

Photoluminescence Studies of Europium (III) Doped Di-Barium Magnesium Silicate Phosphors

Ishwar Prasad Sahu¹, Ravi Shrivastava^{2*}

¹Department of Science and Technology, The ICFAI University Raipur, Raipur, India

²Department of Physics, Indira Gandhi National Tribal University, Amarkantak, India

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***For Correspondence:**

Ravi Shrivastava, Department of
Science and Technology, The ICFAI
University Raipur, Raipur, India

E-mail: ravishrivastava@iuraipur.edu.in

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ABSTRACT

Di Barium Magnesium Silicate ($\text{Ba}_2\text{MgSi}_2\text{O}_7$) doped with various concentrations (0.2, 0.5, 1.0, 2.0 and 2.5 mol %) of Europium (Eu^{3+}) were prepared using solid-state reaction technique. To confirm the proper preparation and the phases available, an X-ray diffraction pattern of the sample with optimal PL concentration was recorded. The recorded sample was matched significantly with crystallographic open database card No. 96-900-6941 reported specifically for $\text{Ca}_2\text{MgSi}_2\text{O}_7$ with a Figure of Merit (FoM) of 0.8051. This FoM confirmed the proper preparation of the sample. Rietveld lattice parameter refinement process using Celref V.2 was carried out for estimating the various crystallographic information of the prepared sample. The prepared samples underwent Photoluminescence (PL) studies. The excitation spectrum, which was monitored at 620 nm, exhibited two distinct peaks centred at 294 nm and 365 nm respectively. Therefore, the emission spectra were recorded at an excitation wavelength of 294 nm. The emission spectra expressed the prominent peaks centred at 592 and 612 nm are attributed to $^5\text{D}_0 \rightarrow ^7\text{F}_2$ of Europium (III) ions accommodated at various lattice sites having different energies, whereas peak centred at 633 nm is due to $^5\text{D}_0 \rightarrow ^7\text{F}_3$ transition of Europium (III). Sample with a dopant concentration of 2 mol % expressed the maximum PL intensity. Overall emission was found in the red colour region which was confirmed using a CIE chromaticity diagram with coordinate (0.611, 0.387). Critical distance for energy transfer in the concentration, beyond which concentration quenching occurred in PL spectra, was calculated. In this case, the critical distance was found to be 19.34 Å, therefore the mechanism involved in concentration quenching of $\text{Ba}_2\text{MgSi}_2\text{O}_7$ doped with 2.0 mol % of Europium (III) must be only multipole-multipole exchange whereas the exchange interaction is ineffective.

INTRODUCTION

Europium activated di alkaline earth (Sr, Ba, Ca) magnesium silicate materials have been investigated extensively because of their excellent luminescence properties like broaden emission peak, long lasting behavior and ability to retain these properties even inside the liquids. Silicate based phosphor has usually a band gap around 7.5 eV, which make these phosphors suitable for Light Emitting Diodes (LEDs) and Plasma Display Panel (PDPs) [1-4]. White LEDs have been produced commercially using a combination of two colour phosphor i.e. blue and yellow colour. In this case fabrication cost is low and luminescence efficiency is quite high but the colour rendering is poor [5-6]. To

get rid of this problem, one of the options was to compensate this deficiency of the red element of Yttrium Aluminum Garnet (YAG) doped with Ce^{3+} phosphor-based LED with another red-emitting phosphor separately^[7-8]. Unfortunately, the phosphors studies were limited to low brightness and could not absorb efficiently in the near UV region, even the lifetime was also not inadequate under near UV irradiation. Tri colour phosphor with strong green, yellow and red luminescence is suitable for high colour rendering white LEDs. Most of the green emitting phosphors for White LED application are nitride phosphors. "The red colour emission of Eu^{3+} is a result of the intra-4f transitions, while the emission of Eu^{3+} from the 5d–4f transition which is dipole allowed varies in a significantly large range from red to UV region which depends in accordance to the crystal structure of the host materials. It is well known that the optical properties of rare-earth ion-doped luminescent materials are highly affected by the matrix^[9]. Therefore environment-friendly and stable red-emitting rare-earth-doped silicate-based phosphors have attracted many researchers. In this article, $\text{Ba}_2\text{MgSi}_2\text{O}_7$ doped with various concentrations of Eu^{3+} were prepared and its photoluminescence studies were done.

