is transferred to a crucible and kept inside the muffle furnace for the calcination process at 900°c for 5 hours. Then the calcined powder was removed from the furnace, cooled at room temperature, and again grounded for 5 mins. The resultant phosphor was used for further characterization studies. X-ray diffraction (XRD) pattern of MgB_4O_7: Sm, Li phosphor was determined by a PANalytical X'pert Powder X-ray Diffractometer in the 2Θ range from 10 to 55º, with CuKα radiation of λ= 1.5406 Å. The surface morphology of the samples was examined using a scanning electron microscope (SEM). The nature of the bonding behavior of the phosphor was carried out through Fourier transform infrared spectroscopy (FTIR) and Raman spectra. To study the IR transmittance spectra, some pellets were prepared by mixing sample powder with potassium bromide (KBr) in the ratio of 1:8. The photoluminescence emission (PLE) and excitation spectra of the phosphor were examined using Spectrofluorophotometer. All the above experimental processes were performed under ambient conditions.

3. RESULTS AND DISCUSSION

3.1 XRD analysis

The crystal structure and phase purity of the synthesized powder sample MgB_4O_7: Sm, Li was identified by Powder X-ray Diffractometer (XRD). Figure 1 displays the XRD pattern of MgB_4O_7: Sm, Li along with JCPDS data 31-0787. It can be observed that the diffraction peak has been well-matched with JCPDS data 31-0787. The crystal structure of the sample was orthorhombic with a space group Pbca and lattice parameters a = 13.475 Å, b = 8.200 Å, c = 7.952 Å. [17].

