

Structural, Morphological and Luminescence Properties of Dy³⁺ Doped Calcium Magnesium Silicate Solid Materials

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Abstract

The CaMgSiO₄:Dy³⁺ phosphor samples were prepared by high temperature solid state reaction method. X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray (EDX) analysis, fourier transform infrared (FT-IR) spectra were used to characterize the structural characterization and surface morphology of CaMgSiO₄:Dy³⁺ phosphors. The optical properties were presented in terms of photoluminescence (PL), photoluminescence excitation (PLE) spectra. The prepared CaMgSiO₄:Dy³⁺ phosphors show higher PL emission intensity at wavelengths 484 and 578 nm. The photoluminescence (PL) properties of the prepared phosphors were carried out at room temperature. The CaMgSiO₄:Dy³⁺ phosphor exhibits improvement in PL intensity and quenching occurs at 0.5 mol% of doping concentration of Dy³⁺ ions. PL results indicate that the prepared phosphors could be potentially useful for in the field of solid state lighting.

Keywords: CaMgSiO₄: Dy³⁺ Phosphor; Photoluminescence; Solid state reaction method

1. INTRODUCTION

In recent years, research on different lanthanides (Ln) - activated materials has established extensive attention due to their structural diversity, thermally stability, larger band gap, higher chemical stability, low cost and eco-friendly characteristics [1-3]. Research on silicate based phosphor materials are suitable to replace conventional light source in the current years. Silicate based phosphor materials with different lanthanides (Ln) activated have been great interest due to their many applications in field of solid state lighting. 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 white light emitting phosphor and commercial available blue phosphor is BaMgAl₁₀O₁₇:Eu²⁺ [1]. But these phosphor materials have the poor color rendering index (CRI) and a less efficiency [7-8]. So it is essential to grow the single doped phosphor materials by simple synthesis technique having high efficiency, less consumption of electricity and low production cost. To generate white light Dy³⁺ ion is used as an activator in many host matrix because it gives emission in the blue and yellow region of the visible spectrum. Dysprosium ions which give the emission line in the blue region wavelength (470 nm-

500 nm) ascribed to transition ⁴F_{9/2}→⁶H_{15/2} and in yellow region wavelength (570 nm- 600 nm) ascribed to transition ⁴F_{9/2}→⁶H_{13/2} [9].

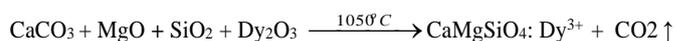
Calcium Magnesium Silicate (CaMgSiO₄) is a useful for inorganic luminescent materials with outstanding structural and optical properties. The luminescence properties of CaMgSiO₄:Eu²⁺ were reported by Blasse et al. [10] and Bhatkar et al. [11]. The two emission bands peaked at 446 and 524 nm were observed in their experiment and the 524 nm band dominated the emission spectrum. The photoluminescence (PL) properties of Eu³⁺ doped CaMgSiO₄ phosphors were also studied by Li et al. [12]. CaMgSiO₄: Eu³⁺ exhibited an intense red emission from the ⁵D₀ →⁷F_J manifold transitions of Eu³⁺, whereas the Eu²⁺-doped phosphors showed an extremely weak emission peaking at 475 nm due to the 4f⁶5d¹→4f⁷ transition of Eu²⁺. but the luminescent characteristics of Dy³⁺ ions doped CaMgSiO₄ phosphors, have not been investigated systematically yet, which were attracted to us for this study.

In this study, CaMgSiO₄ phosphors with Dy³⁺ doping concentrations were synthesized by high temperature solid state reaction method and their structural, morphological and photoluminescence properties were investigated under UV excitation.

