Optical Properties of Eu^{3+} Doped Gadolinium Silicate Phosphors

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Abstract: ***The present paper reports the optical properties of rare-earth-doped Gadolinium Silicate Phosphors. The europium (Eu^{3+}) was used as rare-earth-doped. The phosphor is prepared by using the Solid-state reaction method (conventional method) heated at 1200°C for 2 hrs. The received cakes are grounded for 30 minutes each. The phosphors are prepared and the received powder is subjected to PL, XRD, SEM, and EDAX analysis. The following section discusses and the experimental results are mentioned in these phosphors. The present Phosphor can act as a host for red light emission in many display devices and technological applications.***

Keywords: Gadolinium Silicates Phosphor, Rare earth ion, Conventional Solid state reaction method

1. Introduction

Rare earth ion-doped hosts have demonstrated good photoluminescence (PL) properties and chemical-physical stabilities. Eu^{3+} in such kinds of a host may emit various colors demanded by white lighting. Rare earth ion-doped phosphors have been used in varied fields based on their electronic and optical characters arising from their 4*f* electrons [1-5]. Among the rare earth elements, europium is a special element as dopant, because it exhibits the property of valence fluctuation, i.e. the valence state is divalent or trivalent. And it exhibits different characteristics luminescence due to the different valence. The red light emission of Eu^{3+} is due to the intra-4*f* transition. While the emission of Eu^{3+} from the dipole allowed 5*d*–4*f* transition varies in a wide range from red to ultraviolet which depends on the crystal structure of host materials. It is well known that the optical properties of rare-earth ion-doped luminescent materials are greatly influenced by the matrix. Their exceptional electronic and optical properties result from the properties of the 4f shell of these ions, where the structure of Eu^{3+} is $4f^6$. Fluorescence properties were livelier, excited-state lifetime is long enough and it could transmit good monochromaticity, the high quantum efficiency of red fluorescence, which is widely used in the light-emitting material activator. Spectroscopic studies of these phosphors play a vital role in characterizing the specific luminescence properties such as photoluminescence and thermoluminescence. The rare-earth is usually incorporated in these materials as divalent or trivalent cation for the realization of optically active materials in photonics and optoelectronic applications. The europium is efficiently used as a luminescent center in phosphors for various purposes. Phosphors doped with europium ions are of greater importance for observing red colors on the monitors of various display devices [6-11].

In this research paper, we have studied the optical properties of Eu^{3+} doped Gadolinium Silicates Phosphors prepared by the conventional solid-state reaction method fired at 1200°C for 2h. The prepared phosphors were characterized by subjected to PL, XRD, SEM, and EDAX analysis.

2. Experimental Method

The conventional Solid state reaction method was utilized for preparing these phosphors, which is the simpler and standard method. The inorganic compounds like Gadolinium oxide (Gd_2O_3), Silicon dioxide (SiO_2), and Europium Oxide (Eu_2O_3) of high purity (99.9%) chemicals were used as starting materials. First, we prepared Gd_2SiO_4 phosphor, without adding any dopants, as a host material, by weighing Gadolinium oxide (Gd_2O_3), Silicon dioxide (SiO_2) in stoichiometric proportions of 2:1. The compounds were mixed with a spatula and then ground into a fine powder using an agate mortar and pestle manually about an hour at room temperature. The grounded sample was placed in an alumina crucible and heated at 1200°C in the air for 3 hours in a muffle furnace with a heating/cooling rate of 5°C/min. In the same way and Europium Oxide (Eu_2O_3) rare-earth ion-doped (at different concentrations like 0.1, 0.2, 0.5, 1.0, 1.5, 2.0 and 2.5 mol %) Gd_2SiO_5 phosphor samples were synthesized.

To identify the crystal phase, XRD analysis was carried out with a powder diffractometer (Rigaku-D/max 2500) using Cu Kα radiation. The Photoluminescence emission and excitation spectra were measured by Spectrofluorophotometer (SHIMADZU, RF-5301 PC) using a Xenon lamp as an excitation source. All the spectra were recorded at room temperature. The morphologies (SEM) of the phosphor powders were obtained by using the Nova NanoSEM450. Energy-dispersive X-ray spectroscopy (EDS, EDX, EDXS, or XEDS), sometimes called energy dispersive X-ray analysis (EDXA) or energy dispersive X-ray microanalysis (EDXMA), is an analytical technique used for the elemental analysis or chemical characterization of samples.

