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Solid State Synthesis and Judd - Ofelt Parameter of Europium Doped Barium Magnesium Silicate Phosphors

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ABSTRACT

The europium (Eu^{3+}) doped barium magnesium silicate ($BaMgSiO_4$: Eu^{3+}) phosphors were prepared by the high temperature and conventional solid state reaction (SSR) method. The obtained phosphor samples crystallized in the hexagonal phase with $P6_3$ space group. Excitation and emission spectra as well as luminescence decays were recorded. In the photoluminescence (PL) spectra of the as-synthesized phosphors, two characteristic emission peaks recorded at 596 nm and 614 nm can be attributed to electronic transitions $^5D_0 \rightarrow {}^7F_1$ (orange region) and $^5D_0 \rightarrow {}^7F_2$ (red region) of Eu^{3+} ions. The symmetry of the local environment of Eu^{3+} activators has been described in the frame of Judd–Ofelt (J–O) parameter by using Ω_2 and Ω_4 intensity parameters derived from emission spectra. The Judd–Ofelt parameters have also been used to calculate the relative transition probability, the branching ratio and the relative lifetime. The luminescence decay rates of $^5D_0$ excited state have been measured and the corresponding emission quantum efficiency has been calculated. The effective bandwidth of the Eu^{3+} ($\Delta\lambda_{eff}$) and stimulated emission cross-section (σ_p) were also investigated.

Keywords: Europium, solid state reaction, photoluminescence, J–O parameters.

1. INTRODUCTION

Inorganic photoluminescence (PL) materials have received remarkable research attention of scientific community owing to their applications in fabricating light-emitting

diodes (LEDs)[1-4]. Mostly, the fabrication of a white light emitting diodes (wLEDs) is based on the fractional conversion of the blue illumination of an (In, Ga)N LED by a phosphor material. It is important to mention that in addition to blue or violet LEDs, near ultraviolet (UV) LEDs can also be used as major light sources[5-6]. The required condition states that the emission of the LED chip should be converted to visible light to optimize the light output of the device. These luminescent materials widely known as luminescent phosphors are capable of efficiently absorbing light of a particular wavelength and converting it into visible light. Another technology that has recently come into limelight is the fabrication of white light emitting diodes (wLEDs). The LED technology has revolutionized lighting industry from the last decade owing to their advantages. These advantages include high efficiency, long lifetime and low power consumption[7]. The red phosphors can also be employed to generate white light upon excitation by blue or near-UV light. In order to synthesize phosphors with high emission, the material needs to be chosen very carefully. It must support good physical and chemical stabilities. There occur suggestions for a number of technologies to explore efficient luminescent materials that could facilitate the development of suitable phosphors. When lanthanide (Ln) or rare earth (RE) ions are added to the host, it results in the vacant $4f^N$ electron orbitals which have grabbed a significant attention of researchers worldwide. The resultant phosphors are expected to emit highly luminescent emissions with specific light wavelengths because of variations in the energy level of some free electrons[8-11].

Among many popular dopants, Eu^{3+} ion is an essential activator for many inorganic lattices to produce orange-red emission by the transitions of $^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2, 3). The optical properties of any phosphor/dopant are closely related to its structure. In turn, Eu^{3+} can also be used as a structural probe[12]. In a crystal with inversion symmetry, the $^5D_0 \rightarrow {}^7F_1$ magnetic dipole transition of Eu^{3+} (~590–600 nm) dominates[13]. Due to the incorporation of a dopant ion or changes in the ligand field surrounding the fluorescing ion, the symmetry of site deviates from its ideal form and the electric dipole transition ($^5D_0 \rightarrow {}^7F_2$) becomes dominant giving rise to an enhanced red emission (~ 610 – 630 nm). Thus, to achieve an excellent luminescent intensity, the selection of a suitable host and rare earth ion is important.

Europium (Eu^{3+}) ion, as an excellent luminescent centre, has been the choice of many research groups. It has been incorporated in a variety of hosts, such as $LiAl_5O_8$: Eu^{3+} [14], $Sr_2MgSi_2O_7$: Eu^{3+} [15], $NaBaBO_3$: Eu^{3+} [16] to emit an intense red light coming from $^5D_0 \rightarrow {}^7F_2$ transition. Shinde *et al.*[17] have synthesized Eu^{3+} activated $NaCaPO_4$ phosphors and excited them with 393 nm light. In their emission spectra, the principal peak was observed at 594 nm (orange) while other two peaks so at 614 and 621 nm (red), respectively.

