Luminescent characterization of CaMgSiO₄:Dy³⁺ phosphor for white light emitting diodes

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Abstract. Different concentration of Dy³⁺ doped calcium magnesium silicate (CMS) phosphors are synthesized via solid state synthesis (SSS) method at high temperature. The structural properties are analyzed by X-ray diffraction (XRD). The surface microstructures are confirmed by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectra. The vibrational properties of the synthesized phosphor are carried out using fourier transform infrared (FT-IR) spectra. The luminescence properties are explained in terms of photoluminescence (PL) and thermoluminescence (TL) characteristics. The PL spectra showed maximum emission intensity peaking at 484 and 578 nm, which are attributed to the ⁴F₉/₂ → ⁶H₁₅/₂ and ⁴F₉/₂ → ⁶H₁₃/₂ transitions of Dy³⁺ ion respectively. The PL properties of the prepared phosphors are carried out at room temperature. The maximum PL intensity occurs at 0.5 mol% of doping concentration of Dy³⁺ ions due to concentration quenching. The glow peak and TL parameters of the prepared phosphors are computed by means of peak shape method. The CIE color co-ordinates are originated (x = 0.3263, y = 0.3451) and correlated color temperature (CCT) are determined to be 5769 K. The results indicate that the prepared phosphor produces cool light in the white region.

1. Introduction

In recent years, research on different rare earths (REs) activated compounds have recognized widespread interest owing to their thermally stability, structural diversity, larger band gap, higher elemental stability, low expenditure and environmental individuality [1-3]. The investigation on silicate phosphor matrix is appropriate to substitute conventional light source in the present years. Silicate based phosphor materials with different REs activated have been enormous interest due to their various applications in field of solid state lighting. In the field of lighting technology, these phosphors can be employed as white light emitting diodes (WLEDs), display devices, optical memories, rewritable copy papers, smart windows and photo-switches [4-6]. It is well known that the YAG:Ce³⁺ is a phosphor emitted white light and BaMgAl₁₀O₁₇:Eu²⁺ is phosphor emitted blue light which is available commercially [1]. However these phosphor matrix have the low color rendering index (CRI) and a less luminous efficiency [7-8]. Subsequently it is essential to develop the single rare earth ion doped phosphor matrix by simple preparation method having high efficiency, less electricity consumption, low preparation and production cost. To produce white light, dysprosium (Dy³⁺) ion is...
used as adopant in various host matrix because it produces emission in the blue and yellow region of the visible spectrum. The blue region wavelength (470 nm-500 nm) and yellow region (570 nm-600 nm) are mainly attributed to transition $^4F_{9/2} \rightarrow ^6H_{15/2}$ and $^4F_{9/2} \rightarrow ^6H_{13/2}$ respectively [9].

Calcium Magnesium Silicate (CaMgSiO₄) is a useful for solid state lighting as a luminescent materials with excellent structural and optical properties. Blasse et al. [10] and Bhatkar et al. [11] have synthesized and reported the luminescence properties of CaMgSiO₄:Eu²⁺ phosphor. The two emission bands occurred at 446 and 524 nm were observed in their investigation and the emission spectrum dominated by the spectral band at 524 nm. The photoluminescence (PL) behavior of CaMgSiO₄ phosphors doped with Eu³⁺ were also studied and reported by Li et al. [12]. These phosphors showed an strong red emission from the $^5D_0 \rightarrow ^7F_j$ manifold transitions of Eu³⁺, while the Eu²⁺-doped phosphors showed an extremely weak emission peaked at 475 nm due to the $4f^65d^1 \rightarrow 4f^7$ transition of Eu²⁺. The luminescent characteristics of CaMgSiO₄ phosphors doped with Dy³⁺ ions, have not been investigated systematically yet, which were fascinated to us for the preparation and characterization of phosphor.

In the present investigation, un-doped CaMgSiO₄ and CaMgSiO₄ doped with Dy³⁺ ion were synthesized by solid state synthesis (SSS) method. The phase identification, morphology, photoluminescence, thermoluminescence and colorimetric properties were investigated for optimum dopant concentration.