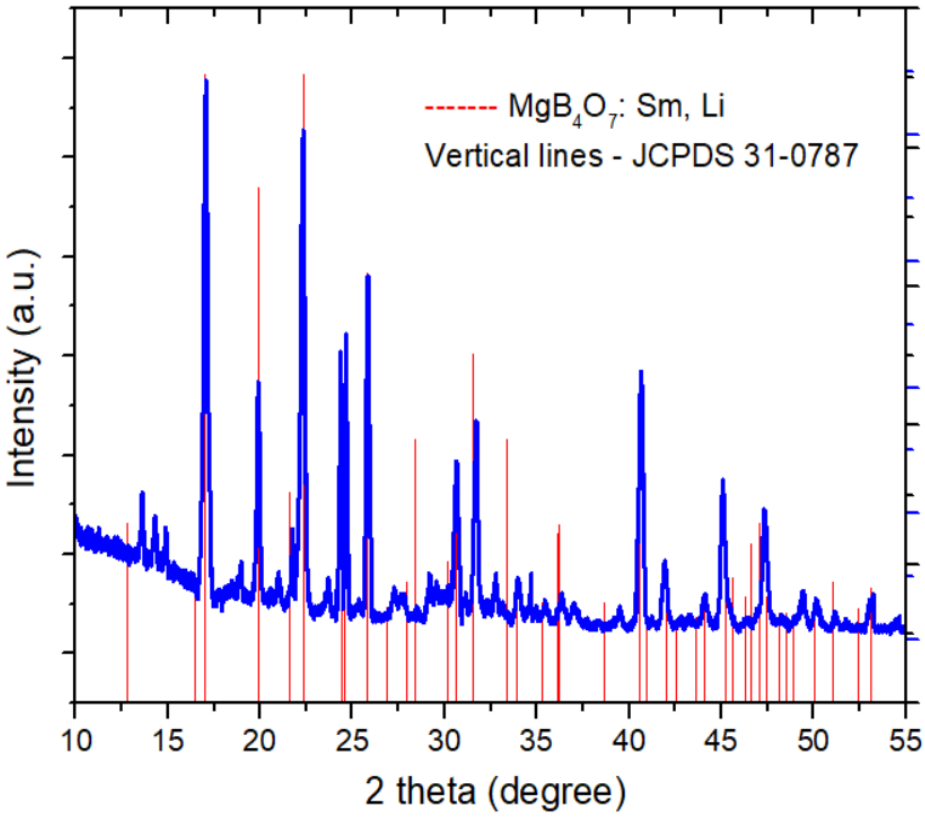
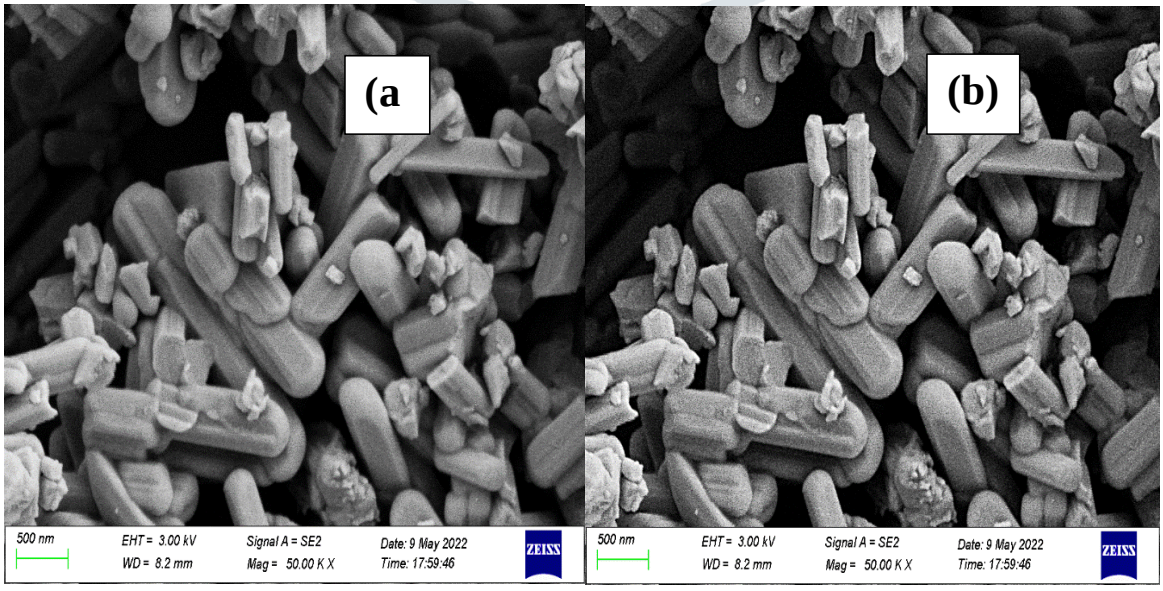


Fig. 1. XRD pattern of MgB_4O_7: Sm, Li (2 mol%) along with JCPDS data 31-0787

3.2 Morphological analysis

The surface morphology of the prepared phosphors was investigated by SEM analysis. Figure 2 shows the SEM images of the MgB_4O_7: Sm, Li phosphor doped with different concentrations. The micrograph shows that all the samples have almost the same morphology. The particles are of non-uniform size and shape but are slightly found in the agglomerated form. The crystalline size of particles was observed to be in the range of 300–500 nm.



