

Synthesis, Structural Parameter Determination and PL Characterization

Sm³⁺ Doped MgB₈O₁₃ Phosphor

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Abstract: A series of Sm doped MgB₈O₁₃ phosphors were synthesized by solid state reaction method and their photo luminescence (PL) properties were systematically investigated. The synthesized materials were characterized using powder x-ray diffraction pattern (XRD) for confirmation. The emission and excitation of these materials were measured at room temperature by spectrofluorophotometer. The PL emission spectra of Sm³⁺ doped MgB₈O₁₃ were observed at 565 nm and 607 nm in yellow and orange region respectively for 401 nm excitation near UV range. Emission at 565 nm and 607nm are assigned to $4G_{5/2} \rightarrow {}^6H_{5/2}$ and $4G_{5/2} \rightarrow {}^6H_{7/2}$ transition of Sm³⁺ ions, respectively. The effects Sm³⁺ concentration on the emission spectrum and luminescent intensity of MgB₈O₁₃:Sm³⁺ were investigated. The photoluminescence properties of MgB₈O₁₃:Sm³⁺ shows that the phosphor emits orange 607nm light and yellow 565nm under excitation 401 nm. Consequently, these materials are promising phosphors for white LEDs

Keywords: Photoluminescence (PL), XRD, Inorganic Borate; LEDs; Lamp phosphor.

1. Introduction

In the past a few decades, rare earth borates have attracted considerable attention due to their practical applications as nonlinear optical (NLO), laser host, and luminescent materials. For example, YAl₃(BO₃)₄, RECa₄O(BO₃)₃ (RE= Y or Gd) [1], La₂CaB₁₀O₁₉ [2], and Na₃La₉O₃(BO₃)₈ [3] can be used as NLO crystals, Yb:YAl₃(BO₃)₄ and Nd:GdCa₄O(BO₃)₃ [4] are potential self frequency doubling laser crystals, Rare earth ions have rich transition channels (f–f transitions and d–f transitions) and the characteristic of being not insensitive to lattice environment, long lifetime, and narrow spectra lines for f– f transitions, so they are widely used in laser and luminescent materials [5-8].

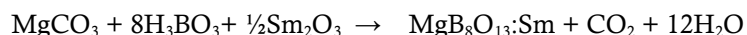
In order to search for new functional materials, considerable research should be carried out in the ternary systems like Li₂O-BaO-B₂O₃. A suitable red-emitting phosphor for near-UV phosphor converted LEDs should have many potential applications, due to their excellent color rendering index, high color tolerance and high conversion efficiency into visible light [9]. Therefore, it is urgent to find new red phosphors that can be excited by NUV-LED chips for the fabrication of white LEDs. The f-f transition absorption and emission of the crystalline host activated by rare earths ions are of great importance due to their applications as luminescent optical materials emitting in the visible and near IR regions [10–12]. The selection of the rare earth ion as an activator is a key factor for the preparation of luminescence materials. Among the different rare earth ions, the Sm³⁺ ion as an activator is regarded as one of the most popular and efficient doping ions, which can produce intense orange light in the visible wavelength range. Sm³⁺ ions in various hosts show bright emission in orange or red regions because of the transitions from the excited state ${}^4G_{5/2}$ to the ground state ${}^6H_{7/2}$ and also to the higher levels 6H_j ($j=7/2, 9/2$, and $11/2$) and found the application in high density optical storage, temperature sensors, undersea communications, various fluorescent devices, color display and visible solid-state lasers [13-14]. Selection of suitable host material is also an important factor for the preparation of luminescent materials for different applications. Among the several inorganic host materials, the borate host matrix constitutes as one of the most important luminescence materials, which can produce plenty of crystal field environments

imposed on emission contents [15, 16]. On realizing the relevance and importance of these rare earth ions doped borate based phosphors, the present investigation is carried out by the authors. We have been synthesized Sm^{3+} ions doped $\text{MgB}_8\text{O}_{13}$ host matrix by a conventional high temperature solid state reaction method in air atmosphere. Its structural, thermal, morphological and photoluminescence properties were systematically studied and also analyzed.