3. Results and Discussion

3.1 Crystal structure analysis

To determine the crystal structure and phase purity of the phosphors, XRD analysis was carried out. The crystal structure of the prepared silicate phosphor was determined by using X-ray diffraction analysis. The XRD pattern of Gd_2SiO_5 phosphor and Gd_2SiO_5: Eu^{3+} phosphors are as shown in Fig.1a & 1b. From the XRD pattern analysis, it was found that the prominent phase formed is Gd_2SiO_5, after the diffraction peaks are well indexed based on the JCPDS card No.40-0287 [12]. The pattern confirms the formation of the monoclinic phase for prepared Gd_2SiO_5 phosphor. Table 1 shows the calculated crystallite sizes of the phosphors from the XRD pattern using Scherer's formula. $D = K \lambda / \beta \cos \theta$, Where D = crystallite size, K = constant, λ = X-ray wavelength, β = Full width at half maxima (FWHM), θ = Angle of the big peak [13]. From table 1 it is found that all the crystallite sizes are in nano form and we conclude majority phosphor crystallites are in nano form. It is also observed that as Eu^{3+} concentration increases the average crystallite size gradually increases. Fig. 2 shows the relation between Eu(mol%) percentages concentration in the present phosphor vs crystallite size. It is concluded that as Eu(mol%) percentages concentration increases in Gd_2SiO_5 phosphor crystallite size is also increasing.

Table 1

S.No	Name of the phosphor	The crystallite size (nm)
1	Gd_2SiO_5: Base	30.12
2	Gd_2SiO_5: Eu^{3+} (0.1mol %)	30.53
3	Gd_2SiO_5: Eu^{3+} (0.2mol %)	31.32
4	Gd_2SiO_5: Eu^{3+} (0.5mol %)	33.03
5	Gd_2SiO_5: Eu^{3+} (1.0mol %)	37.53
6	Gd_2SiO_5: Eu^{3+} (1.5mol %)	40.80
7	Gd_2SiO_5: Eu^{3+} (2.0mol %)	42.61