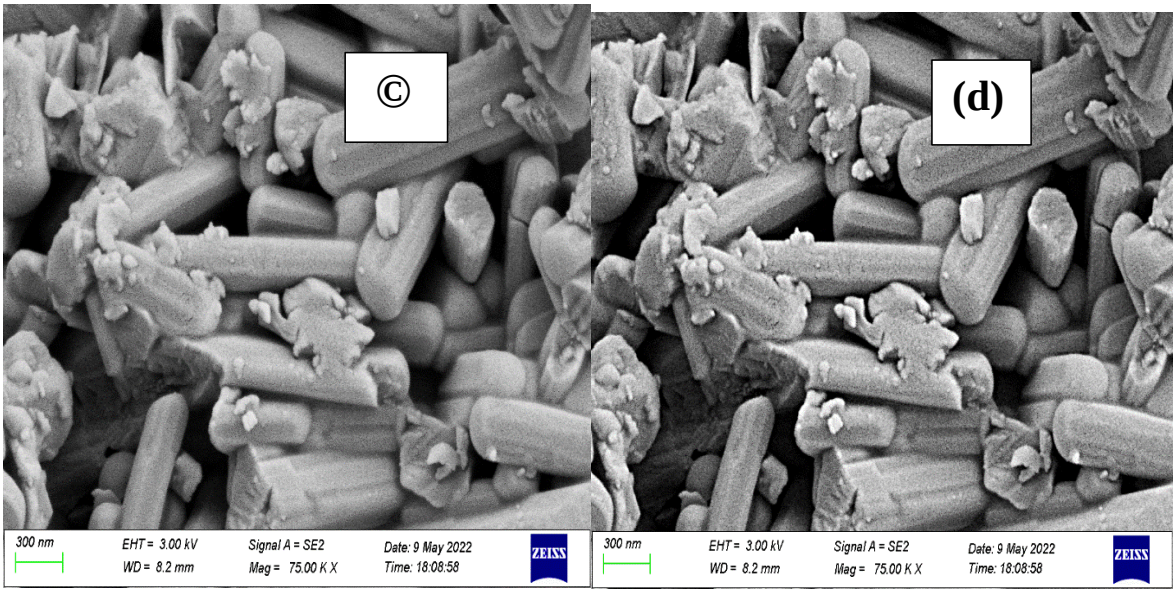


Fig. 2. SEM images of MgB_4O_7: Sm, Li (1-4 mol %) phosphors

3.3 FTIR study

The molecular and vibrational behavior of the prepared samples were investigated by Fourier transform infrared (FTIR) spectroscopy. Figure 3 shows the FTIR spectrum of MgB_4O_7: Sm, Li in the range of 3500 – 400 cm^{-1}. The band obtained at 3432 cm^{-1} corresponds to the OH^- groups of the material which was observed due to humidity in the air. The peak between 1515 to 1292 cm^{-1} might be the asymmetric stretching of tri-coordinate boron (BO_3) units. The asymmetric stretching of four-coordinate boron BO_4 units lying in the region 1292 – 1025 cm^{-1}. The symmetric stretching of trigonal BO_3 units can be observed in the region between 1025 to 840 cm^{-1}, and the band below 840 cm^{-1} describes the out-of-plane OH^{-1} bending band and vibration nature of the B-O-B bending borate network.

