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Synthesis, Structural Parameter Determination and PL Characterization Sm^{3+} Doped Mgb_8o_{13} Phosphor

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Abstract: A series of Sm doped MgB_8O_{13} 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 Sm^{3+} doped MgB_8O_{13} 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 Sm^{3+} ions, respectively. The effects Sm^{3+} concentration on the emission spectrum and luminescent intensity of MgB_8O_{13}:Sm^{3+}were investigated. The photoluminescence properties of MgB_8O_{13}:Sm^{3+} 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, $YAl_3(BO_3)_4$, $RECa_4O(BO_3)_3$ (RE= Y or Gd) [1], $La_2CaB_{10}O_{19}$ [2], and$Na_3La_9O_3(BO_3)_8$ [3] can be used as NLO crystals, Yb:$YAl_3(BO_3)_4$ andNd:$GdCa_4O(BO_3)_3$ [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 Li_2O-BaO-B_2O_3.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 Sm^{3+} ion as an activator is regarded as one of the most popular and efficient doping ions, which can produces intense orange light in the visible wavelength range. Sm^{3+} 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, and11/2) 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 MgB_8O_{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 MgB_8O_{13}:Sm phosphor,host compound using other chemical element like Magnesium Carbonate ($MgCO_3$:99.9%), and Boric acid (H_3BO_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 chinacrucible which is then introduced into preheated muffle furnace maintained and sintered at 500ºC 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 800ºC for 5 hrs. Again, the phosphors is then cooled to room temperature inside the closed furnace itself; subsequently, phosphors in silica crucible is then transferred in an morter pestle for grounding for 30 minutes..

Reaction:

$$MgCO_3 + 8H_3BO_3 + \tfrac{1}{2}Sm_2O_3 \rightarrow MgB_8O_{13}:Sm + CO_2 + 12H_2O$$

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 Cu Kα radiation (λ=1.54 Å) 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 Cu Kα radiation with λ=1.54060(Å). The crystallite size (D) was calculated using the Debye Scherrer formula from the full-width at half-maximum (FWHM) (β2θ).

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

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 (Ɛ) and the dislocation density (ρ) of $LiCaBO_3$ material were evaluated using the equations

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

and

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

XRD pattern of MgB_8O_{13}: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.

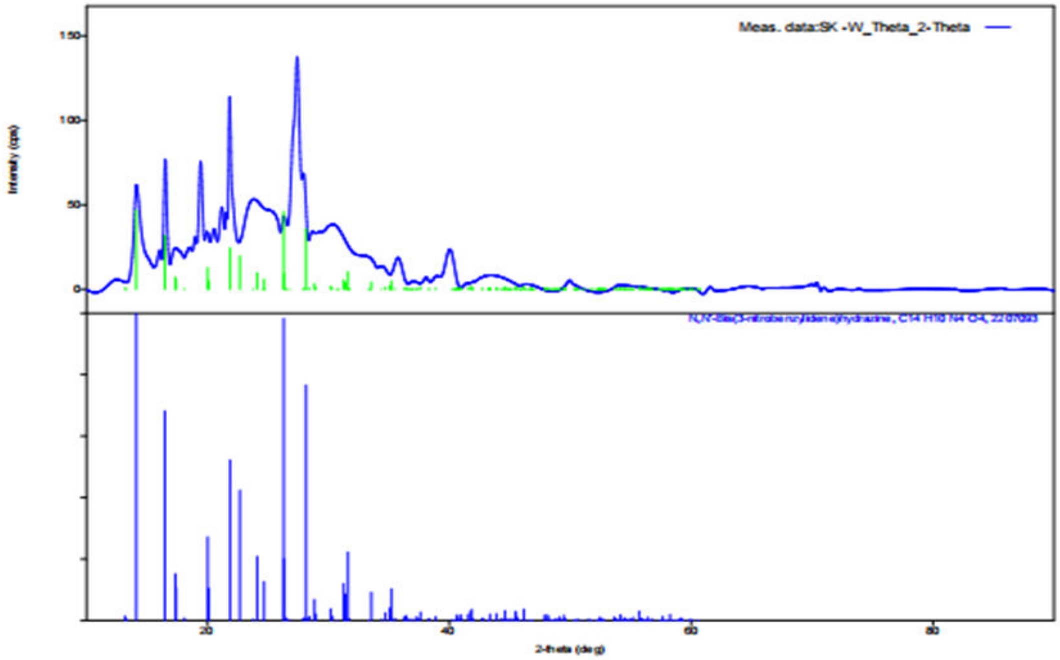

Fig 3.1 (A) X-ray diffraction pattern of MgB_8O_{13} for without dopant.