MATERIALS AND METHODS

Eu^{3+} doped $\text{Ba}_2\text{MgSi}_2\text{O}_7$ phosphors doped with different concentration of Eu^{3+} (0.5, 1.0, 1.5, 2.0 mol %) were prepared using solid state reaction technique. The starting materials used were SiO_2 , BaCO_3 , MgO , and Eu_2O_3 with proper stoichiometric proportions were thoroughly ground for approximately 1 h in a mortar, pre-sintered at 900°C , then fired at 1200°C for approximately 2 h, with 1.6 mol% of H_3BO_3 used as flux^[10-13]. The Photoluminescence (PL) excitation and emission spectra were measured by a spectrofluorophotometer (SHIMADZU, RF-5301 PC, Kyoto, Japan) using a Xenon lamp of power 150 watt as excitation source. X-Ray Diffraction (XRD) characterization of the sample is done using Panalytical Xpert PRO MPD (Singapore) with copper k alpha anode of wavelength 1.5405 \AA .

RESULTS AND DISCUSSION

XRD analysis:

Figure 1 exhibits the comparison of observed and calculated XRD pattern of $\text{Ba}_2\text{MgSi}_2\text{O}_7$ having 0.5 mol% of Europium (III). The results show a good resemblance between the two graphs. Match! v. 2.3.1 was used to match the standard (Crystallographic open database) and experimental XRD pattern. It was observed that, experimental XRD pattern was matched convincingly with Crystallographic Open Database (COD) card No. 96-900-6941 with Figure of Merit (FoM) of 0.8051. This is already reported XRD pattern of $\text{Ca}_2\text{MgSi}_2\text{O}_7$.

The lattice parameter refinement process was carried out using software Celref v.2. The crystallographic information file (1010215.cif) corresponding to the Crystallographic Open Database COD 96-900-6941 was downloaded from the website <http://www.crystallography.net/>. The information contained in the crystallographic information file was utilized as reference in the process of lattice parameter refinement. Initial and refined lattice parameters are shown in the Table 1.

Figure 1. Comparison between calculated and observed XRD.

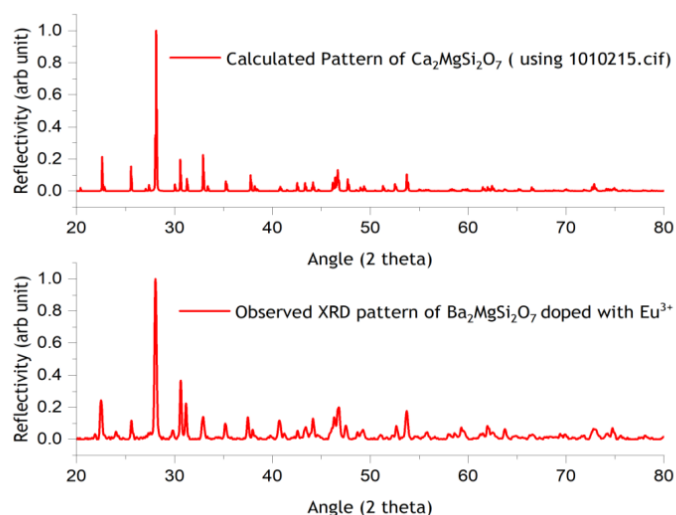


Table 1. Initial and refined lattice parameter of Ba₂MgSi₂O₇ doped with Eu³⁺.