2. Experimental

There are several low temperature methods such as hydrothermal and microwave methods which can be used instead of the conventional solid state reaction. But solid state synthesis is found to be more convenient than other methods due to economical interest and enhancement of the properties of the material. This paper describes the chemical composition of $\text{MgB}_8\text{O}_{13}:\text{Sm}$ phosphor, host compound using other chemical element like Magnesium Carbonate ($\text{MgCO}_3:99.9\%$), and Boric acid ($\text{H}_3\text{BO}_3:99.9\%$) with rare earth elements like Sm_2O_3 , etc., are used as starting materials. The stoichiometric amounts of the individual ingredients calculated on the basis of molar ratio are thoroughly blended and grounded thoroughly in an agate mortar with bricks and obtained a homogeneous mixture. This homogeneous mixture transferred into a china crucible which is then introduced into preheated muffle furnace maintained and sintered at 500°C for 3 hrs. The phosphor is then cooled to room temperature inside the closed furnace itself; subsequently, the china crucible is removed from the furnace and transferred the material in an mortar pestle for grounding for 30 minutes. The crushed powder is then transferred into silica crucible and is then introduced into preheated muffle furnace maintained and sintered at 800°C for 5 hrs. Again, the phosphor is then cooled to room temperature inside the closed furnace itself; subsequently, phosphor in silica crucible is then transferred in an mortar pestle for grounding for 30 minutes..

Reaction:



The XRD technique was used in order to identify the product and check their crystallinity. The phase composition and phase structure were characterized by X-ray diffraction (XRD) pattern using a PAN-analytical diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda=1.54 \text{ \AA}$) operating at 40Kv, 30mA. The XRD data were collected in a 2θ range from 10 to 80° , with the continuous scan mode. The photoluminescence (PL) emission spectra of the samples were measured at room temperature by using SHIMADZU Spectrofluorophotometer (RF-5301 PC) equipped with a 150W Xenon lamp as the excitation source. The same amount of sample was used in each case. Emission and excitation spectra were recorded using a spectral slit width of 3nm.

3. Results and Discussion:

The structure of the samples were analyzed by an X-ray diffractometer (using $\text{Cu K}\alpha$ radiation with $\lambda=1.54060(\text{\AA})$. The crystallite size (D) was calculated using the Debye Scherrer formula from the full-width at half-maximum (FWHM) ($\beta_{2\theta}$).

$$D=0.9\lambda/(\beta_{(2\theta)}\cos\theta)$$

Where λ is the wave length of X –rays used, β is the FWHM, and θ is the angle between the incident and scattered X-rays.

The micro strain (ϵ) and the dislocation density (ρ) of LiCaBO_3 material were evaluated using the equations

$$\epsilon = \frac{\beta_{(2\theta)}\cos\theta}{4}$$

and

$$\rho = \frac{1}{D^2}$$

XRD pattern of $\text{MgB}_8\text{O}_{13}:\text{Sm}$ phosphors results indicates that the final product was formed in homogeneous form. It is also observed that all the in different concentrations match with the standard peaks shown in figures 3.1 A,B,C,D. It indicates that samples are prepared correctly. The average size of the particle to be at 70.36569354 nm which proves that the prepared sample is nanomaterial. Mean dislocation density to be 0.002623- nm^{-2} and mean strain to be XRD pattern of 0.003526 phosphors result indicates that the final product shows crystalline nature.