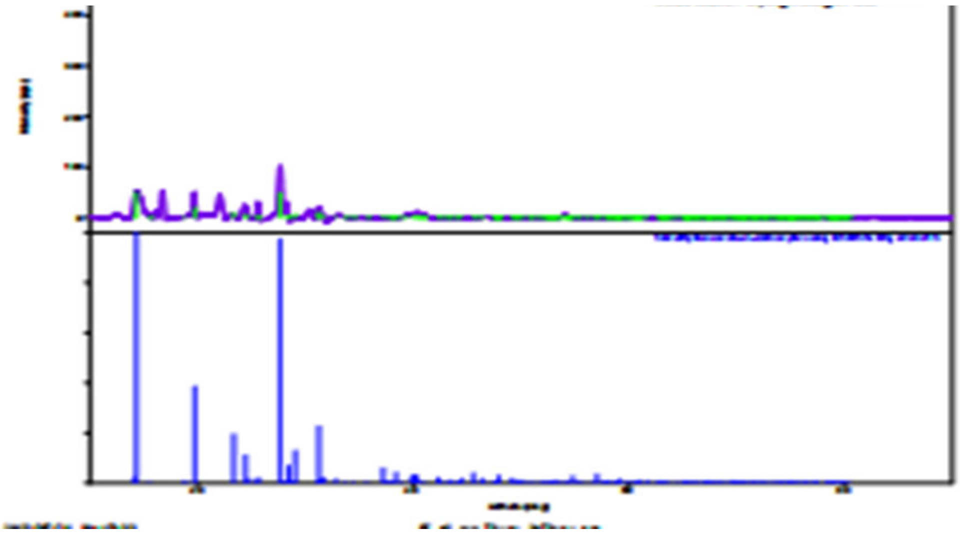

Fig 3.1 (B) X-ray diffraction pattern of MgB_8O_{13}:$Sm^{3+}$for 1mol%

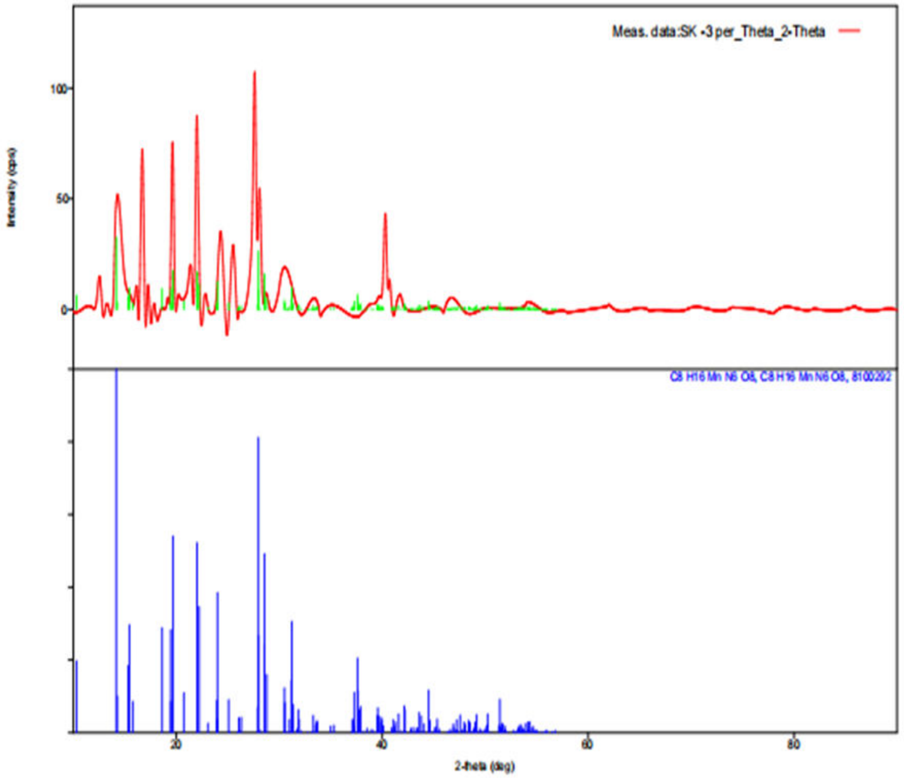

Fig 3.1 (C) X-ray diffraction pattern of MgB_8O_{13}:Sm^{3+} for 2 mol%