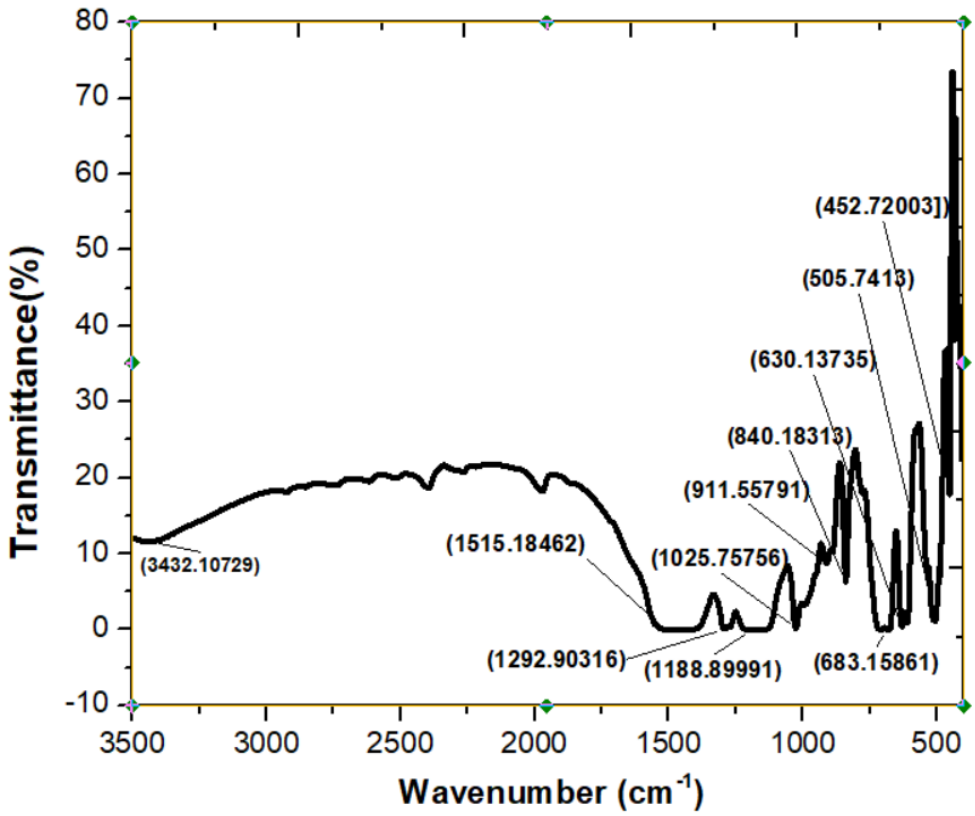


Fig. 3. FTIR spectrum of MgB_4O_7: Sm, Li phosphor (2 mol%)

3.3 Raman spectroscopy

To identify the vibrational, rotational, and other states of molecules, Raman spectroscopy was carried out. Figure 4 displays the recorded Raman spectra of MgB_4O_7: Sm, Li Phosphors in the wavenumber range of 1800–200 cm^{-1}. On increasing the dopant concentration, only the intensity of the peak increases after 2 mol concentration, and no Raman peak shifting was observed in the host matrix. Generally, the boron atoms that are attached to the polyhedron of the borates are either triagonal or tetrahedral. It is observed that the band at around 1096 cm^{-1} is ascribed to the symmetric stretching vibrations of trigonal boron in the $[BO_3]$ groups, and the band at 1303 cm^{-1} may correspond to the antisymmetric stretching modes of trigonal boron.