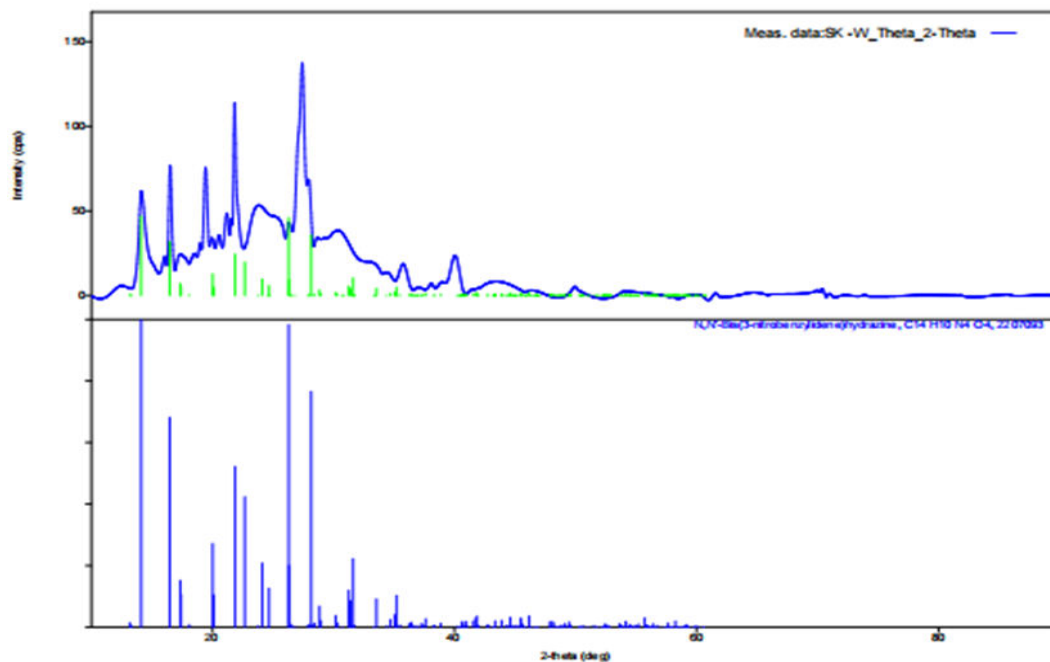


Fig 3.1 (A) X-ray diffraction pattern of $\text{MgB}_8\text{O}_{13}$ for without dopant.

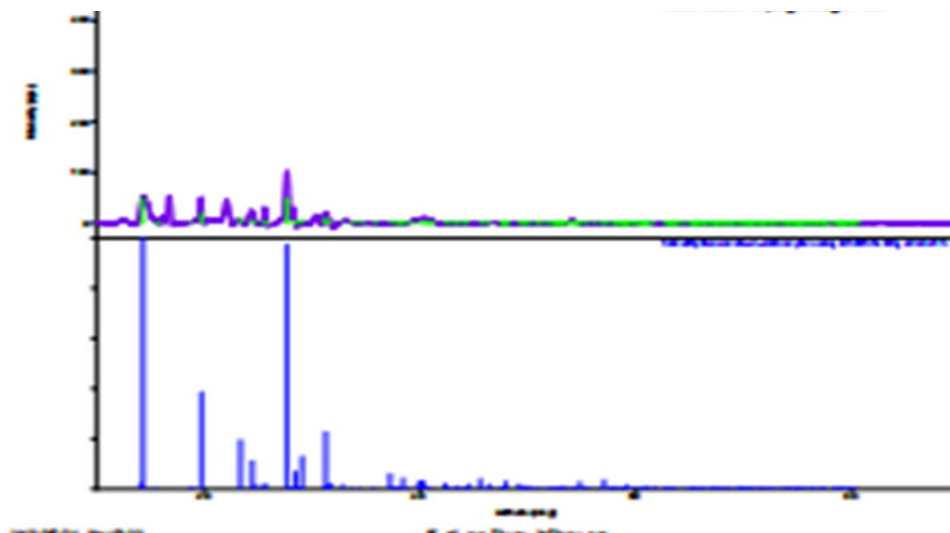


Fig 3.1 (B) X-ray diffraction pattern of $\text{MgB}_8\text{O}_{13}:\text{Sm}^{3+}$ for 1mol%