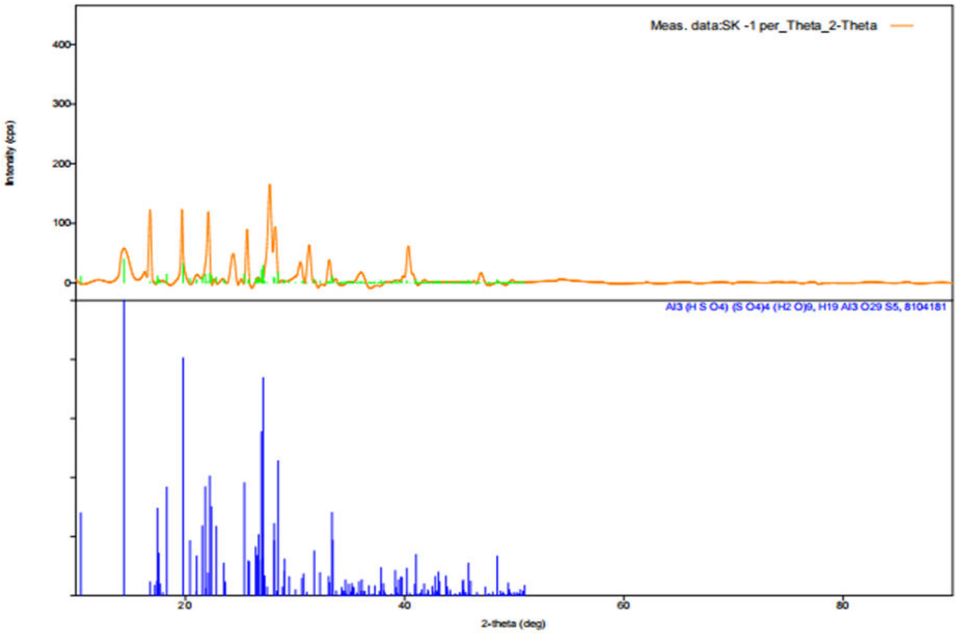

Fig 3.1 (D) X-ray diffraction pattern of MgB_8O_{13}:Sm for 3 mol%

Table 3.2.Structure parameters of intrinsic MgB_8O_{13}

Sr. No.	2θ	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 $MgB_8O_{13}:Sm^{3+}$ phosphor

