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Synthesis and Optical Properties of Ce^{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 Cerium Oxide (Ce^{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 blue light emission in many display devices and technological applications.

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

Introduction

In daily life of urban civilization, luminescence devices have become so significant that without these devices our life cannot be imagined. These devices have usage in several forms such as LED TVs, LED lamps, simple lamps, TVs, signals, displays and mobile displays etc. Luminescence devices have two common types "incandescence" and "luminescence". Light generated from heat energy is incandescence. If we heat something to enough high temperature, then it will begin to glow due to heat, this phenomenon is known as "incandescence". For example, when a metal or electric stove's heater in a flame begins to glow "red hot" and produce light. In an ordinary incandescent light bulb, when tungsten filament is heated, it produces "white hot" light and glows brightly. The stars and sun also glow by the process of incandescence. Recently various red phosphors materials have been actively investigated to improve their luminescent properties and to meet the development of different display and luminescence devices. Inorganic compounds doped with rare earth ions form an important class of phosphors as they possess a few interesting characteristics such as excellent chemical stability, high luminescence efficiency, and flexible emission colors with different activators (Yokota et al., 2010; Murthy & Virk, 2013; Shionoya & Yen, 1999; Blasse & Grabmaier, 1994; Rao & Devine, 2000).

Rare earth ion-doped hosts have demonstrated good photoluminescence (PL) properties and chemical-physical stabilities. Ce^{3+} in such kinds of a host may emit various colors demanded by blue lighting. Rare earth ion-doped phosphors have been used in varied fields based on their electronic and optical characters arising from their $^4f_2$ electrons. 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 blue light emission of Ce^{3+}at 438nm is due to transition $^5D_2 \rightarrow {}^7F_0$ with energy 2.6572ev. While the emission of $Ce^{3+}$from the dipole allowed $^5D_2 \rightarrow {}^7F_0$ transition varies in a wide range from blue to ultraviolet which depends upon 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 (Rao & Devine, 2000; Köstler et al., 1995; Sankar & Subba Rao, 2005; Nazarov et al., 2010). Their exceptional electronic and optical properties result from the properties of the 4f shell of these ions, where the structure of Ce^{3+} is $^4f_2$. Fluorescence properties were livelier, excited-state lifetime is long enough and it could transmit good monochromaticity, the high quantum efficiency of blue 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 cerium is efficiently used as a luminescent center in phosphors for various purposes. Phosphors doped with cerium ions are of greater importance for observing blue colors on the monitors of various display devices (Nazarov & Noh, 2010; Kao & Chen, 2002; Li et al., 2007; Ghildiyal, Page, & Murthy, 2007). In this research paper, we have studied the optical properties of Ce^{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.

Methodology

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 Cerium Oxide (Ce_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 5ºC/min. In the same way and Cerium Oxide (Ce_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.