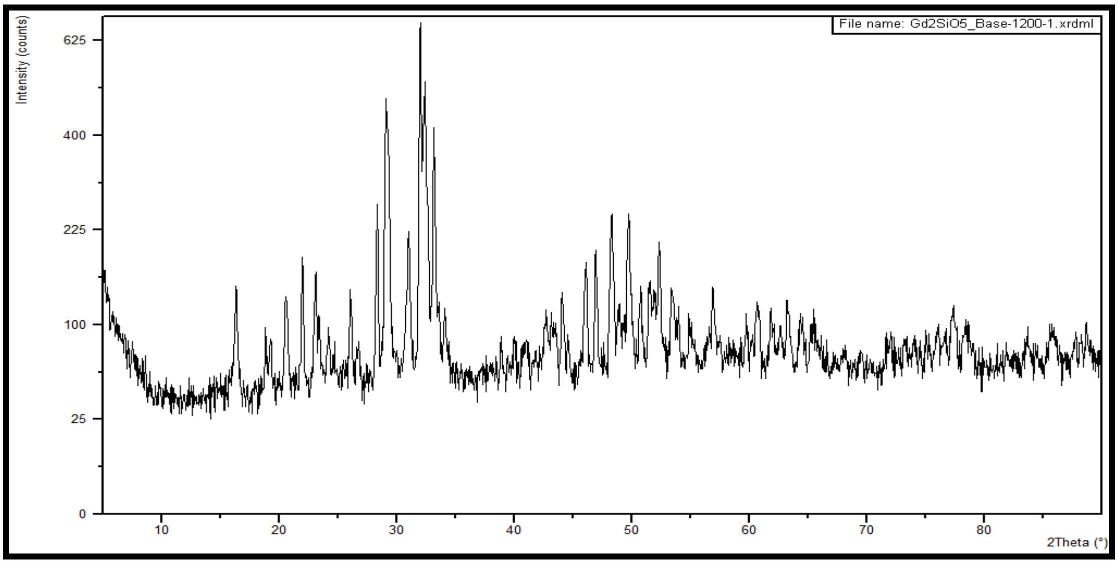

Figure 1 (a): XRD pattern of Gd_2SiO_5 phosphor

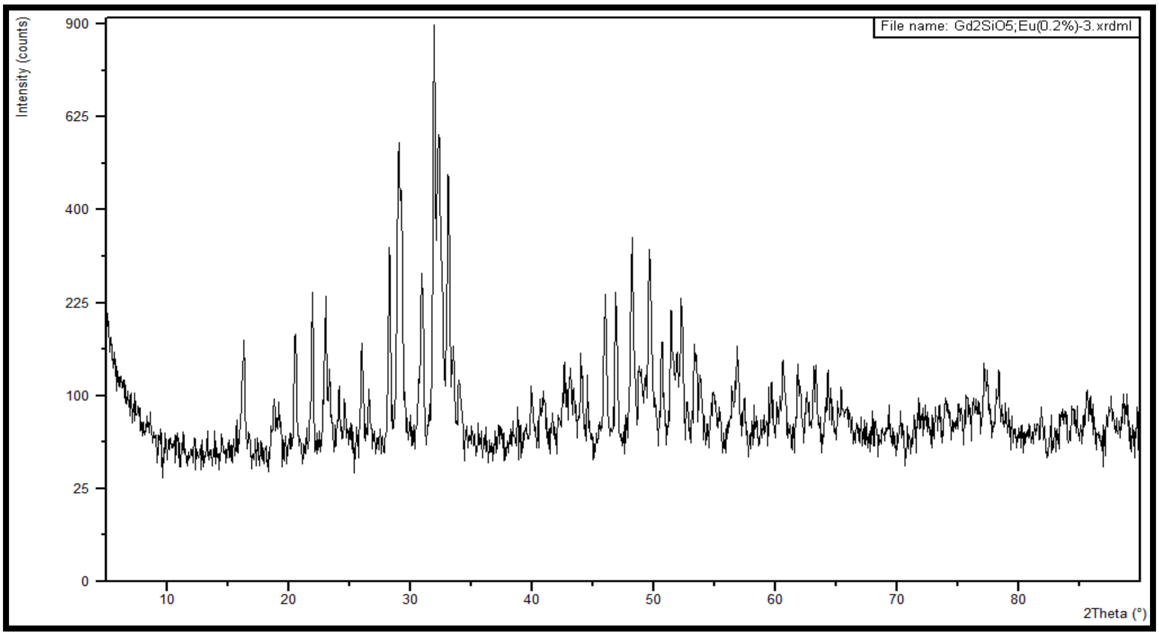

Figure 1 (b): XRD pattern of Gd_2SiO_5: Eu^{3+}(0.2mol %) phosphor

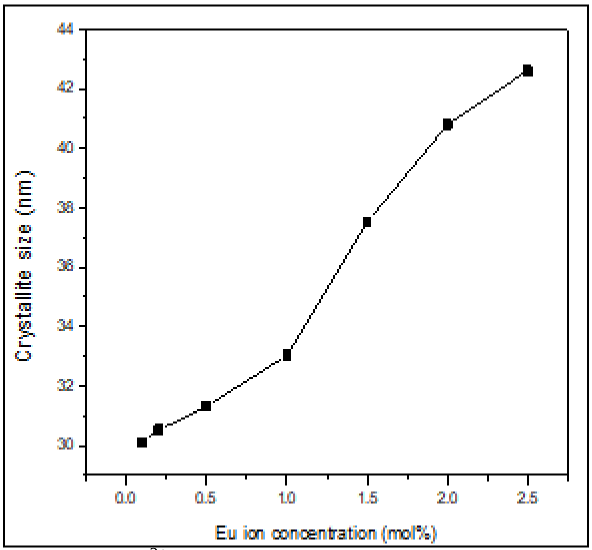

Figure 2: Eu^{3+} (mol %) percentages concentration Vs crystallite size

3.2 Photoluminescence behavior

Fig.3 shows the PL excitation spectra of the Gd_2SiO_5: Eu^{3+} phosphor monitored at 615 nm for the 0.1 - 2.5 mol% of Eu^{3+} samples. The excitation peak at 275 nm corresponds to the 4-4f transitions of Gd^{3+} from the $^8S_{7/2}$ ground state to the ^6I_J. The peak nearby at 265 nm corresponds to the higher energy $^8S_{7/2} \rightarrow {}^6D_J$ transitions of Gd^{3+}, and the 312 nm peak originates from the $^8S_{7/2} \rightarrow {}^6P_J$ transitions of Gd^{3+}. The PL emission spectra of the Gd_2SiO_5: Eu^{3+} prepared at different Eu^{3+} doping concentration (0.1–2.5mol %) excited at 275 nm are shown in Fig.4. There was no change in the peak position of the emission spectra with an increasing concentration of Eu^{3+} and all the intense fluorescence peaks originated from the $^5D_0$ state of Eu^{3+}. The strongest one (615 nm) is the forced electric dipole transition $^5D_0 \rightarrow {}^7F_2$, and it gave the intense red emission [14]. From the emission spectrum, the features and the high intensity of the $^5D_0 \rightarrow {}^7F_2$ transition indicated that Eu^{3+} occupied asymmetry site without a center of inversion. When the host matrix Gd_2SiO_5 phosphor absorbed the ultraviolet light energy, the Eu^{3+} ion was excited by the energy transfer from the absorption energy and then non- radiatively relaxed to the higher energy state of the Eu^{3+} ion. The distinct emission band between 580 and 632 nm was observed due to the transitions from the $^5D_0$ to the ^7F_j (J=0, 1, 2, 3) level of Eu^{3+} as shown in fig.5. The origin of