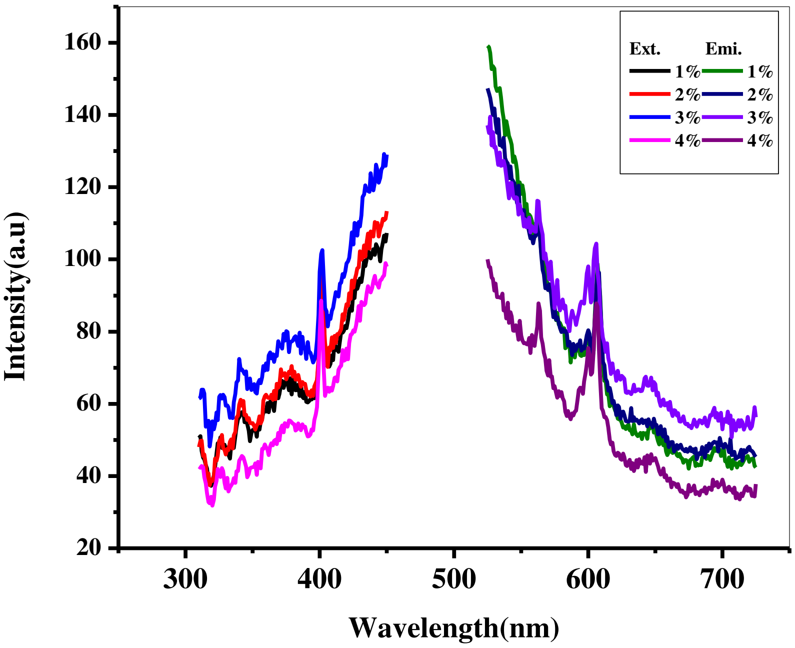

Fig 3.2(A) : PL characterization of $MgB_8O_{13}Sm^{3+}$Phosphor

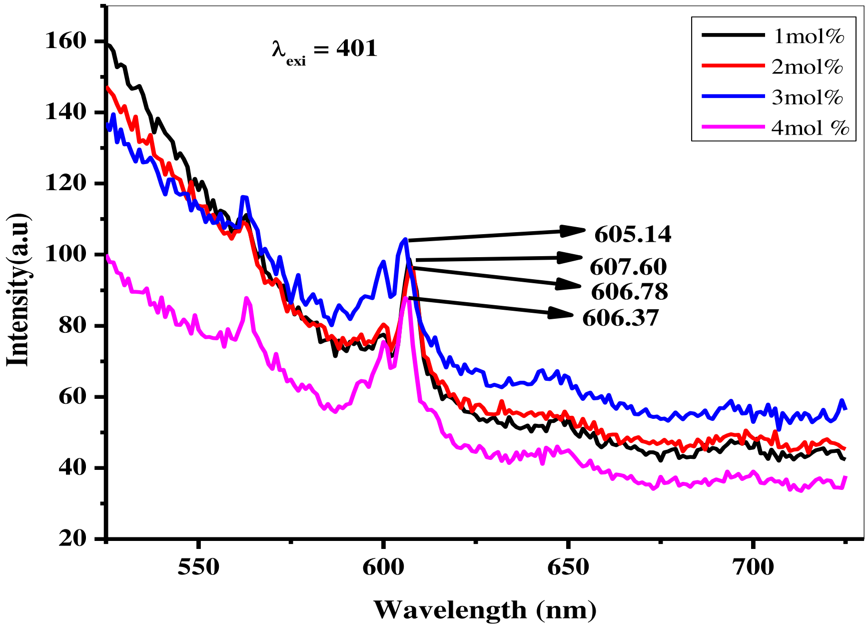

Fig3.2(B) PL emission spectra of $MgB_8O_{13}:Sm^{3+}$ monitored at 401nm excitation

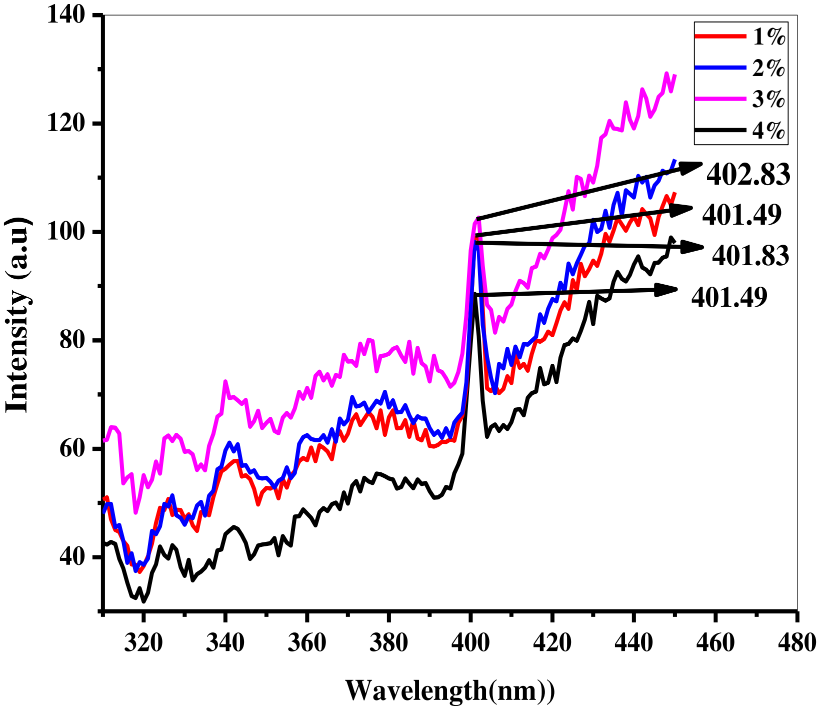

Fig 3.2(C) : PL excitation spectra of $MgB_8O_{13}:Sm^{3+}$ monitored at 607nm emission