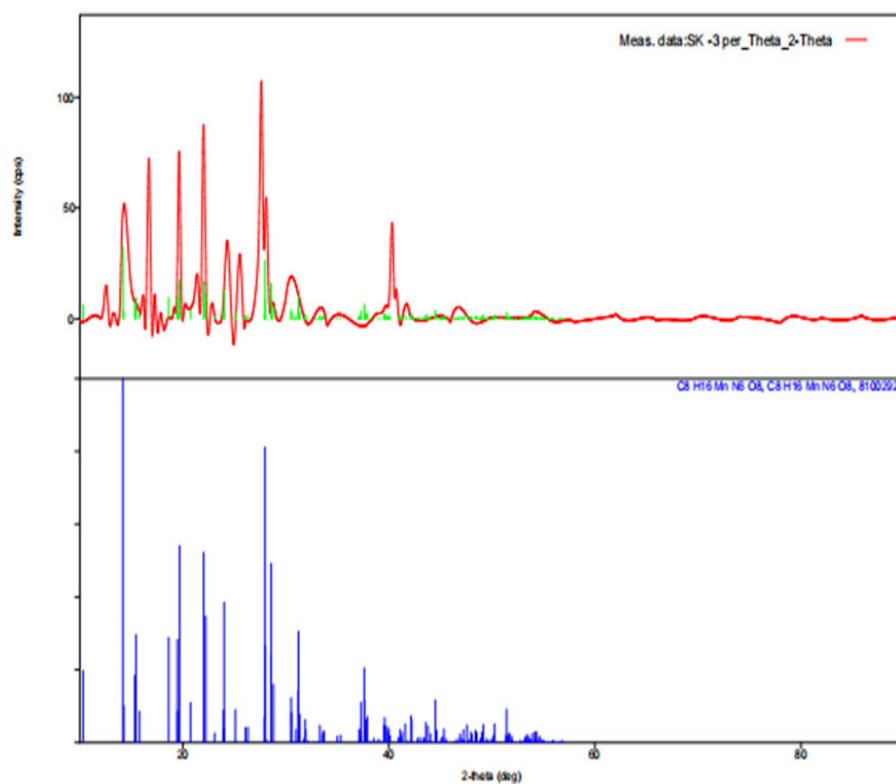


Fig 3.1 (C) X-ray diffraction pattern of $\text{MgB}_8\text{O}_{13}:\text{Sm}^{3+}$ for 2 mol%

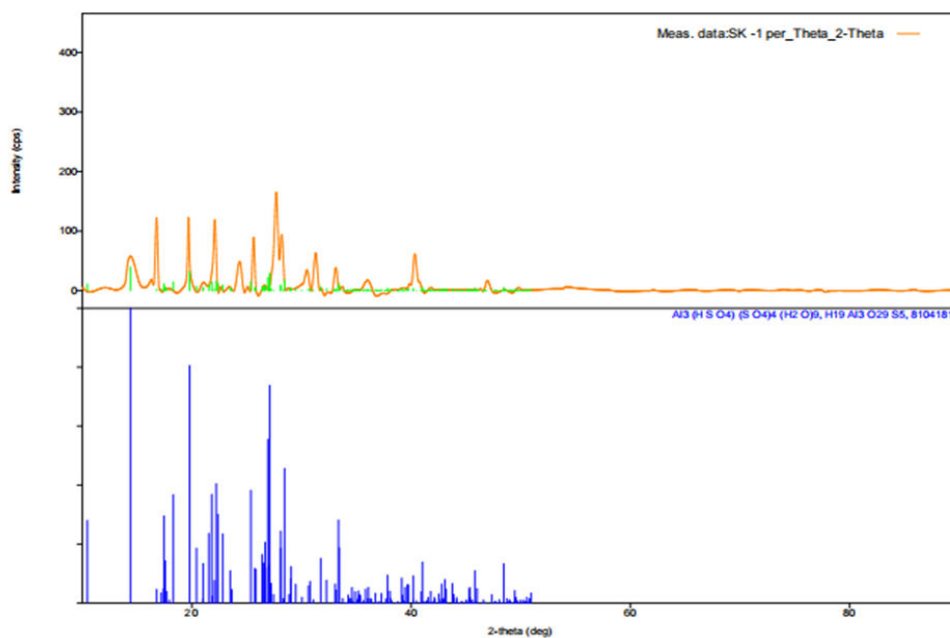


Fig 3.1 (D) X-ray diffraction pattern of $\text{MgB}_8\text{O}_{13}:\text{Sm}$ for 3 mol%