Results and Discussion

Crystal structure analysis

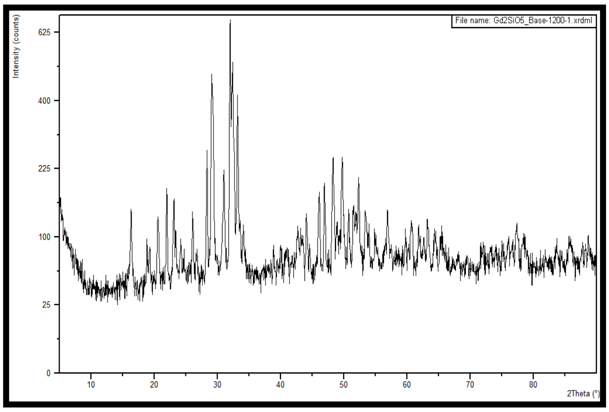


Figure 1(a). XRD Pattern of Gd_2SiO_5: Base Phosphor

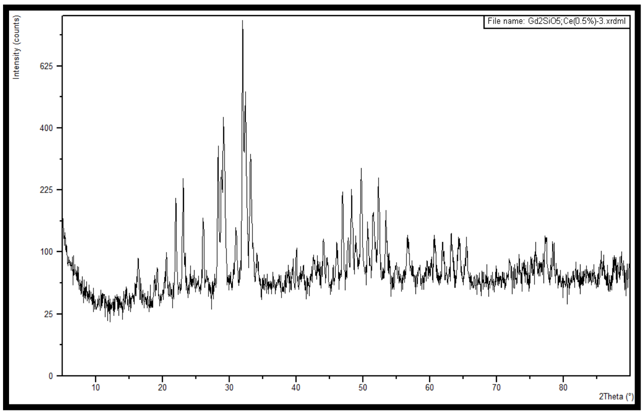


Figure 1(b). XRD Pattern of Gd_2SiO_5: Ce^{3+} (0.5mol %) Phosphor

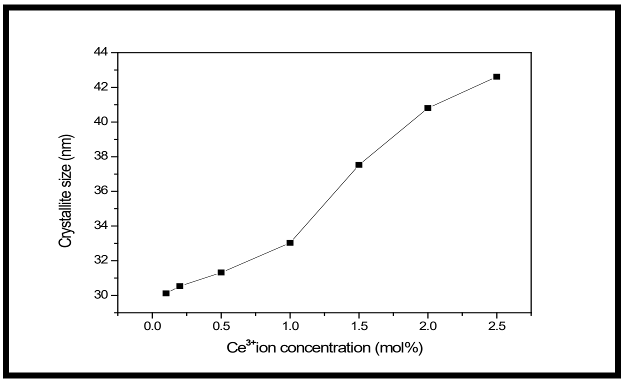


Figure 2. Ce^{3+} (mol %) Percentages Concentration Vs Crystallite Size

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: Base phosphor and Gd_2SiO_5: Ce^{3+} (0.5mol %) phosphors are as shown in Figure 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 XRD pattern confirms the formation of the phosphor it may be majority is in single phase, since the sintering temperature required for silicate phosphor is around 1300°C. This may be the reason many peaks are observed in the XRD pattern of prepared Gd_2SiO_5: Base phosphor and Gd_2SiO_5: Ce^{3+} (0.5mol %) phosphors. 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 (Kohale, & Dhoble, 2012). 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 Ce^{3+} concentration increases the average crystallite size gradually increases. Figure 2 shows the relation between Ce^{3+} (mol %) percentages concentration in the present phosphor vs crystallite size. It is concluded that as Ce^{3+} (mol %) percentages concentration increases in Gd_2SiO_5 phosphor crystallite size is also increasing.

Table 1. Calculated Crystallite Sizes of the Phosphors

S. No	Name of the phosphor	Crystallite size (nm)
1	Gd_2SiO_5: Base	26.73
2	Gd_2SiO_5: Ce^{3+} (0.5mol %)	29.34
3	Gd_2SiO_5: Ce^{3+} (0.2mol %)	30.58
4	Gd_2SiO_5: Ce^{3+} (0.5mol %)	33.14
5	Gd_2SiO_5: Ce^{3+} (1.0mol %)	34.41
6	Gd_2SiO_5: Ce^{3+} (1.5mol %)	34.49
7	Gd_2SiO_5: Ce^{3+} (2.0mol %)	34.62
8	Gd_2SiO_5:Ce^{3+} (2.5mol %)	42.31