2. Experimental section

2.1 Synthesis

The phosphor CaMgSiO₄:Dy³⁺ were prepared using solid-state synthesis (SSS) method at high temperature. The high purity of starting reagents CaCO₃ (99.9%), MgO (99%), SiO₂ (99.9%) and Dy₂O₃ (99.99%) were used for preparation of sample. First, the reagents are taken in stoichiometric amounts mixed by hand-grinding for 2 hour in an agate mortar. The mixture was placed in crucible and heated at 1050 °C for 5 h in high temperature furnace to obtain the desired product. The heating and the cooling rate of furnace were fixed at 10 °C min⁻¹. Further, the obtained mixtures were reground in fine powder and used for further characterization. The following chemical reaction takes place during solid state synthesis process

$$\text{CaCO}_3 + \text{MgO} + \text{SiO}_2 \xrightarrow{1050^\circ C} \text{CaMgSiO}_4 + \text{CO}_2 \uparrow$$

$$\text{CaCO}_3 + \text{MgO} + \text{SiO}_2 + \text{Dy}_2\text{O}_3 \xrightarrow{1050^\circ C} \text{CaMgSiO}_4: \text{Dy}^{3+} + \text{CO}_2 \uparrow$$

2.2 Characterization

The phase identification and structure of the prepared phosphor CaMgSiO₄: Dy³⁺ was analyzed by Powder X-ray diffraction (XRD, 40 kV and 30 Ma, Cu Ka target, scanning step 0.001, PANalytical 3 kW X'pert Powder – Multifunctional X-ray Diffractrometer) and the data were collected in the diffraction angle 2θ range from 10° to 60°. The surface morphology of powder was carried out by using scanning electron microscopy (ZEISS-EVO 60 m) and the elemental composition was quantified by energy dispersive X-ray spectrometer coupled with an Oxford Inca. The vibrational properties of the sample were performed by Fourier transform infrared (FTIR) spectroscopy. The photoluminescence (PL) spectra were obtained on a Shimadzu Spectrofluorophotometer (RF model 1009I) with a spectral resolution slit width of 3.0 nm. Thermoluminescence (TL) glow curve were also recorded using 1009I TL reader (Nucleonics, Hyderabad) after the sample exposed UV with 254 nm for 10 min.

3. Results and Discussion

3.1. X-ray Diffraction (XRD) Analysis

In order to determine the phase composition, purity and crystal structure of the as-prepared phosphor, XRD analysis was carried out. Figure 1 depicts the typical XRD patterns of the undoped and Dy³⁺ ion doped CaMgSiO₄. All the reflection planes observed in sample were matched with the JCPDS data file.
From the XRD pattern of the sample, we can deduce that dopant ions Dy\(^{3+}\) were expected to occupy the Ca\(^{2+}\) sites in the CaMgSiO\(_4\) host matrix due to the close radii and identical valence of the ions. CaMgSiO\(_4\) has an orthorhombic structure with space group Pnma and its unit cell volume V = 338.42Å\(^3\). The lattice parameters of refined values of CaMgSiO\(_4\) are found as; a = 11.0510 Å, b = 6.3640 Å, c = 4.8120 Å, α = β = γ = 90° and Z = 4, which signifies the proper preparation of the sample. The peaks at 24.60, 28.10, 30.65, 33.82, 34.83 and 50.44 are indexed the reflection planes of (111), (020), (301), (311), (121) and (222) respectively. Due to maximum diffraction intensity, the reflection plane (311) is used to calculate the crystallite size of the sample. The crystallite sizes (D) of samples can be calculated using Scherrer’s Formula [13]:

\[
D = \frac{K\lambda}{\beta \cos \theta}
\]

where K is a Scherrer constant (taken as 0.94), λ = 1.5418 Å is wavelength of X-rays, β is half maxima line width and θ is the diffraction angle. The crystallite sizes of host and Dy\(^{3+}\) doped sample CaMgSiO\(_4\) were calculated to be as 52.34 nm and 63.62 nm respectively.

![Figure 1. XRD patterns of (a) CaMgSiO\(_4\) and (b) CaMgSiO\(_4\) : Dy\(^{3+}\) (0.5 mol%) phosphors.](image)

3.2 Surface Morphology

The morphologies of the prepared samples were investigated by SEM images. Figure 2 represents the SEM images of undoped and Dy\(^{3+}\) doped sample, respectively. It is noticed from figure 2, the particles in undoped sample shows compact and irregular shape. On the other hand Dy\(^{3+}\) doped sample having particles more clear and uniform size, which may be due to that the surface energy distribution of sample is uneven, resulting in abnormal growth of crystals in certain crystal, leading to the...
agglomerate of particles. From the images, it is clear that the approximate size of the particles is in micrometer range which is in favour of its applications in the field of solid state lighting.