Zero	Lambda	a	b	c	alpha	beta	gamma
0	1.5418	7.73	7.73	5.01	90	90	90
0	0	1	0	1	0	0	0

Final values: (Standard errors on 2 nd line)							
Zero	Lambda	a	b	c	alpha	beta	gamma
0	1.5418	7.6306	7.6306	5.2039	90	90	90
0	0	0.1259	0	0.1325	0	0	0

H	K	L	2T(Obs)	2T-Zero	2T(Cal)	Diff
1	2	0	25.601	25.601	26.1123	-0.5113
1	2	1	31.175	31.175	31.3458	-0.1708
2	2	0	32.926	32.926	33.2074	-0.2814
2	2	0	35.178	35.178	33.2074	1.9706
2	2	1	37.494	37.494	37.5517	-0.0577
2	1	2	44.141	44.141	43.7491	0.3919
0	4	0	46.792	46.792	47.671	-0.879
3	3	1	53.72	53.72	53.9373	-0.2173
5	1	2	72.795	72.795	72.9207	-0.126

Photoluminescence studies

Photoluminescence Excitation spectrum (Figure 2) of the Ba₂MgSi₂O₇ doped with 1.5 mol% Europium (III) was monitored at 592 nm. Observed spectrum exhibited two peaks centered at 294 and 364 nm respectively, therefore the emission spectra of the samples with various concentration of Europium (III) i.e. 0.2, 0.5, 1.0, 2.0, and 2.5 mol% were recorded for an excitation wavelength of 294 nm. The emission spectra which were monitored by giving an excitation wavelength 294 nm are expressed in Figure 3.

Figure 2. Excitation Spectrum of Ba₂MgSi₂O₇ doped with Eu³⁺ (1.5 mol %).

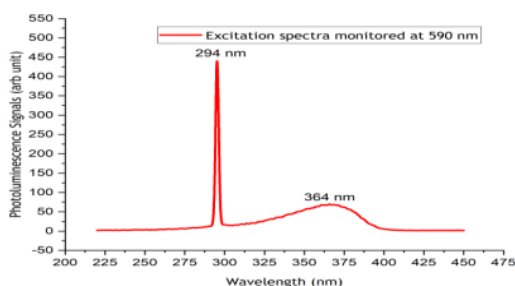
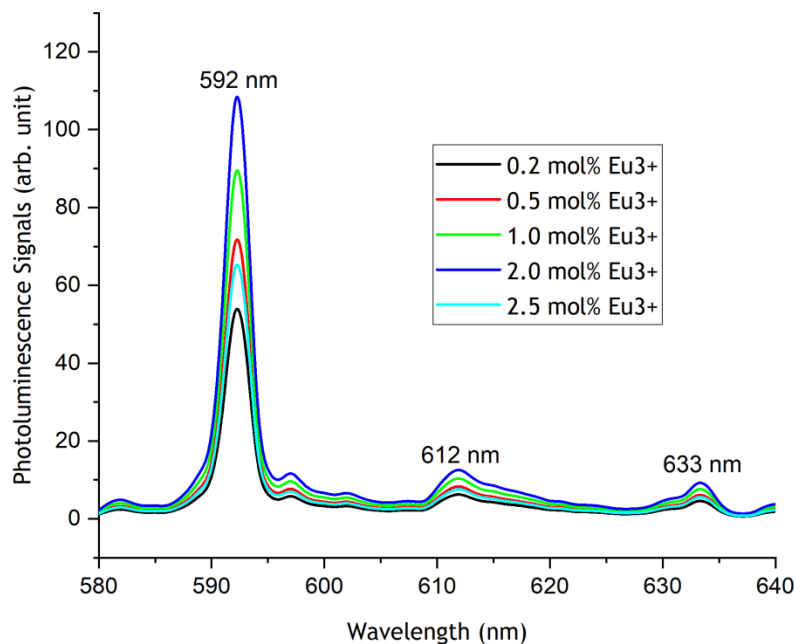


Figure 3. Emission Spectra of Ba₂MgSi₂O₇ doped with Eu³⁺.