Table 3.2. Structure parameters of intrinsic $\text{MgB}_8\text{O}_{13}$

Sr. No.	2 θ	d (obs.)	Height (cps)	FWHM (deg)	D (nm)	Strain	Dislocation density
1.	14.071	6.289	46	0.52	15.40117	0.00904	0.004215
2.	16.495	5.370	63	0.125	63.7411	0.00184	0.0002461
3.	17.37	5.10	9	1.1	7.3095	0.00153	0.01871
4.	19.44	4.562	33	0.98	8.2574	0.00121	0.01466
5.	21.829	4.068	50	0.42	19.3407	0.00457	0.002673
6.	24.38	3.698	39	1.27	6.4253	0.00122	0.02422
7.	27.38	3.255	66	1.33	6.1724	0.00111	0.026247
8.	31.10	2.873	33	0.72	11.4989	0.00520	0.007562
9.	32.85	2.724	21	0.60	13.8592	0.00405	0.005206
10.	35.86	2.502	13	0.66	12.7020	0.00398	0.006198
11.	40.15	2.2444	21	0.40	21.2303	0.00206	0.002218
12.	44.26	2.045	7	2.5	3.4442	0.00111	0.084299
13.	50.01	1.8223	7	0.21	41.9099	0.00768	0.000569
14.	54.09	1.6940	8	0.16	55.9716	0.00505	0.0003192
15.	55.93	1.6427	10	0.11	82.0968	0.00324	0.0001483

3.2 Photoluminescence (PL) characterization of $\text{MgB}_8\text{O}_{13}:\text{Sm}^{3+}$ phosphor

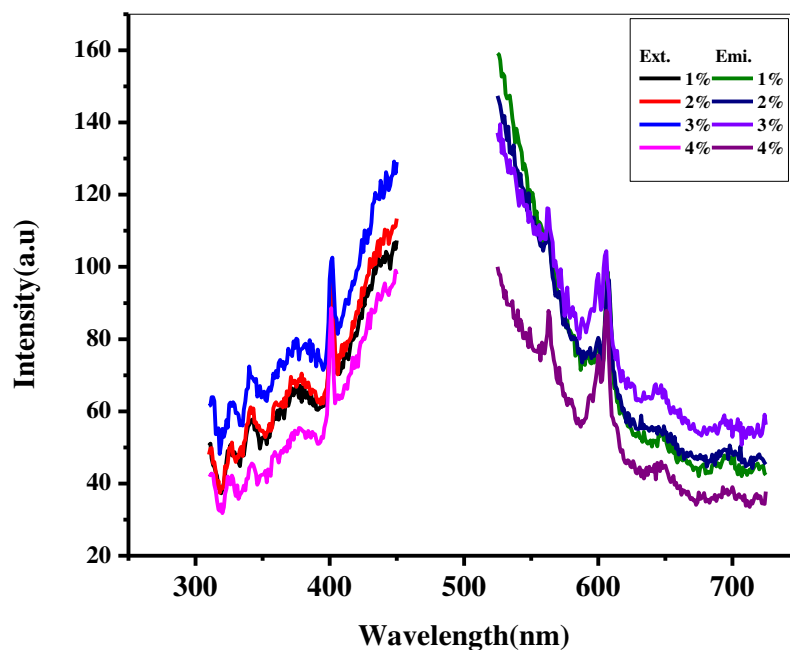


Fig 3.2(A) : PL characterization of $\text{MgB}_8\text{O}_{13}:\text{Sm}^{3+}$ Phosphor