2. MATERIALS AND METHODS

2.1 Materials Preparation

The sample CaMgSiO₄:Dy³⁺ investigated in this work were synthesized using solid-state reactions method at high temperature. CaCO₃ (99.9%), MgO (99%), SiO₂ (99.9%) and Dy₂O₃ (99.99%) were used as starting reagents for preparation of sample. These reagents are taken in stoichiometric ratio mixed by hand-grinding for 2 hour in an mortar and pestle, then the sample was placed in crucible and calcined at 1050°C for 5 h in high temperature furnace to obtain the desired phosphor. Boric acid (1 mol%) was mixed as a flux in the sample. The heating and the cooling rate were recorded as 10 °C min⁻¹. In this experiment, the dopant concentration were taken from 0.1 mol% to 2 mol%. The following chemical reaction during solid state reaction method follows



2.2 Analysis Methods

The structures of the phosphor were established by Powder X-ray diffraction (XRD, 40 kV and 30 Ma, Cu K α target, scanning step 0.001, PANalytical 3 kW X'pert Powder – Multifunctional X- ray Diffractometer) and morphology of particles was observed by a ZEISS-EVO 60 m German make scanning electron microscope (SEM) coupled with an Oxford Inca energy dispersive X-ray spectrometer. The photoluminescence (PL) spectra were observed at RT on a Shimadzu Spectrofluorophotometer (RF model 5301 PC) with a spectral resolution slit width of 3.0 nm.

3. RESULTS AND DISCUSSION

3.1. Structural Analysis

In order to analyze the structural properties of the phosphors, X-ray diffraction (XRD) was performed to determine the phase composition, purity and crystal structure of the as-prepared phosphors. Figure 1 depicts the XRD patterns of CaMgSiO $_4$: Dy $^{3+}$ which calcined at 1050 °C for 5 h and the ICSD Code No.(202281). No other phases of the peak were detected, which indicates that the prepared samples were single phase. 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 a orthorhombic structure with space group P nma and its unit cell volume V= 338.42 Å 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, $\alpha = \beta = \gamma = 90^\circ$ 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) are used to calculate the crystallite size of the sample.

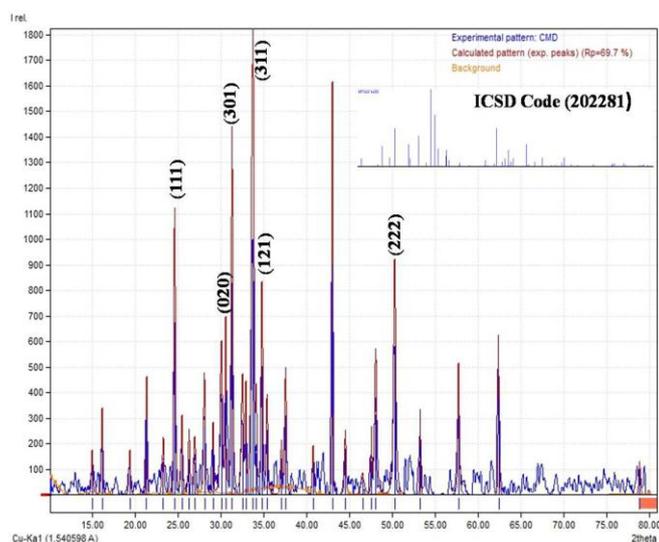


Fig. 1 XRD patterns of CaMgSiO $_4$ phosphors.

The crystallite size (D) of sample in (311) direction was calculated using Debye Scherrer's Formula [13] which is given by equation (1)

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

where K= 0.94 is a Scherer constant, λ the wavelength of radiation, β - the full width at half maxima (FWHM) and θ is the diffraction angle. The crystallite size of sample was calculated to be as 63.62 nm.

3.2 Morphology and EDS Studies

The morphologies of the prepared samples were investigated by SEM images. Figure 2 represents the SEM images of un-doped and Dy $^{3+}$ doped sample, respectively. From figure, we noticed that the samples with Dy $^{3+}$ doped shows smaller particles and more uniform size (Figure 2b). Dy $^{3+}$ un-doped sample shows larger particles and irregular shape, 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 particle. 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. To determine the elemental composition and distribution of element in the sample, an EDX measurement was carried out and the spectrum shown in Figure 3. It is found that the phosphors are composed of Ca, Mg, Si and O. The weight and atomic weightage of the elements in synthesized phosphor are tabulated in Table 1.