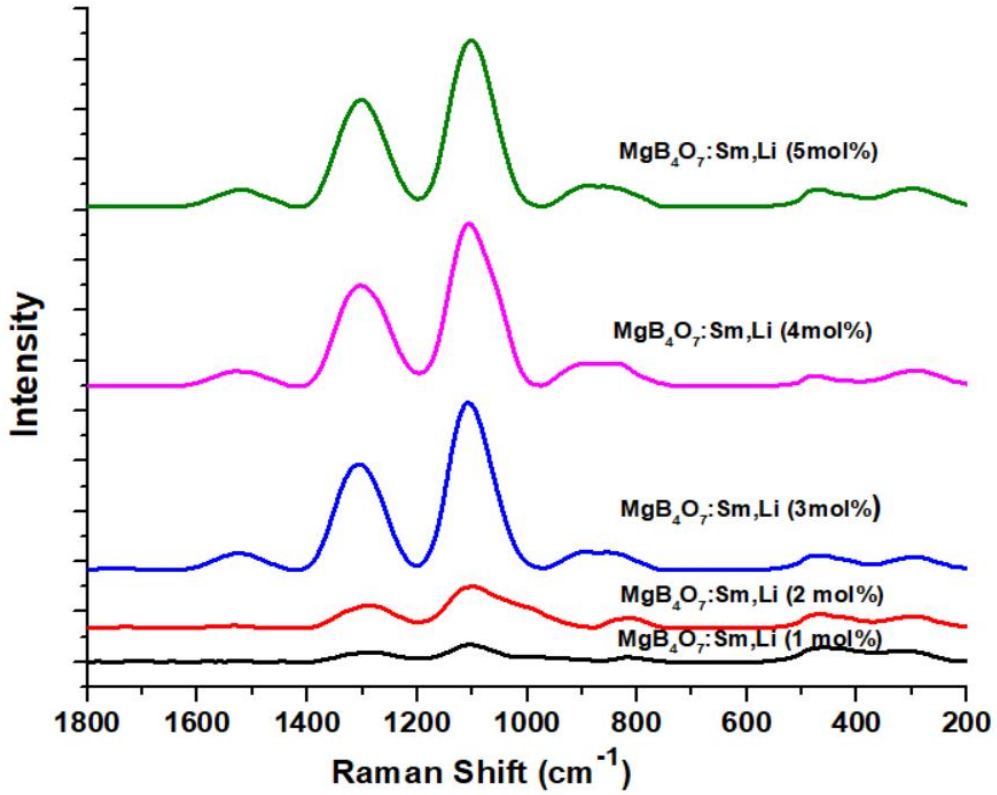


Fig. 4 Raman spectrum of MgB_4O_7: Sm, Li Phosphors

3.4 Photoluminescence (PL) studies

Figure 5 shows the excitation spectra of the MgB_4O_7 phosphor doped with Sm and codoped with Li ions. The excitation spectrum was obtained by monitoring the sample at an emission wavelength of 612 nm. The characteristic transition consists of sharp and intense peaks at 336, 346, 378, 408, and 468 nm which corresponds to the electronic transition from $^6H_{5/2}$ to upper excited states within Sm^{3+}. The most intense peak is obtained at 408 nm ($^6H_{5/2} \rightarrow {}^4K_{11/2}$).