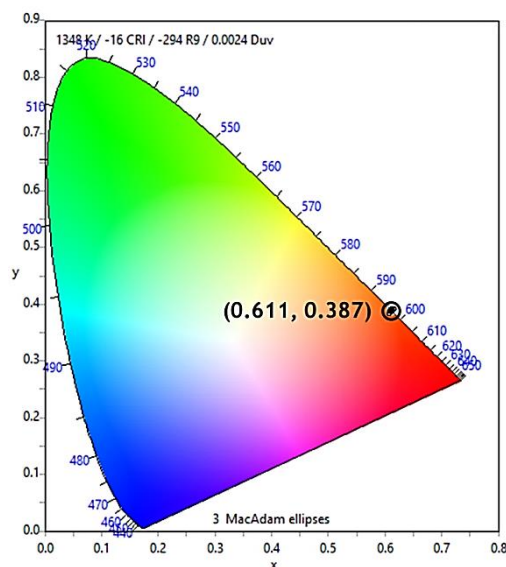


The emission spectra expressed the prominent peaks centred at 592 and 612 nm are attributed to ⁵D₀ → ⁷F₂ of Europium (III) ions accommodated at various lattice sites having different energies, whereas peak centred at 633 nm is due to ⁵D₀ → ⁷F₃ transition of Europium (III) [12]. Sample with a dopant concentration of 2 mol % expressed the maximum PL intensity. Overall emission was found in the red colour region which was confirmed using a CIE chromaticity diagram (CIE 1931) with coordinate (0.4805, 0.3763) (Figure 4) which is the point belonging to the intense red colour region.

Figure 3 expressed the variation in peak emission intensity for various Eu³⁺ doping concentrations. We noticed from Figure 4 that the emission intensity increases with increasing concentration of Eu³⁺ ion till it reaches 2.0 mol% and then decreases for 2.5 mol% doping of Eu³⁺. This is due to concentration quenching. When the concentration of Eu³⁺ ions increases, the distance between the Eu³⁺ ions decreases. This results in the non-radiative transitions in Eu³⁺ ions. It points an important fact that the transfer of excitation energy strongly depends on the distance between the Eu³⁺ ions. Blasse [13,15] gave an important formula to estimate the critical distance for energy transfer (R).

$$R \approx 2 \left(\frac{3V}{4\pi X_c N} \right)^{\frac{1}{3}}$$

Where V is the unit cell – volume, N is the number of atoms per unit cell, and X_c is the critical concentration of the dopant. In present case (Ba₂MgSi₂O₇ doped with Eu³⁺ - 2.0 mol %) the unit cell volume is 303.0 (Å)³, Number of atoms per unit cell is 4 and the critical concentration is 0.020. Using the Blasse’s formula, the value of critical distance was found as 19.34 Å. The non-radiative energy transfer of the luminescence of oxidic phosphors is based the resonance transfer by electric multipole -multipole interaction or exchange interaction [16].

Figure 4. Colour Chromaticity Diagram (CIE 1931) of Ba₂MgSi₂O₇ doped with Eu³⁺.

This situation was explained by the Blasse's theorem [13,17]. It was reported that exceeding critical distance beyond 5 Å, only a multipole-multipole interaction is important where the exchange interaction becomes ineffective. When the critical distance is found less than 5 Å then, the exchange interaction becomes effective [18]. In present case the critical distance is calculated as 19.34 Å therefore the mechanism involved in concentration quenching of Ba₂MgSi₂O₇ doped with 2.0 mol % of Eu³⁺ is considered to be the multipolar interaction.