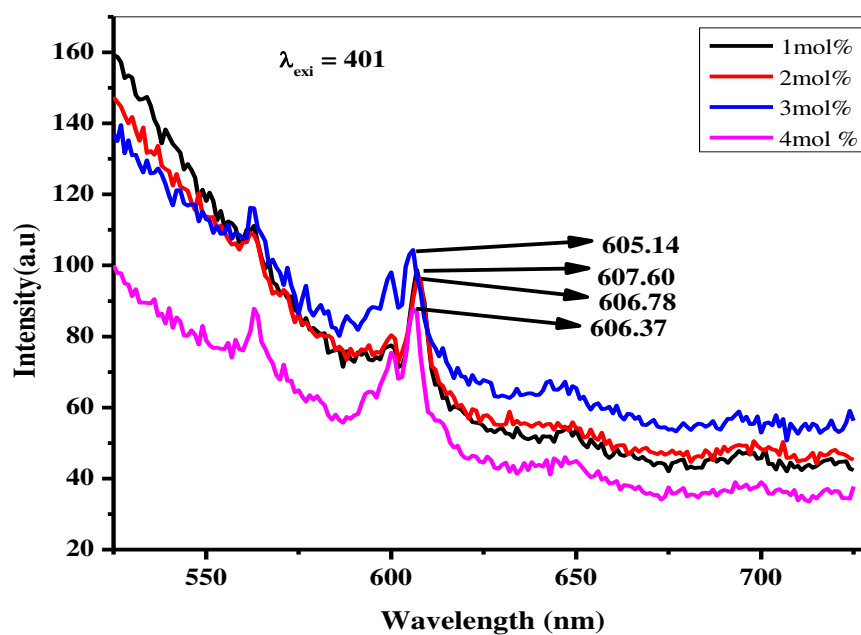


Fig3.2(B) PL emission spectra of $\text{MgB}_8\text{O}_{13}:\text{Sm}^{3+}$ monitored at 401nm excitation

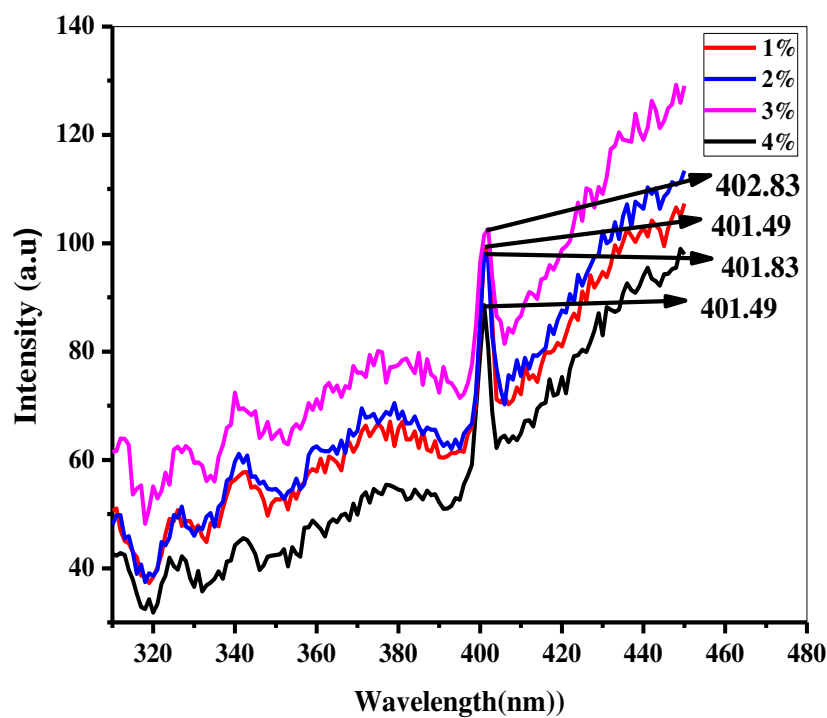


Fig 3.2(C) : PL excitation spectra of $\text{MgB}_8\text{O}_{13}:\text{Sm}^{3+}$ monitored at 607nm emission

Table 3.3: Variation in emission intensity of $\text{MgB}_8\text{O}_{13}:\text{Sm}^{3+}$ with concentration of Sm