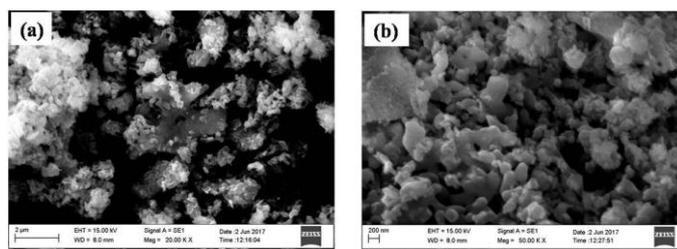


Fig. 2. SEM images of CaMgSiO $_4$ phosphor (a) Un-doped (b) doped with Dy $^{3+}$ (0.5 mol%)

Table 1. Elemental composition of host BaMgSiO $_4$ phosphor

S.No.	Standard	Elements	Weight %	Atomic%
1	SiO $_2$	O K	58.91	74.02
2	MgO	Mg K	7.92	6.55
3	SiO $_2$	Si K	13.02	9.32
4	Wollastonite	Ca L	20.15	10.11
Total			100.00	100.00

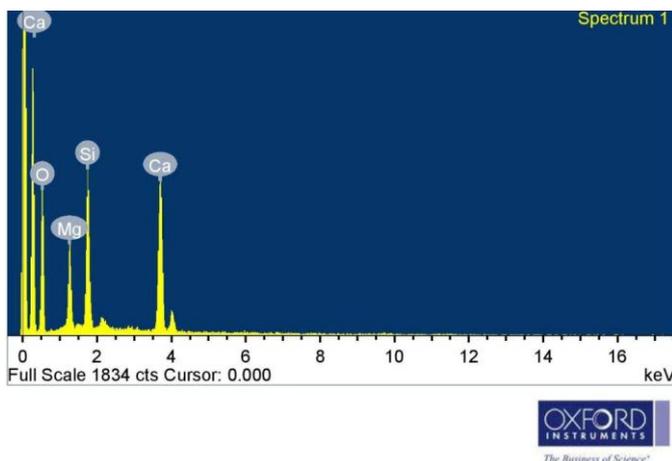


Fig. 3 EDX spectrum of CaMgSiO₄ phosphor.

3.3 Fourier transform infrared (FT-IR) Spectrum of CaMgSiO₄

The FTIR spectrum of CaMgSiO₄ for the 4000-600 cm⁻¹ spectral region is given in Figure 4. It is known from the literature that this spectrum is typical silicates. The most intense complex band at 1042 cm⁻¹ is assigned to the asymmetric stretching modes of the external Si-O-Si groups. The bands at 420, 441, 515, and 580 cm⁻¹ are assigned to the vibrational mode of bending. The band around 710 cm⁻¹ may also be assigned to Ca-O bending vibrations. Mg-O bending is responsible for peak at 851 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 highly covalent in character and dopant Dy³⁺ occupies the site created by Ca²⁺ because of having similar ionic radii [14]. This might create distortion in the lattice resulting in 1445 and 1638 cm⁻¹ vibration modes assigned to vibration in Ca²⁺ and Mg²⁺ ions respectively.

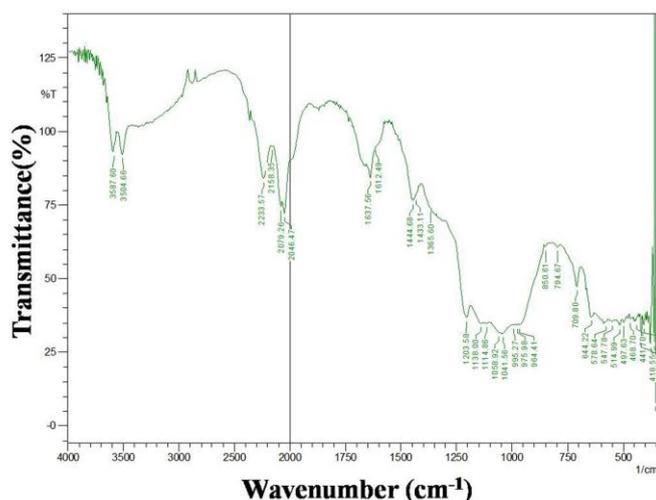


Fig. 4. The FTIR spectrum of CaMgSiO₄ phosphor.