CONCLUSION

Di Barium Magnesium Silicate (Ba₂MgSi₂O₇) doped with various concentrations (0.2, 0.5, 1.0, 2.0 and 2.5 mol %) of Europium (Eu³⁺) were prepared using solid-state reaction technique. The sample with optimum PL emission was characterized by means of X-ray diffraction pattern, which was well matched with the standard reported for the similar sample. The PL excitation spectrum, which was monitored at 620 nm, exhibited two distinct peaks centred at 294 nm and 365 nm respectively. Therefore, the emission spectra were recorded at an excitation wavelength of 294 nm. The emission spectra expressed the prominent peaks centred at 592 and 612 nm are attributed to ⁵D₀ → ⁷F₂ of Europium (III) ions accommodated at various lattice sites having different energies, whereas peak centred at 633 nm is due to ⁵D₀ → ⁷F₃ transition of Europium (III). Sample with a dopant concentration of 2 mol % expressed the maximum PL intensity. Overall emission was found in the red colour region which was confirmed using a CIE chromaticity diagram with coordinate (0.611, 0.387). The CIE coordinate was in the region of intense red colour region. As per the literature this intense red colour emission can be a potential candidate for being red colour Light Emitting Diodes. Critical distance for energy transfer in the concentration, beyond which concentration quenching occurred in PL spectra, was calculated which indicated that there must be only multipole-multipole exchange whereas the exchange interaction is ineffective.

REFERENCES

1. Yan j, et al. VUV-vis photoluminescence, low-voltage cathodoluminescence and electron-vibrational interaction of Mn²⁺ in Ba₂MgSi₂O₇. *Optical Materials*. 2015; 43: 59-65.
2. Hou D J, et al. A high efficiency blue phosphor BaCa₂MgSi₂O₈:Eu²⁺ under VUV and UV excitation. *J Mater Chem C*.2013;1: 493-499.

3. Xie M, et al. Yellow-white emission of Ce³⁺ and Eu²⁺ doped Li₂SrSiO₄ under low-voltage electron-beam excitation. *Opt Express*. 2012; 20(14):15891-15898.
4. Zhang X G, et al. Photo-physical behaviors of efficient green phosphor Ba₂MgSi₂O₇:Eu²⁺ and its application in light-emitting diodes. *J Am Ceram Soc*.2010; 93: 1368-1371.
5. Tam T T H, et al. Co-precipitation synthesis and optical properties of green-emitting Ba₂MgSi₂O₇:Eu²⁺ phosphor. *J Lumin*. 2014; 147: 358-362.
6. Setlur A A, et al. Crystal Chemistry and Luminescence of Ce³⁺-Doped Lu₂CaMg₂(Si,Ge)₃O₁₂ and Its Use in LED Based Lighting. *Chem Mater*. 2006;18: 3314-3322.
7. Kim J S, et al. White-light generation through ultraviolet-emitting diode and white-emitting phosphor. *Appl Phys Lett*. 2004;85:3696-3698.
8. Gonggong Lu, et al. 4th International Conference on Mechatronics, Materials, Chemistry and Computer Engineering (ICMMCCE 2015). 2015;1751-1756.
9. Rao A, et al. *Indian Journal of Science & Research*. 2021;10:516-521.
10. Yen W M, et al. Inorganic phosphors compositions, preparation and optical properties. CRC Press LLC. 2004.
11. Shrivastava R, et al. Studies on long lasting optical properties of Eu²⁺ and Dy³⁺ doped di-barium magnesium silicate phosphors. *Chin Chem Lett*.2015; 26:1187-1190.
12. Shrivastava R, et al. Characterisation and mechanoluminescence studies of Sr₂MgSi₂O₇: Eu²⁺, Dy³⁺. *J Radiat Res Appl Sci*.2015; 8:201-207.
13. Shrivastava R. Near white light emission and concentration quenching of calcium titanate doped with dysprosium (iii) phosphors. *Journal of Fluorescence*. *J Fluoresc*. 2019; 29:369-374.
14. Vikas Dubey, et al. Synthesis and characterization of Eu³⁺ doped SrY₂O₄ phosphor. *Optik*. 2013; 124 (22): 5585-5587.
15. Blasse G. Energy transfer between inequivalent Eu²⁺ ions. *J Solid State Chem*. 1986; 62: 207-211.
16. Blasse G, et al. *Luminescent Materials*. Springer. 1994; 99.
17. Blasse G. Energy transfer in oxidic phosphors. *Philips Res Rep*. 1969; 24:131.
18. Ilhan M, et al. Photoluminescence and concentration quenching of Pr³⁺ doped BaTa₂O₆ phosphor. *Metalurgija*. 2015; 54(2): 407-410.