$BaMgSiO_4$ (BMS) is a useful applicant for inorganic photochromatic materials with outstanding opto-electronic and nonlinear optical properties[18-19]. BMS has attracted the attention of researchers worldwide owing to its applications in high density optical memories, smart windows, photo switches and LEDs[20-21]. Therefore, $BaMgSiO_4$ is a suitable candidate to be used as a host in rare earth (RE)-doped host compounds. Blasse *et al.*[22] and Poort *et al.*[23] have witnessed the maximum photoluminescent (PL) intensity in $BaMgSiO_4$:

Eu^{2+} ions occurring at 440 nm, 510 nm and 570 nm wavelength. Peng *et al*.[24] and Li *et al*.[25] have investigated PL properties of $BaMgSiO_4$: Eu^{2+} compounds with peaks centered at 405 nm and 500 nm.

In present paper, we have reported the light emitting phosphors $AMgSiO_4$ (A= Ba, Ca and Sr) with different concentration of the Eu^{3+} ions, synthesized by the well-known solid state reaction (SSR) method. The structural, morphological and luminescence properties of BMS phosphors doped with Eu^{3+} ions have been investigated and explained.

2. EXPERIMENTAL SECTIONS

The phosphors $BaMgSiO_4$ doped with Eu^{3+} ions have been synthesized at a high temperature using conventional solid-state reaction method. $BaCO_3$ (99.9%), MgO (99.9%), SiO_2 (99.9%) and Eu_2O_3 (99.99%) have been used as raw materials for preparation of the samples. The raw materials taken in the appropriate stoichiometric ratios were ground manually for 1 hr with an mortar and pestle followed by sintering at $1050^{\circ}C$ for 5 h. Boric acid (1 mol%) was mixed as a flux in the sample. The heating and the cooling rates were kept at 10 °C/min. The chemical reaction takes place during solid state reaction synthesis is given below.

$$BaCO_3 + MgO + SiO_2 + Eu_2O_3 \xrightarrow{1050\ ^{O}C} BaMgSiO_4: Eu^{3+} + CO_2\uparrow$$

The phase purity of prepared samples was ascertained using a PANalytical make powder X-ray diffractometer (Cu Kα radiation λ = 0.15406 nm) operated at 40 KV and 30 mA. The scanning was done in the range: $10° < 2\theta < 80^0$. The photoluminescence excitation (PLE) and photoluminescence (PL) spectra were recorded on RF-5301 PC spectrofluorophotometer (Shimadzu, Japan) with a Xe lamp as the exciting source. Time-resolved measurements (fluorescence decay times) were performed by using pico second time resolved (PSTR) fluorimeter (Make: Eddinburg Instruments, Model: Lifespec II).

3. RESULTS AND DISCUSSIONS

3.1 XRD pattern

The powder X-ray diffraction (PXRD) spectra were performed on $BaMgSiO_4$: Eu^{3+} to validate the phase purity and crystallinity. Fig.1 shows the typical XRD patterns of pure $BaMgSiO_4$ and $BaMgSiO_4$: Eu^{3+} (5 mol%) phosphors. From the XRD data, the hexagonal phase of $BaMgSiO_4$ with space group $P6_3$ and unit cell volume V= 628.23 $Å^3$ has been established. The lattice parameters of refined values of $BaMgSiO_4$ were found as; a = 9.1120 Å, c = 8.7370 Å, which signified the proper preparation of the sample.

The crystallite sizes (D) of samples are computed using Scherrer's formula[27] given as follows

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where K is the Scherrer constant with value = 0.94, λ is the wavelength of X-rays used, β - the full width at half maxima (FWHM) and θ is the Bragg's angle. The values of average crystallite sizes have been calculated to be as 43.85 nm and 91.69 nm, respectively.