these transitions (electric dipole or magnetic dipole) from emitting levels to terminating levels depends upon the location of the Eu^{3+} ion in the Gd_2SiO_5 lattice, Gd^{3+} sites replaced by Eu^{3+} sites which are responsible for the emission spectra in the host matrix and the type of transition is determined by the selection rule [15–18]. The peak at 580 nm was ascribed to the transition of the $^5D_1$ and $^7F_0$ levels. The emission intensity of the Gd_2SiO_5: Eu^{3+} phosphors were strongly affected by the Eu^{3+}doping concentration. The optimum intensity was obtained at a doping concentration of 1.5 mol% of Gd_2SiO_5: Eu^{3+} phosphor. As shown in Fig.4, it is also observed that the emission intensity of the phosphor increased with the increase of Eu^{3+} concentration up to 2.5mol%. Beyond the limit value (2.5mol %) the PL emission intensity of the phosphor increased due to the effect of concentration Eu^{3+}. As the results the excessive Eu^{3+} ions were doped into the Gd_2SiO_5 host, the distance of the Eu^{3+}– Eu^{3+} increased. Then the immigration of excitation energy via resonant energy transfer occurred between the Eu^{3+} ions, increasing the PL emission intensity. The peak position of the PL emission spectra did not show any shift with a changing Eu^{3+}doping concentration only a change in the relative intensities of the different emission peaks[19-24]. Higher symmetry of the crystal field near the activator Eu^{3+} ion resulted in a higher ratio of the red and orange peak intensity (R/O value). In this study, the emission intensity of the magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$ (orange) was weaker than that of the electric dipole transition $^5D_0 \rightarrow {}^7F_2$ (red). This indicated that the Eu^{3+} ions located at the high symmetric sites might occupy the Gd^{3+} crystallographic sites in the Gd_2SiO_5 with a monoclinic structure.