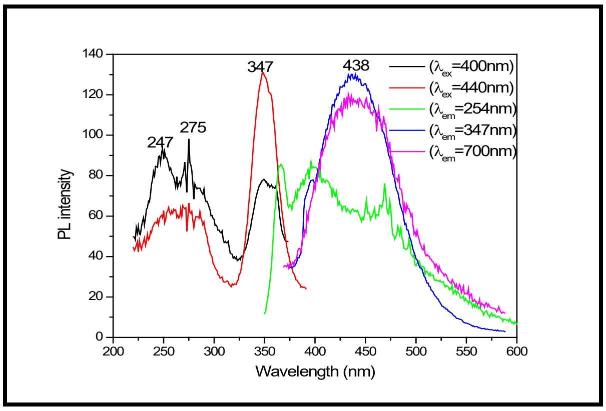


Figure 3. PLE & PL Spectrum of Gd_2SiO_5: Ce^{3+} (0.1mol %) Phosphor

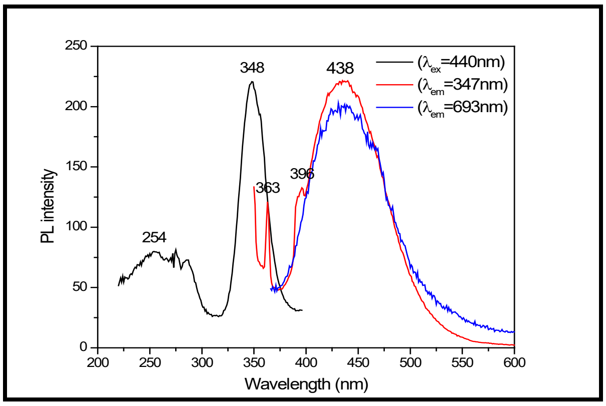


Figure 5. PLE & PL Spectrum of Gd_2SiO_5: Ce^{3+} (2.0mol %) Phosphor

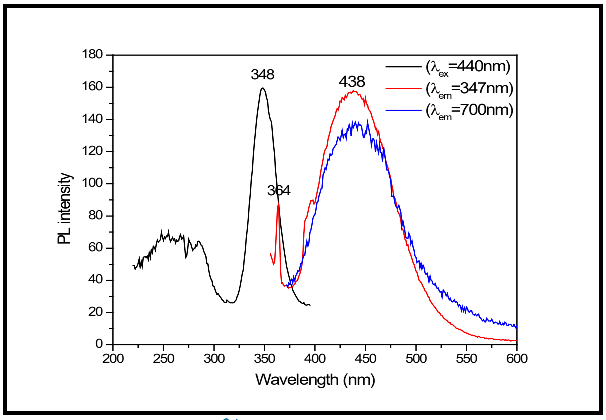


Figure 4. Ce^{3+} (0.5 mol %) Phosphor

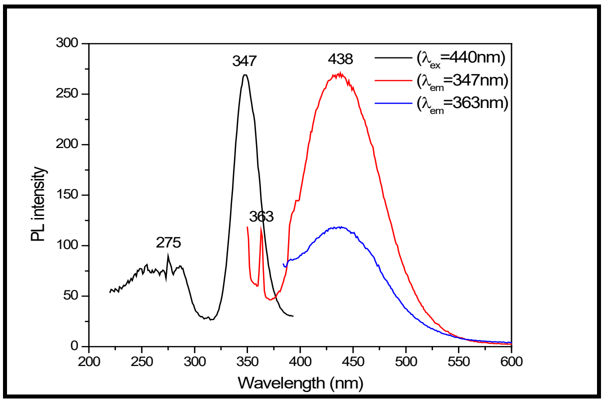


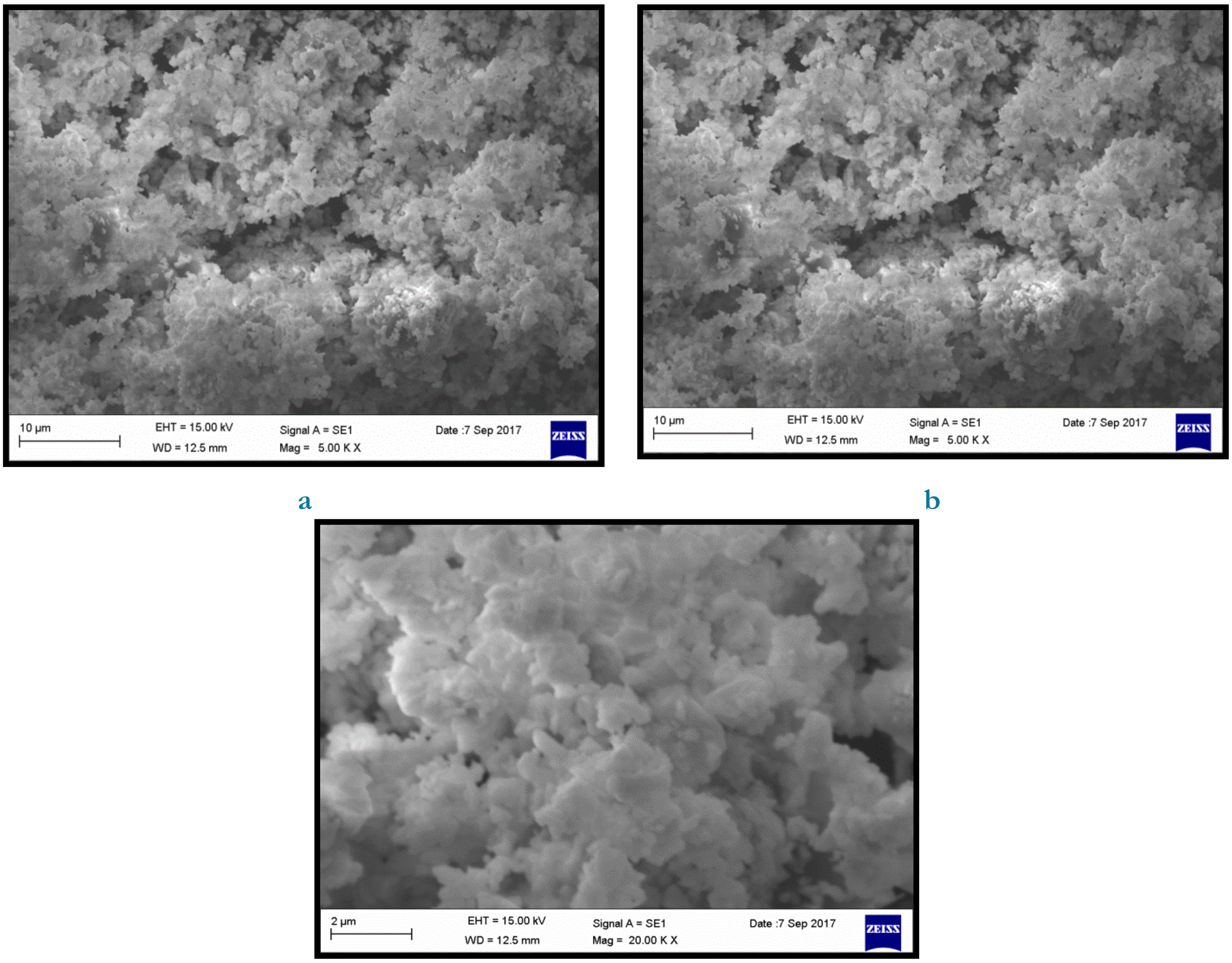
Figure 6. PLE & PL Spectrum of Gd_2SiO_5: Ce^{3+} (2.5mol %) Phosphor

Table 2. Emission Wavelength vs Emission Intensity

S. No	Name of the Phosphor	Emission intensity of 438nm peak under	
		λ_{ex}=347nm	λ_{ex}=700nm
1	Gd_2SiO_4: Ce^{3+} (0.1mol %)	130	120
2	Gd_2SiO_4: Ce^{3+} (0.5 mol %)	160	140