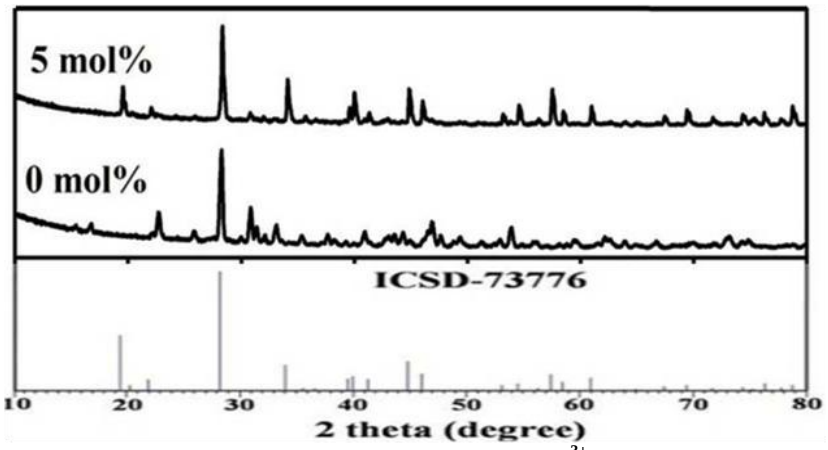

Fig. 1 XRD patterns of $BaMgSiO_4$ and $BaMgSiO_4$: Eu^{3+} (5 mol%) phosphors.

3.2 Photoluminescence (PL) characteristics

The PL emission spectrum of $BaMgSiO_4$: Eu^{3+} (5 mol%) powders were excited at a wavelength of 396 nm. The emission spectrum consists of two strong peaks centered at 596 nm and 614 nm as shown in Fig. 2. The emission peak at 596 nm wavelength can be attributed to transition ($^5D_0 \rightarrow {}^7F_1$) magnetic dipole (MD) origin while the stronger peak transition ($^5D_0 \rightarrow {}^7F_2$) at 614 nm wavelength so to the electric dipole (ED) origin[28]. The peak obtained at 596 nm corresponding to ($^5D_0 \rightarrow {}^7F_1$) transition dominates over that at 614 nm corresponding to ($^5D_0 \rightarrow {}^7F_2$), while the Eu concentration was 5 mol %.

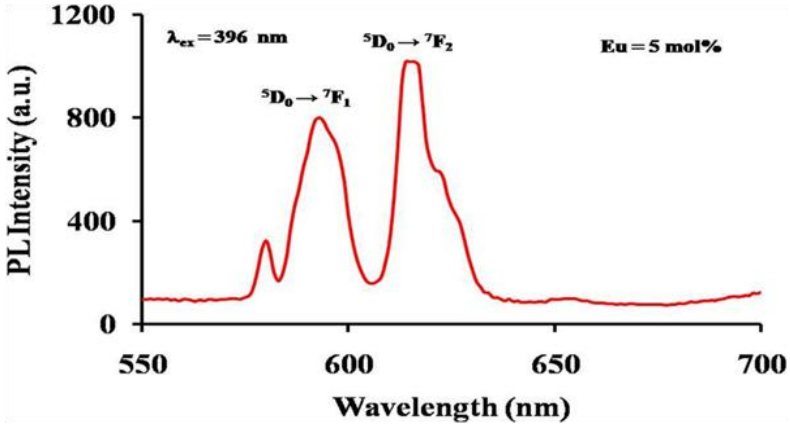

Fig. 2 PL emission spectrum of $BaMgSiO_4$: Eu^{3+} (5 mol%) phosphor at λ_{ex} = 396 nm

3.3 Decay curve

The luminescence decay studies were performed on $BaMgSiO_4:Eu^{3+}$ (5 mol%) phosphor. Fig. 3 represents the luminescence decay behavior of a silicate phase under excitation at wavelength of λ_{ex}= 396 nm and monitoring wavelength at 614 nm.

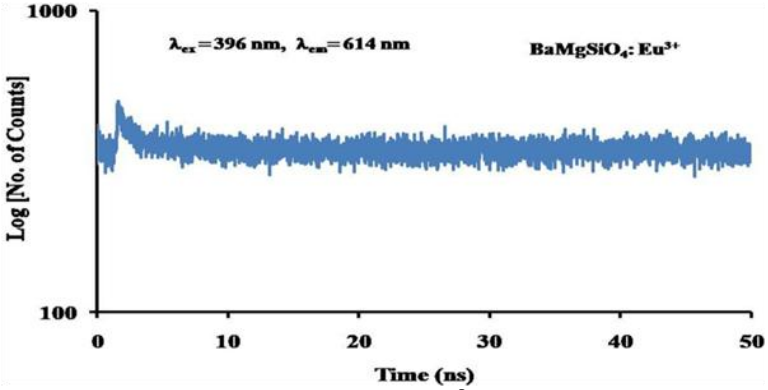

Fig. 3 Decay profile of $BaMgSiO_4$: Eu^{3+} (5 mol%) phosphor.