Table 3.3: Variation in emission intensity of MgB_8O_{13}:Sm^{3+} with concentration of Sm

Concentration	Excitation Wavelength (nm)	Emission wavelength (nm)	Intensity (a.u)
MgB_8O_{13}:Sm (1%)	401.49	607.60nm	98
MgB_8O_{13}:Sm (2%)	401.83	606.78 nm	99
MgB_8O_{13}:Sm (3%)	402.83	606.96 nm	105
MgB_8O_{13}:Sm (4%)	401.49	606.37 nm	87

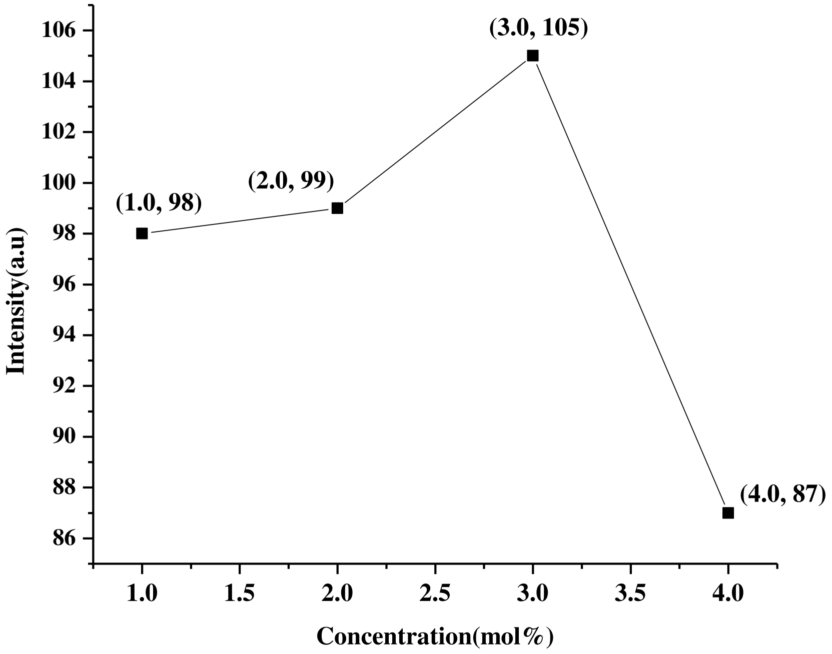

Fig 3.4: Graph between concentration and emission intensity

To study photoluminescence characteristics the excitation spectra was recorded for MgB_8O_{13}:Sm^{3+} phosphor by monitoring emission at 607 nm as depicted in Fig3.2(C).The excitation spectra MgB_8O_{13}:Sm^{3+} phosphor shows dominant. peak at 401 nm due to $^6H_{5/2} \rightarrow$ $^4F_{7/2}$ 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 MgB_8O_{13}:Sm^{3+} the peak is located at 607 nm which is due to $^4G_{5/2} \rightarrow {}^6H_{7/2}$ and other peak is located at 565 nm which is due to $^4G_{5/2} \rightarrow$ $^6H_{5/2}$.It shows the significant orangered emission at 607 nm and yellow emission at 565nm.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 MgB_8O_{13}:Sm^{3+} phosphors indicate that the final product was formed in homogeneousform. 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 theXRD patterns of MgB_8O_{13}:Sm^{3+} phosphors indicates that the final products are incrystalline form.

Sm^{3+} doped MgB_8O_{13} phosphor have been synthesized by high temperature solid state reaction method. The photoluminescence properties of MgB_8O_{13}:Sm^{3+} shows that the phosphor emitsyellow (565nm) and orange red(607nm) light under excitationof 401 nm wavelength. The result indicates that MgB_8O_{13}:Sm^{3+} is an efficientyellow and orange red emitting phosphors and is suitable material for UV LEDs.

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