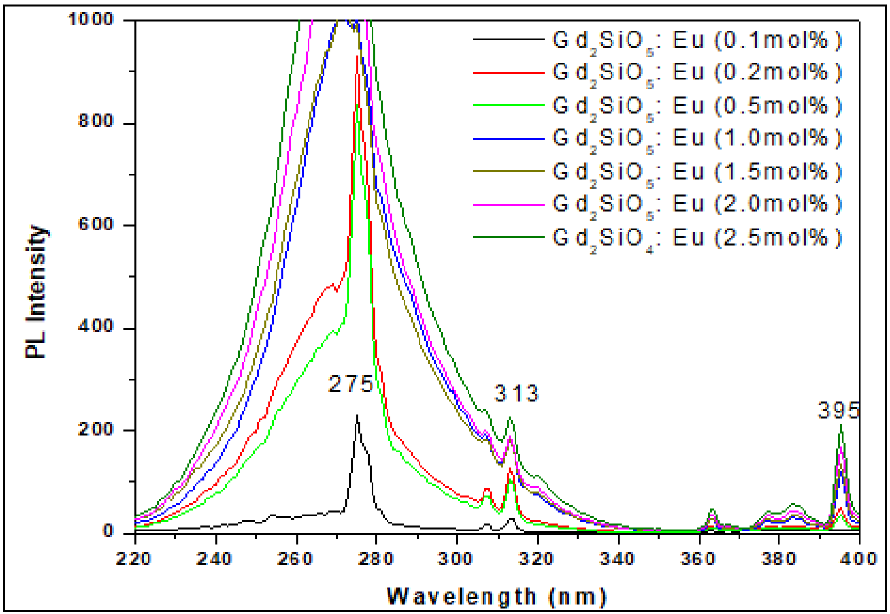

Figure 3: Excitation spectra of Gd_2SiO_5: Eu^{3+} (0.1 – 2.5 mol %) phosphor monitored at 615nm wavelength

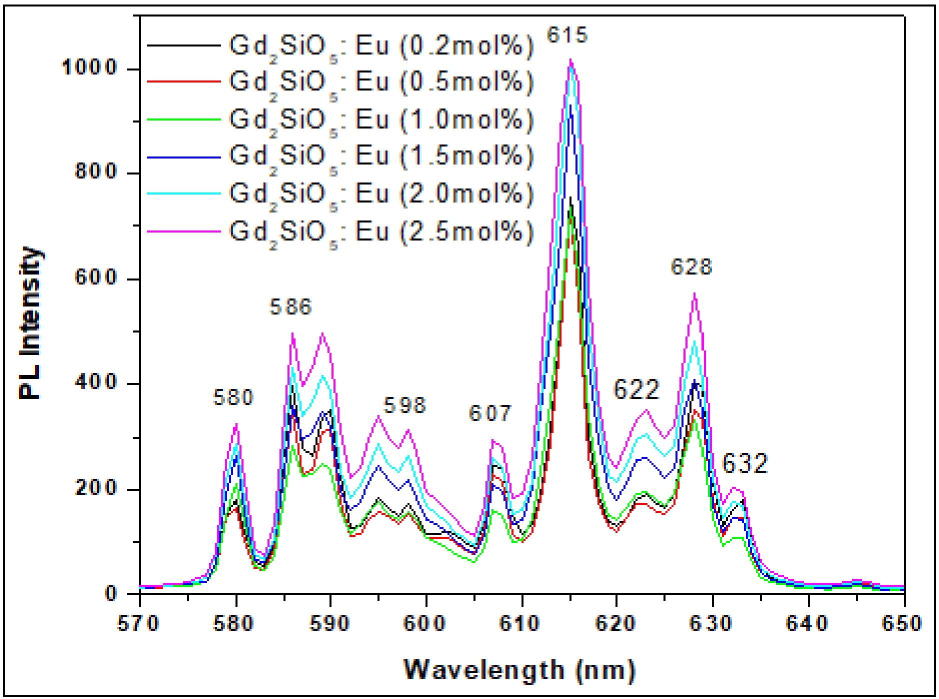

Figure 4: Emission spectra of Gd_2SiO_5: Eu^{3+} (0.2 – 2.5 mol %) phosphor under 275nm excitation