3	Gd_2SiO_4: Ce^{3+} (2.0mol %)	225	200
4	Gd_2SiO_4: Ce^{3+} (2.5 mol %)	275	--

SEM study

Figure 7 (a,b,c) shows the SEM images of Ce^{3+} doped Gd_2SiO_5 phosphor with different concentrations and different resolutions. It is observed that from the SEM images of Ce^{3+} doped Gd_2SiO_5 phosphors particles are highly agglomerated with irregular size shape distribution look bunch of the flowers (Rao, Babu, & Murthy, 2022), and also just like as cutting of the cauliflower flakes. The particle sizes are in the size range is 2-10μm is seen.

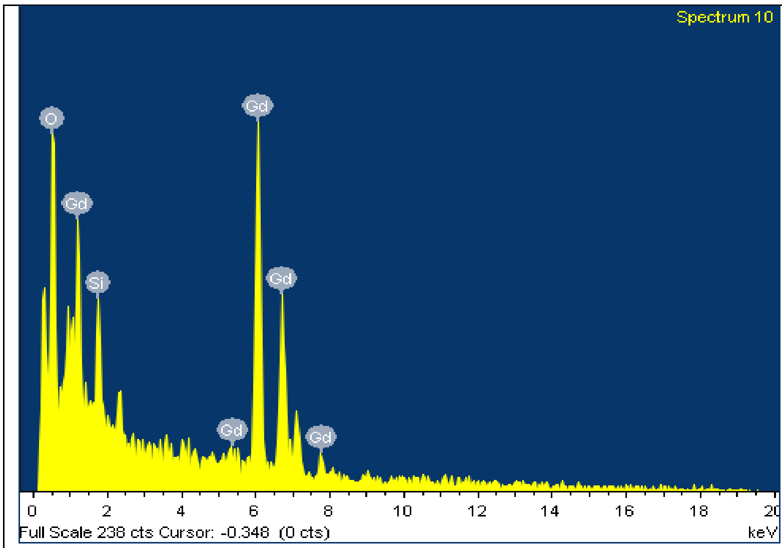


a b c

Figure 7 (a,b,c). SEMIimages of Gd_2SiO_5: Ce^{3+} phosphor with different concentrations and different resolutions