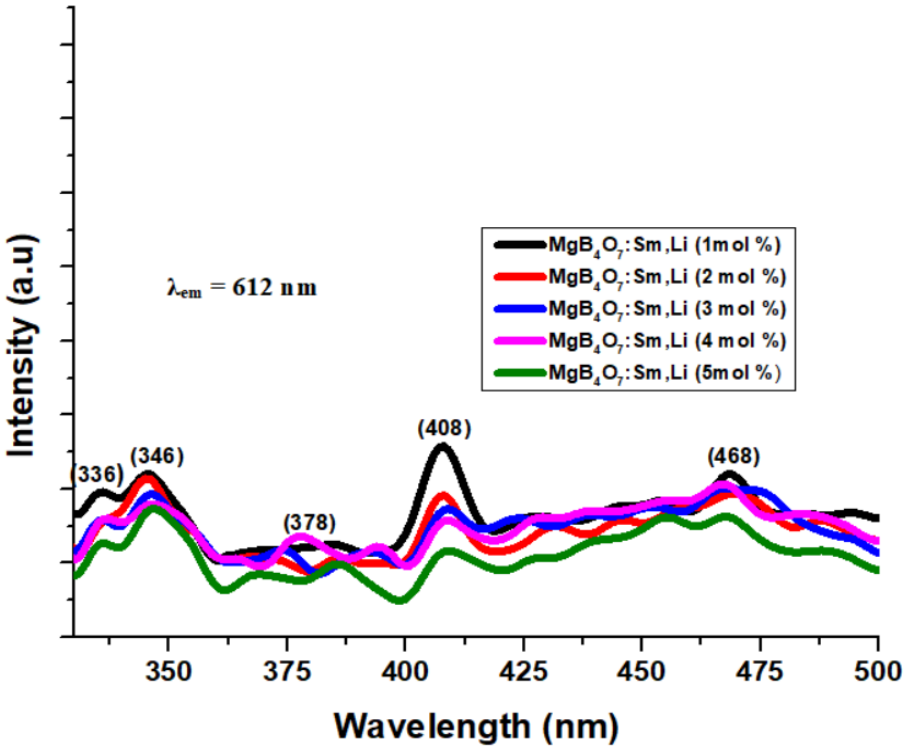


Fig. 5. Excitation spectra of MgB_4O_7:Sm,Li at λ_{em} = 612 nm

Figure 6 shows the emission spectra of Sm and Li codoped MgB_4O_7 phosphor. Under an excitation with a 406 nm wavelength, the emission spectra contain the characteristic lines of Sm^{3+} ion at 578 nm and 602 nm. The emission peak at 602 nm ($^4G_{5/2}$ to $^6H_{7/2}$) was observed to be the strongest intense peak, which satisfies the selection rule of $\Delta J = \pm 1$ where J; is the angular momentum. It is also observed that the excitation and emission peaks of Sm^{3+} show a slight shift and slight increase in the PL intensity for the Li codoped MgB_4O_7: Sm compared to that of Sm^{3+} singly doped powder phosphor. This could be due to the energy transfer mechanism between Sm to Li ions, which enhanced the PL intensity in the MgB_4O_7 host matrix. Li is co-doped usually as a sensitizer, which increases the luminescent properties of materials Therefore, it is indicated that this phosphor may have the potential application for the UV-based LEDs.

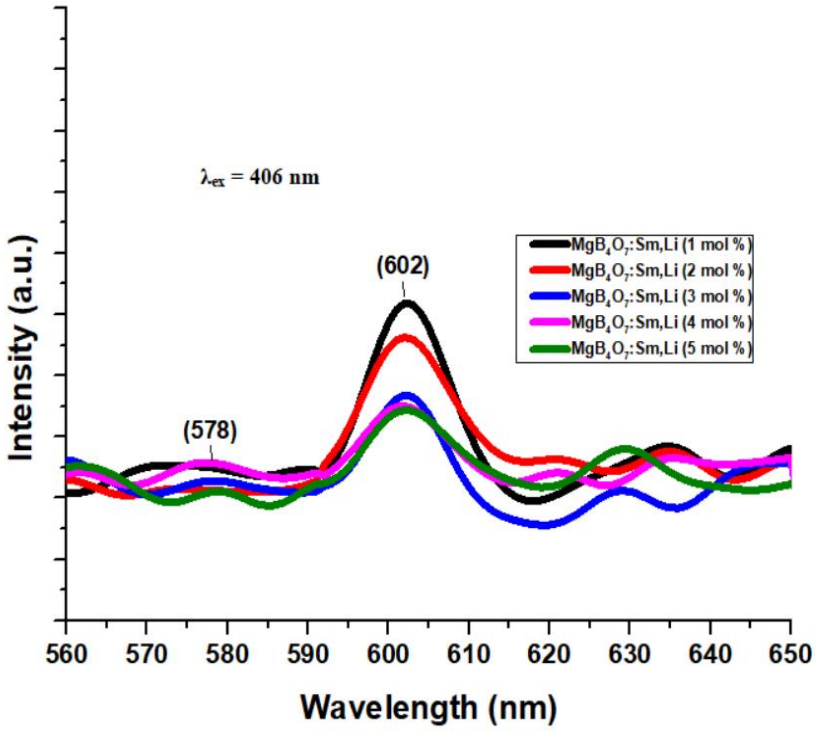


Figure 6. Emission spectra of MgB_4O_7:Sm,Li at λ_{ex} = 406 nm

4 Conclusion

MgB_4O_7:Sm, Li phosphors have been successfully prepared by the solid-state method. The morphology and structure properties of the prepared phosphor were investigated by X-ray diffraction (XRD) scanning electron microscopy (SEM), Fourier Transform Infrared (FTIR), and Raman spectroscopy. The excitation spectra of MgB_4O_7:Sm, Li exhibit a strong peak at 408 nm which corresponds to $^6H_{5/2} \rightarrow {}^4K_{11/2}$ transition and emission spectra show the two-characteristic lines at 578 nm and 602 nm due to the excitation of Sm^{3+} ions from $^4G_{5/2}$ to $^6H_{7/2}$ transition. Raman spectroscopy shows that no peak shifting was detected in the host matrix after a 2 mol concentration. It is also noticed due to cooping of Li ions the excitation and emission peaks of Sm^{3+} were slightly shifted and PL intensity also increases as compared to that of Sm^{3+} singly doped powder phosphor. Thus, Li is co-doped usually as sensitizers, which enhanced the luminescent properties of materials and this phosphor may be the suitable candidate for the UV-based LEDs.

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