The decay curve can be fitted using double exponential equation as follows[29]:

$$I = I_1 \exp(-t/\tau_1)+I_2 \exp(-t/\tau_2) \quad (2)$$

where I_1 and I_2 are constants, τ_1 and τ_2 are decay times, respectively. The decay profile comprises of both fast and slow decay processes. The obtained decay times of prepared phosphor summarized are given in Table 1.

Table 1 Decay time of $BaMgSiO_4$: Eu^{3+} (5 mol%) phosphor.

Sample	Decay time	
$BaMgSiO_4:Eu^{3+}$ (5 mol%)	Fast decay (τ_1)	Slow decay (τ_2)
	4.0 ns	6.52 ns

3.4 Judd – Ofelt parameters

The theory proposed by Judd and Ofelt[30,31] is commonly applied to determine spectroscopic properties of Ln^{3+} - doped materials, such as ED transition probabilities, radiative lifetimes and branching ratios, in terms of three intensity parameters, Ω_i (i = 2, 4, 6), that can be determined from the knowledge of the absorption spectra.

In case of Eu^{3+}-doped compounds, it is also possible to apply for calculation of Judd-Ofelt (JO) parameters based on emission spectrum[32,33]. The magnetic dipole (MD) transition $5D_0 \rightarrow {}^7F_1$ can be taken as a reference to evaluate the other electric dipole (ED) transitions originated in the transitions ${}^5D_0 \rightarrow {}^7F_j$ (j = 2, 4, 6). It is widely used to calculate the oscillator strength for an induced electric dipole transition from the emission spectra using relation cited in literature[30,31] and optical parameters can be calculated i.e. emission peak wavelength (λ_p), J-O intensity parameters (Ω_2, Ω_4), radiative transition probability (A_{rad}), total radiative

transition probability (A_T), experimental branching ratio (β_{exp}), theoretical branching ratio (β_{th}), barycentres (ν), stimulated emission cross section (σ), theoretical life time (τ_{th}), calculated life time (τ_{cal}), experimental life time (τ_{exp}), non-radiative relaxation rate (W_{NR}), optical gain parameter (P) and luminescence quantum efficiency (η) have been listed in Table 2.

Table 2 Calculated optical properties of $BaMgSiO_4$: Eu^{3+} (5 mol%) phosphor.

Eu^{3+} Concentration	Parameters	Transitions		
		$^5D_0 \rightarrow {}^7F_1$	$^5D_0 \rightarrow {}^7F_2$	$^5D_0 \rightarrow {}^7F_4$
5 mol%	λ_p	593 nm	614 nm	
	Ω_2 x 10^{-20} (cm^2)	3.04		
	Ω_4 x 10^{-20} (cm^2)	1.01		
	A_{rad} (s^{-1})	342.45	464.99	71.55
	A_T (s^{-1})	878.99		
	β_{exp}	0.35	0.46	0.06
	β_{th}	0.39	0.52	0.08
	ν (cm^{-1})	33653.59	32284.95	28953.26
	σ X 10^{-22} (cm^2)	6.66	12.26	0.007
	τ_{th} (ms)	8.11		
	τ_{cal}	11.3		
	τ_{exp}	5.63		
	W_{NR} (s^{-1})	89.1		
	$P = \sigma$ x τ_{exp}	3.72	69.02	0.04
	η (%)	49.8		

4. CONCLUSIONS

In the present study, a novel Eu^{3+} doped $BaMgSiO_4$ phosphors have been successfully synthesized by SSR method. The formation, phase purity and structure of $BaMgSiO_4$: Eu^{3+} phosphor have been confirmed by the XRD analysis. The strong PL emission at 596 nm and 614 nm for the excitation of 396 nm have been observed in phosphors for optimal concentration 5 mol% . The decay lifetime of the prepared phosphor for fast and slow decay have been found to be 4.0 ns and 6.52 ns, respectively. The Judd–Ofelt parameters and related parameters like the relative transition probability, branching ratio and relative lifetime have been also calculated.

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