EDAX analysis of Gd2SiO5: Ce3+ phosphor

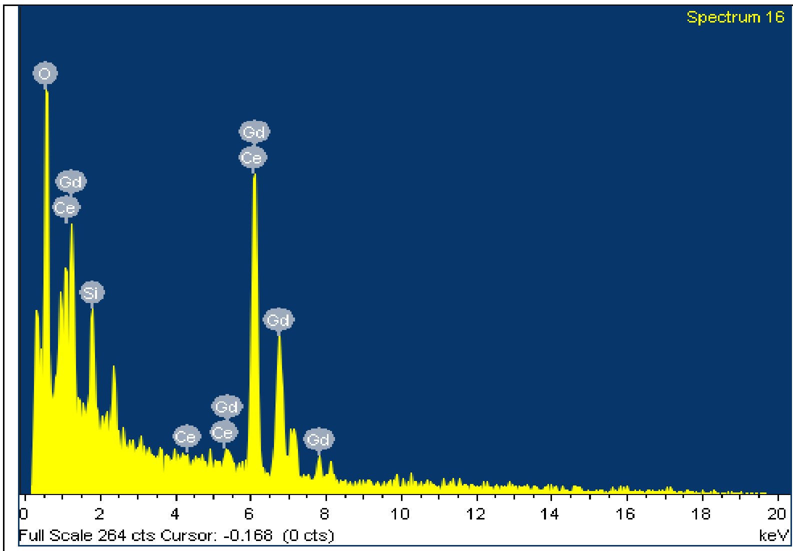
Gd_2SiO_5: Ce^{3+} phosphor subjected to another optical property which is "Energy Dispersive through X-ray Elemental Analysis" (EDAX). Figure. 8 and 9 are the electron images of EDAX analysis of Gd_2SiO_5 base phosphor and Ce^{3+} doped Gd_2SiO_5 phosphor, and the table containing the element, weight %, 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 Ce^{3+} ion, as well as Oxygen, Si, and Gd of various percentages, are seen which are compared with the calculations made while preparing the phosphors (Rao, & Murthy, 2020). 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 %
O K	22.77	68.69
Si K	5.38	9.25
Gd L	71.85	22.05
Totals	**100.00**	

Figure 8. Electron image of the Gd_2SiO_5: Ce^{3+} phosphor



Spectrum processing:
Peaks possibly omitted: 0.266, 2.312 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
Ce CeO2 1-Jun-1999 12:00 AM
Gd GdF3 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
O K	27.86	74.02
Si K	5.20	7.87
Ce L	0.65	0.20
Gd L	66.29	17.92
Totals	**100.00**	

Figure 9. Electron image of the Gd_2SiO_5:Ce^{3+} phosphor

Conclusions

From the XRD studies the phosphor it may be majority is in single phase, since the sintering temperature required for silicate phosphor is around 1300°C. This may be the reason many peaks are observed in the XRD pattern of prepared Gd_2SiO_5: Base phosphor and Gd_2SiO_5: Ce^{3+} (0.5mol %) phosphors.

From the PL studies the excitation spectra were recorded by monitoring 440nm wavelength.

From PL emission spectra is found very good broad peak at 438nm is due to transition $^5D_2 \rightarrow {}^7F_0$ with energy 2.6572ev.

It is also observed that the Ce^{3+} ion concentration increases the emission at 438nm is gradually increases and the 700nm excitation gives the emission around 440nm nearly.

Therefore, it is concluded this phosphor with less concentration Ce^{3+} ion may be a good blue emitting phosphor when excited with 350nm.

It is also concluded the high concentration of Ce^{3+} ion gives rise very good blue emission when excited with 350nm is a good LED material when excited with nUV LED chip (350nm).

It is concluded from all the EDAX figures and tables the dopant Ce^{3+} ion, 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.

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