![Figure 2. SEM micrographs of (a) un-doped and (b) CaMgSiO$_4$: Dy$^{3+}$ (0.5 mol%) phosphor.](image)

3.3 Elemental Analysis

To verify the elemental composition and distribution of elements in the sample, EDX spectra were recorded and are shown in figure 3. It is found that the phosphors are composed of Ca, Mg, Si, O and Dy which are displayed in spectra in the form of peaks. No extra peaks are detected during the observation of EDX profile. The percentage of the elements in synthesized phosphor are tabulated in Table 1.

![Figure 3. EDX profile of (a) Un-doped (b) CaMgSiO$_4$: Dy$^{3+}$(0.5 mol%) phosphor.](image)

**Table 1.** Elemental percentages of CaMgSiO$_4$ and CaMgSiO$_4$: Dy$^{3+}$ phosphor.

| S.No. | Standard     | Elements | Weight % | Atomic% |
|-------|--------------|----------|----------|---------|
| 1     | SiO$_2$      | O K      | 55.91    | 70.70   |
| 2     | MgO          | Mg K     | 13.80    | 11.48   |
| 3     | SiO$_2$      | Si K     | 11.70    | 8.43    |
| 4     | CaWollastonite| Ca L     | 18.59    | 9.39    |
|       |              |          | Total 100.00 | 100.00  |
3.4 FTIR analysis

The FTIR spectrum of CaMgSiO₄ for the 4000-400 cm⁻¹ spectral region is given in figure 4. It is known form the literature that this spectrum is typical silicates. The most intense complex band at 964 cm⁻¹ is assigned is the asymmetric stretching modes of the external Si-O-Si groups. The band at 588 cm⁻¹ to the vibrational mode of bending. The band around 1265 cm⁻¹ band may also be assigned to Ca-O bending vibrations. Mg-O bending is responsible for peak at 903 cm⁻¹ due to asymmetric stretching. According to Jiang et al. Ca²⁺ is preferred for tetrahedral sites rather than Mg²⁺ because of the larger radius of Ca²⁺ than Mg²⁺. When Ca²⁺ is located in tetrahedral sites, Ca-O bonds are exceedingly covalent in nature and dopant Dy³⁺ ions occupy the site created by Ca²⁺ owing to having similar ionic radii [14]. This might create deformation in the lattice resulting in 1514 and 1649 cm⁻¹ vibration modes assigned to vibration in Ca²⁺ and Mg²⁺ ions respectively. The broad peak centered at 3414 cm⁻¹ is visible because of stretching of O-H which supports the presence of moisture in the sample.

3.5 Photoluminescence (PL) studies

Figure 5 presents photoluminescence excitation (PLE) spectrum of the as-prepared CaMgSiO₄: Dy³⁺ (0.5 mol%) phosphor monitored at wavelength 577 nm ascribed to transition (⁴F₉/₂ → ⁶H₁₃/₂). The sample shows broad excitation band from 340 to 360 nm and an intense band from 380 to 400 nm with a maximum at 384 nm transition (⁴H₅/₂ → ⁴I₇/₂) due to the 4f-4f transition of the Dy³⁺ ions. Upon
excitation at 384 nm, the emission spectrum of CaMgSiO$_4$: Dy$^{3+}$ of the sample is shown in figure 6. It consists of the characteristic transition between Dy$^{3+}$ levels. The emission spectrum exhibits main two groups of emission peaking at 484 and 578 nm, which are assigned to the $^4$F$_{9/2} \rightarrow ^6$H$_{15/2}$ and $^4$F$_{9/2} \rightarrow ^6$H$_{13/2}$ transitions of Dy$^{3+}$ ion respectively. Obviously, the emission spectrum were dominated by the $^4$F$_{9/2} \rightarrow ^6$H$_{13/2}$ transition of the Dy$^{3+}$, which is due to an electric-dipole-allowed transition and hypersensitive to the environment [15].

In order to show the effect of doping concentration on PL luminescence properties, a series of CaMgSiO$_4$: Dy$^{3+}$ (0.1, 0.2, 0.5, 1, 2 mol%) phosphors were prepared. Figure 7 shows the dependence of PL intensity on dopant concentration of Dy$^{3+}$ ion. When the doping concentration of Dy$^{3+}$ increases, the PL intensity increases gradually and reaches a maximum at 0.5 mol% of Dy$^{3+}$.
ion. With further increasing of Dy\(^{3+}\) concentration, the emission intensity begins to decrease due to concentration quenching. According to the Dexter's energy transfer theory [16], concentration quenching is mainly caused by the non-radiative energy migration among the Dy\(^{3+}\) ions at the higher concentration.