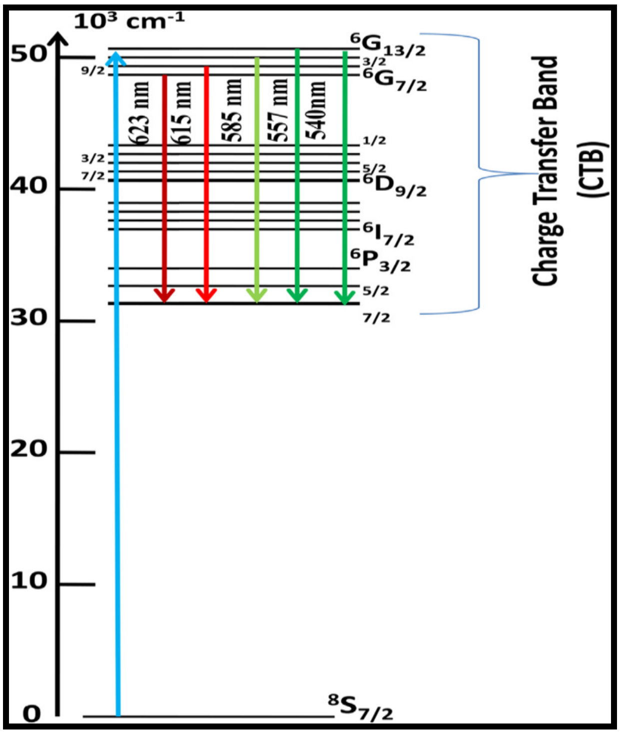

Figure 5: Energy level diagram for emission transitions for Gd_2SiO_5: Eu^{3+}phosphor

3.3 SEM analysis of Gd_2SiO_5: Eu^{3+} phosphor

The structure was further confirmed by scanning electron microscopy techniques. Fig. 6a and 6b are the SEM images of Eu(0.1mol%) doped Gd_2SiO_5 and Eu(2.5mol%) doped Gd_2SiO_5 phosphors respectively under different resolutions. From the images, it is observed that the phosphor is in non-uniform-sized particles with high agglomeration. Also observed that the Eu(0.1mol%) doped Gd_2SiO_5 and Eu(2.5mol%) doped Gd_2SiO_5 phosphors agglomeration of crystals which results in increased particle size of the Bessel diameters are around 2–5 microns.

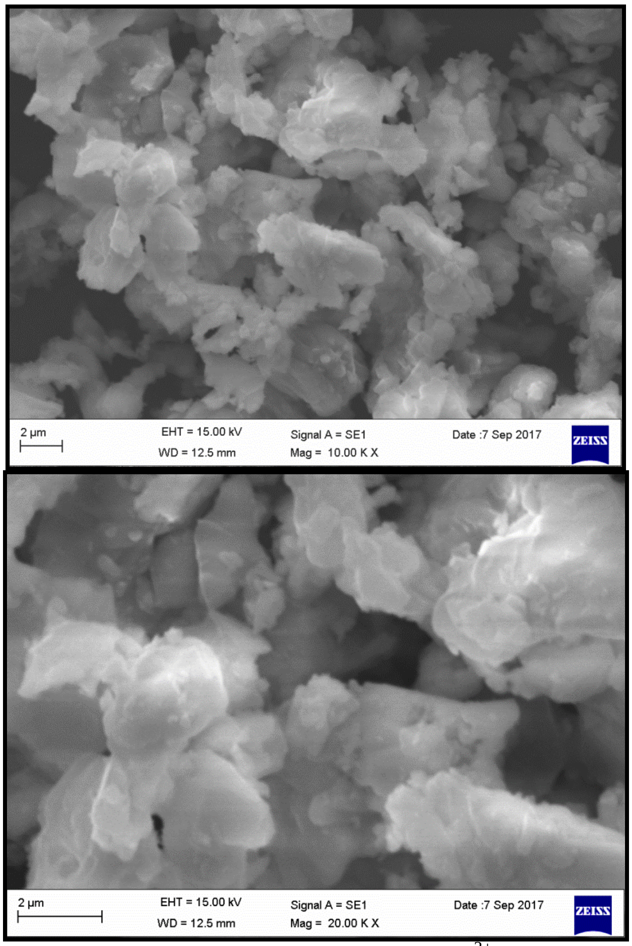

Figure 6 (a): SEM images of Gd_2SiO_5: Eu^{3+}(0.1mol %) phosphor under different resolutions