Concentration	Excitation Wavelength (nm)	Emission wavelength (nm)	Intensity (a.u)
$\text{MgB}_8\text{O}_{13}:\text{Sm}$ (1%)	401.49	607.60nm	98
$\text{MgB}_8\text{O}_{13}:\text{Sm}$ (2%)	401.83	606.78 nm	99
$\text{MgB}_8\text{O}_{13}:\text{Sm}$ (3%)	402.83	606.96 nm	105
$\text{MgB}_8\text{O}_{13}:\text{Sm}$ (4%)	401.49	606.37 nm	87

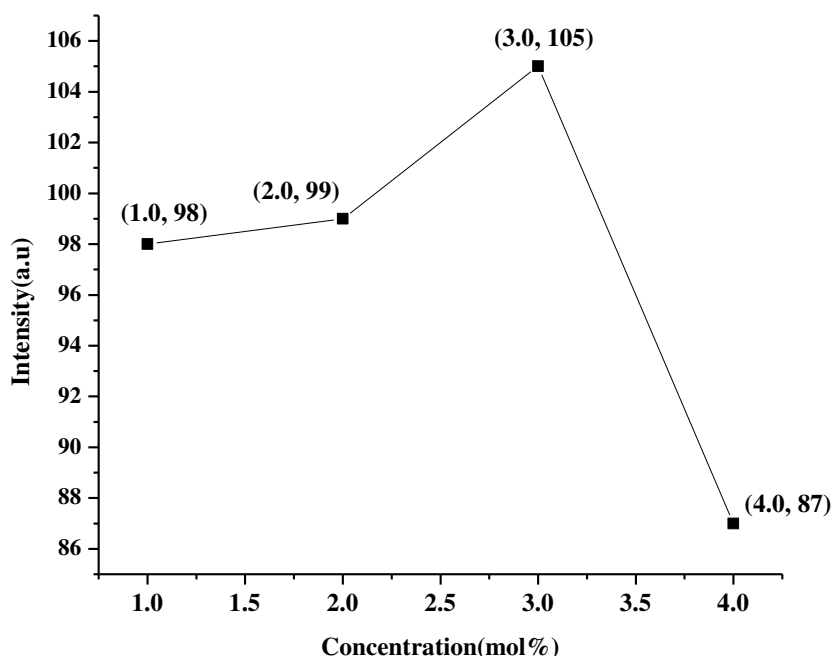


Fig 3.4: Graph between concentration and emission intensity

To study photoluminescence characteristics the excitation spectra was recorded for $\text{MgB}_8\text{O}_{13}:\text{Sm}^{3+}$ phosphor by monitoring emission at 607 nm as depicted in Fig3.2(C). The excitation spectra $\text{MgB}_8\text{O}_{13}:\text{Sm}^{3+}$ phosphor shows dominant peak at 401 nm due to $^6\text{H}_{5/2} \rightarrow ^4\text{F}_{7/2}$ transition. Upon this excitation the photoluminescence emission spectra for different concentration of Sm^{3+} ion were recorded in the spectral range 550-750 nm shown in Fig 3.2(B). In the emission spectra of $\text{MgB}_8\text{O}_{13}:\text{Sm}^{3+}$ the peak is located at 607 nm which is due to $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ and other peak is located at 565 nm which is due to $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$. It shows the significant orange-red emission at 607 nm and yellow emission at 565 nm. It is found that the shape and profile for the emission spectra do not vary with the change of the Sm^{3+} doping concentration, but the PL intensity

changes greatly. The optimum concentration was determined to be 3 mole % to obtain strongest PL emission intensity.

4. Conclusion:

All the XRD patterns of $\text{MgB}_8\text{O}_{13}:\text{Sm}^{3+}$ phosphors indicate that the final product was formed in homogeneous form. The average size of the particle to be at 24.62403 nm which proves that the prepared sample is nanomaterial. Mean dislocation density to be 0.013166 nm^{-2} and mean strain to be 0.003526. Results of all the XRD patterns of $\text{MgB}_8\text{O}_{13}:\text{Sm}^{3+}$ phosphors indicates that the final products are incrySTALLINE form.