Figure 7. Variation of PL intensity with doping concentration of Dy\(^{3+}\) ion

3.6 CIE co-ordinates of CaMgSiO\(_4\): Dy\(^{3+}\) phosphor

Figure 8 depicts the CIE diagram of synthesized CaMgSiO\(_4\): Dy\(^{3+}\) phosphors. The chromaticity coordinate for the CaMgSiO\(_4\): Dy\(^{3+}\) (0.5 mol\%) phosphor was originated to be (x= 0.3263, y= 0.3451) which is close to the NTSC standard white light (0.33, 0.33). This parameter was estimated as per the emission spectra in CaMgSiO\(_4\): Dy\(^{3+}\) (\(\lambda_{ex}= 384\) nm). To further estimate the temperature of the light emission, the CCT was calculated using McCamy formula [17] and found to be 5769 K. Since the CaMgSiO\(_4\): Dy\(^{3+}\) phosphor can display a bright white emission with good CIE chromaticity coordinate. The CCT of CaMgSiO\(_4\): Dy\(^{3+}\) phosphor lies above 5000 K which indicates that the prepared phosphor produces cool light in the white region.
3.7 Thermoluminescence (TL) characteristics

Figure 9 shows the TL glow curves of CaMgSiO$_4$: Dy$^{3+}$ phosphor materials exposed to UV excitation source at room temperature. The TL data were collected in the temperature range 50 to 300 °C with linear heating rate (LHR) of 5°C/s. The peak temperature remains almost same for all dopant concentration. In contrast to PL results, the TL intensity of CaMgSiO$_4$: Dy$^{3+}$ was found to decrease with Dy contents. From the results presented here it is evident that TL of CaMgSiO$_4$: Dy$^{3+}$ phosphor shows good enhancement in TL intensity up to the concentration of 0.5 mol% of Dy$^{3+}$ subsequently it starts decreasing. The decrease in TL intensity may possibly be attributed to concentration quenching. The optimal TL intensity was observed at 0.5 mol% of doping concentration Dy$^{3+}$ ion.

Figure 8. CIE diagram of CaMgSiO$_4$: Dy$^{3+}$(0.5 mol%) phosphor.

Figure 9. TL glow curves for CaMgSiO$_4$: Dy$^{3+}$ phosphor.
To further evaluate the symmetry factor, trap depth and frequency factor, applying peak shape method proposed by Chen [18]. The value of trap depth energy ($E$) and frequency factor ($s$) for optimum concentration of dopant Dy (0.5 mol%) are presented in Table 2.

Table 2. Values of E (eV) and s (s$^{-1}$) for CaMgSiO$_4$: Dy$^{3+}$ phosphor.

| Dopant (mol%) | $T_1$(°C) | $T_2$(°C) | $T_M$(°C) | $\mu_g$ | $E$ (eV) | $s$ (s$^{-1}$) |
|---------------|------------|------------|------------|---------|----------|-----------|
| 0.5           | 114.11     | 242.78     | 176.21     | 0.52    | 0.39     | $1.50 \times 10^5$ |

4. Conclusion

In summary, CaMgSiO$_4$: Dy$^{3+}$ phosphors were synthesized via solid state synthesis method. The XRD spectra showed that the phosphors were matched with reported JCPDS data and the grain size of the phosphor in micron range and uniformity better. From the results of SEM and photoluminescence intensity, the property of the light-emitting substance was improved with the increasing of concentration. The as-obtained CaMgSiO$_4$: Dy$^{3+}$ phosphors showed higher PL emission intensity at 484 and 578 nm. These peaks were attributed to electronic transition $^4F_{9/2} \rightarrow ^6H_{15/2}$ and $^4F_{9/2} \rightarrow ^6H_{13/2}$ of Dy$^{3+}$ respectively. The optimal doping concentration of Dy$^{3+}$ was obtained at 0.5 mol%. The chromaticity coordinate for the synthesized phosphor was found to be ($x = 0.3263$, $y = 0.3451$) and CCT was calculated and found to be 5769 K which produces cool light in the white region. The shape factor and trap depth energy were found 0.52 and 0.39 eV respectively. These results indicate that synthesized phosphor may be good promising candidate phosphors in the field of solid state lighting.

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