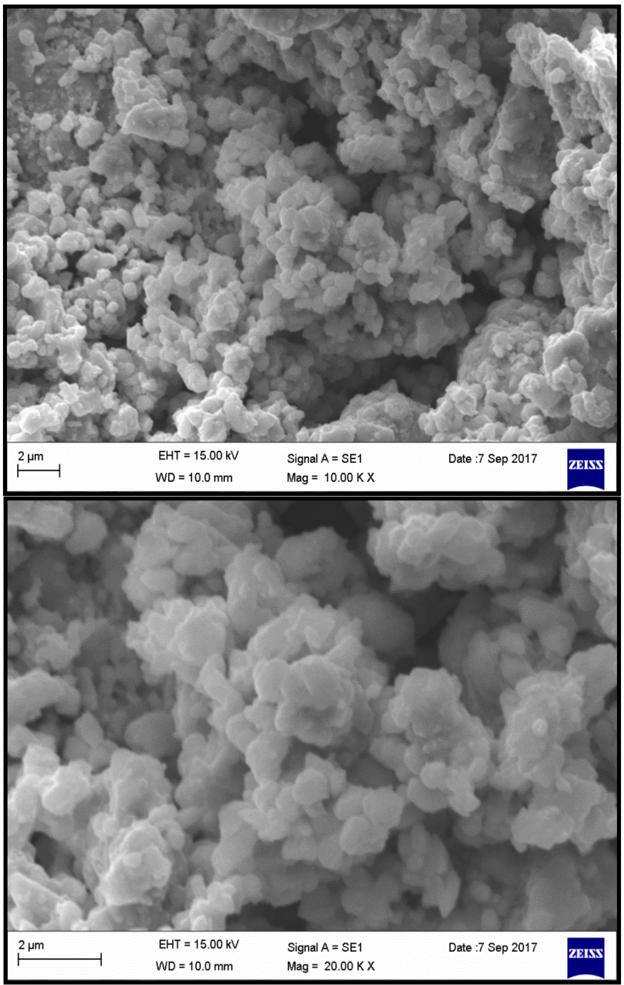

Figure 6 (b): SEM images of Gd_2SiO_5: Eu^{3+}(2.5mol %) phosphor under different resolutions

3.4 EDAX analysis of Gd_2SiO_5: Eu^{3+} phosphor

Gd_2SiO_5: Eu^{3+} phosphor subjected to another optical property which is “Energy Dispersive through X-ray Elemental Analysis” (EDAX). Fig. 7a and 7b are the electron image, EDAX, and the table containing the element, weight %, and atomic % of the phosphors under study. From the figures of EDAX and the tables, the basic phosphor elements are shown. It is concluded from all the EDAX figures and tables the dopant Eu, as well as Si and Oxygen of various percentages, are seen which are compared with the calculations made while preparing the phosphors. Therefore it is mainly concluded the formation of the phosphor is as per the empirical formula and weight percentage used to prepare the phosphors using a solid-state reaction (SSR) method. It is also concluded the SSR method is to synthesize the phosphors under study is a very good method.

Spectrum processing:
Peaks possibly omitted: 0.274, 2.316 keV
Processing option: All elements analyzed (Normalized)
Number of iterations = 2
Standard:
O SiO2 1-Jun-1999 12:00 AM
Si SiO2 1-Jun-1999 12:00 AM
Gd GdF3 1-Jun-1999 12:00 AM

Element	Weight %	Atomic %
OK	22.77	68.69
Si K	5.38	9.25
Gd L	71.85	22.05
Totals	100.00	

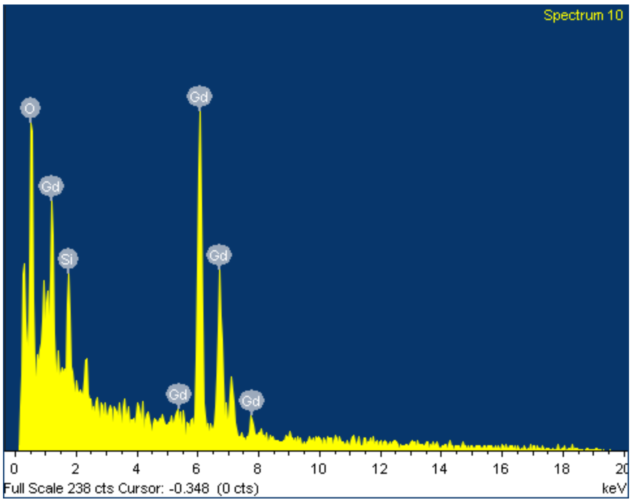

Figure 7 (a): Electron image of the Gd_2SiO_5 base phosphor

Spectrum processing:
Peak possibly omitted: 2.305 keV
Processing option: All elements analyzed (Normalized)
Number of interactions = 2
Standard:
O SiO2 1-Jun-1999 12:00 AM
Si SiO2 1-Jun-1999 12:00 AM
Eu EuF3 1-Jun-1999 12:00 AM
Gd GdF3 1-Jun-1999 12:00 AM