Sm^{3+} doped $\text{MgB}_8\text{O}_{13}$ phosphor have been synthesized by high temperature solid state reaction method. The photoluminescence properties of $\text{MgB}_8\text{O}_{13}:\text{Sm}^{3+}$ shows that the phosphor emits yellow (565nm) and orange red (607nm) light under excitation of 401 nm wavelength. The result indicates that $\text{MgB}_8\text{O}_{13}:\text{Sm}^{3+}$ is an efficient yellow and orange red emitting phosphors and is suitable material for UV LEDs.

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References:

1. Iwai M, Kobayashi T, Furuya H, Mori Y, Sasaki T, Crystal Growth and Optical Characterization of Rare-Earth (Re) Calcium Oxyborate $\text{ReCa}_4\text{O}(\text{BO}_3)_3$ (Re=Y or Gd) as New Nonlinear Optical Material Jpn. J. Appl. Phys 1997; 36; 276-279.
2. Wu YC, Liu JG, Fu PZ, Wang JX, Yun HY, Wang GF, Chen CT, A New Lanthanum and Calcium Borate $\text{La}_2\text{CaB}_{10}\text{O}_{19}$ Chem. Mater. 2001; 13; 753-755.
3. Reshak AH, Auluck S, Kityk IV, Investigation of the linear and nonlinear optical properties of $\text{Ag}_2\text{In}_2\text{SiS}_6$ and $\text{Ag}_2\text{In}_2\text{GeS}_6$ J. Phys. Condens. Matter 2008; 20; 145209- 145215.
4. Liu, Wenbin, et al. "2.44 KW laser output of Nd: YAG ceramic slab fabricated by a solid-state reactive sintering." Journal of alloys and compounds 538 (2012): 258-261.
5. Ye S, Xiao F, Pan YX, Ma YY, Zhang QY, Phosphors in phosphor-converted white light- emitting diodes: Recent advances in materials, techniques and properties. Mater. Sci. Eng. 2010; R 71;1-34.
6. Brown MR, Cox AFJ, Shand WA, William JM, Sensitization of rare earth photoluminescence in II-VI compounds. II. Site sensitive excitation mechanisms in zinc selenide. J. Phys. C: Solid State Phys. 1972; 5; 502.
7. Song E, Zhao W, Zhou G, Dou X, Yi C, Zhou M, Luminescence properties of red phosphors $\text{Ca}_{10}\text{Li}(\text{PO}_4)_7:\text{Eu}^{3+}$. J. Rare Earths 2011; 29; 440-443.
8. Li YL, Chang YH, Lin YF, Chang YS, Lin YJ, Synthesis and luminescent properties of Ln^{3+} (Eu^{3+} , Sm^{3+} , Dy^{3+}) doped lanthanum aluminum germanate $\text{LaAlGe}_2\text{O}_7$ phosphors. J. Alloys Comp. 2007; 439; 367-375.
9. Setlur AA, Shiang JJ, Happek U, $\text{Eu}^{2+}-\text{Mn}^{2+}$ phosphor saturation in 5mm5mm light emitting diode lamps. Appl. Phys. Lett. 2008; 92; 081104.
10. Sange Zhao, Jiyong Yao, Erpan Zhang, Guochun Zhang, Jianxiu Zhang, Peizhen Fu, Yicheng Wu. Preparation, structure, and photoluminescence properties of new layered borates $\text{KBaRE}(\text{B}_3\text{O}_6)_2$ (RE=Y, Eu, and Tb) Solid State Sciences 2012; 14; 305-310
11. Hisanori Yamane, Tetsuya Kawano, Kentaro Fukuda, Takayuki Suehiro, Tsugio Sato. Preparation, crystal structure and photoluminescence of lithium magnesium manganese borate solid solutions, $\text{LiMg}_{1-x}\text{Mn}_x\text{BO}_3$. J. Alloys and Compounds. 2012; 512; 223– 229.