Element	Weight %	Atomic %
OK	25.04	70.69
Si K	5.89	9.47
Eu L	0.60	0.18
Gd L	68.47	19.35
Totals	100.00	

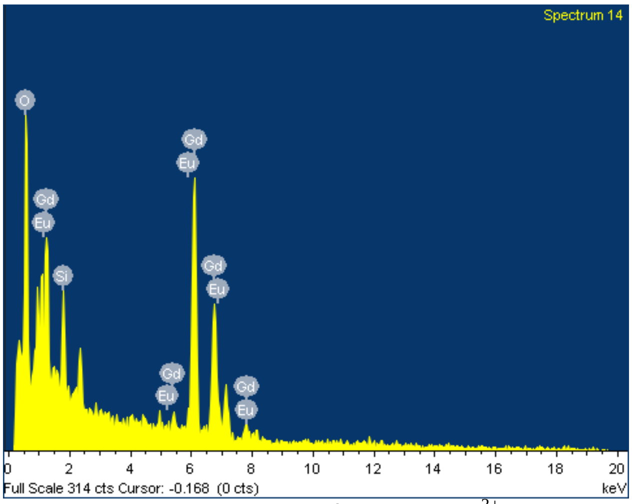

Figure7 (b): Electron image of Gd_2SiO_5: Eu^{3+} (2.5mol %) phosphor

4. Conclusions

- The PL excitation and emission studies of the phosphors mentioned above. Fig. 3 is the excitation spectra of Eu (0.1 – 2.5mol %) doped Gd_2SiO_5 phosphor monitored at 615nm wavelength. From the excitation spectra, it is found the intensity is out of range of the observations at 275nm wavelength and also at 313, 395, and 465nm excitations are observed. By considering the application potential only, the emissions are recorded under the excitation of 275, 395, and 465nm.
- Fig.4 is the 275nm excited emission spectra of various concentrations (0.2-2.5 mol %) of $Gd_2SiO_5:Eu^{3+}$ phosphor. From the figure, it is found many emissions with different intensities are found they are 580, 586, 598, 607, 615, 622, 628, and 632nm with different intensities. However 615nm intensity is highest for all the concentrations. This observation confirmed that the prepared phosphor is a good emitting phosphor for UV light excitation and useful for display device applications.
- Finally, we conclude that many emissions are found from the figure which is yellow to the red region with various intensities. All the emissions are allowed transitions of Gd^{3+} as well as Eu^{3+} ions. Among the observed peaks, the 615nm peak is the highest in intensity. The transitions are allowed which are attributed to a magnetic dipole (552–600nm) and electric dipole (600nm and above) components of the Eu^{3+}doped phosphors.
- The XRD pattern of Gd_2SiO_5 phosphor and Gd_2SiO_5: Eu^{3+}phosphors are as shown in Fig.1a & 1b. From the XRD pattern analysis, it was found that the prominent phase formed is Gd_2SiO_5, after the diffraction peaks are well indexed based on the JCPDS card No.40-0287. The pattern confirms the formation of the monoclinic phase for prepared Gd_2SiO_5 phosphor.
- Fig. 6a and 6b are the SEM images of Eu^{3+}(0.1mol %) doped Gd_2SiO_5 and Eu^{3+}(2.5mol %) doped Gd_2SiO_5 phosphors respectively under different resolutions. From the images, it is observed that the phosphor is in non-uniform-sized particles with high agglomeration.
- Fig. 7a and 7b are the electron image, EDAX, and the table containing element, weight %, and atomic % of the phosphors under study. It is concluded from all the EDAX figures and tables the dopant Eu, as well as Si and Oxygen of various percentages, are seen which are compared with the calculations made while preparing the phosphors. Therefore it is observed that the formation of the phosphor is as per the empirical formula and weight percentage used to prepare the phosphors using the conventional Solid-state reaction (SSR) method. Finally, it is also concluded that the SSR method is to synthesize the phosphors under study is a very good method.

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