3.5 Photoluminescence (PL) Characteristics

3.5.1 Excitation and Emission Spectrum

In order to study and analyze the PL properties of the as-prepared phosphor, fluorescence spectrofluorophotometer was used to test the material. Figure 5 presents photoluminescence excitation (PLE) spectra of the as-prepared CaMgSiO₄: Dy³⁺ phosphor monitored at wavelength 577 nm ascribed to transition (⁴F_{9/2} → ⁶H_{13/2}). The sample shows broad excitation band from 340 to 360 nm and a intense band from 380 to 400 nm with a maximum at 384 nm transition (⁶H_{15/2} → ⁴I_{13/2}) due to the 4f-4f transition of the Dy³⁺ ions. Upon excitation at 384 nm, the emission spectra of CaMgSiO₄: Dy³⁺ of the sample is shown in Figure 6. It consists of the characteristic transition lines between Dy³⁺ levels. The emission spectrum exhibits main two groups of emission peaking at 484 and 578 nm, which are assigned to the ⁴F_{9/2} → ⁶H_{15/2} and ⁴F_{9/2} → ⁶H_{13/2} transitions of Dy³⁺ respectively. Obviously, the emission spectrum were dominated by the ⁴F_{9/2} → ⁶H_{13/2} (578 nm) transition of the Dy³⁺, which is due to an electric-dipole-allowed transition and hypersensitive to the environment [15].

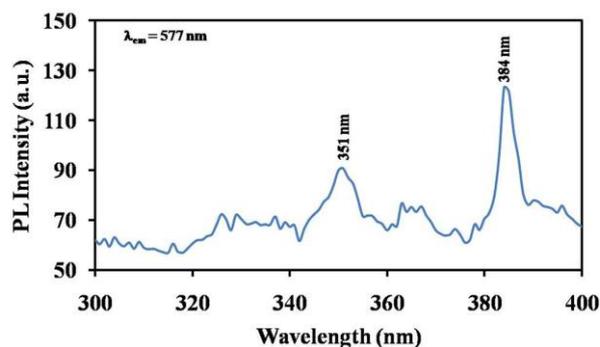


Fig.5 PL excitation spectrum of CaMgSiO₄: Dy³⁺ (0.5 mol%) monitored at λ_{em} = 577 nm.

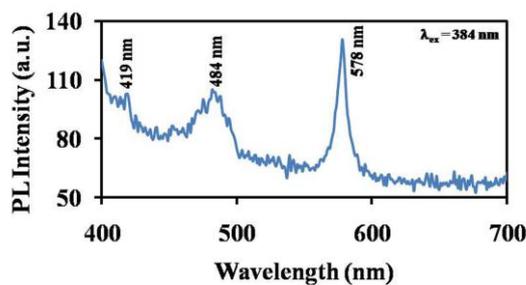


Fig.6 PL emission spectrum of CaMgSiO₄: Dy³⁺ (0.5 mol%) monitored at λ_{ex} = 384 nm.

3.5.2 Effect of Calcination Temperature

Figure 7 depicts the emission spectra of as-prepared sample with the calcinations temperature from 900 °C to 1100 °C. When sample was calcined at 900 °C, the PL intensity remains low. With the increasing of the temperature, the PL intensity enhanced. As the temperature was over 1050 °C, the PL intensity saturated and begins to gradually decrease. When at

1050 °C all the emission peak reaches the maximum. With increases of calcination temperature, the PL intensity increases at first, then gradually decreases. It's because with the increasing of calcination temperature, the degree of crystallinity increases at the same time, and had a uniform particle size. However, when the calcination temperature was too high, the phase was over-burning and liquefaction phenomenon, thus leading the emission peaks luminous intensity decrease. The PL intensity shows that the optimum calcination temperature is 1050 °C.

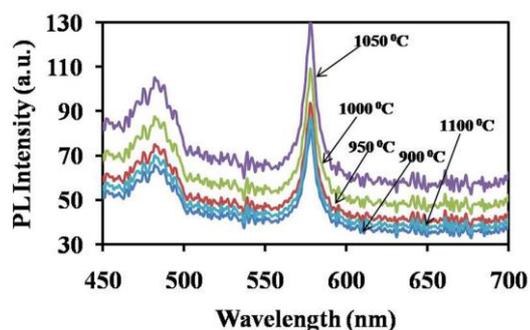


Fig. 7 PL emission spectra of CaMgSiO₄: Dy³⁺ (0.5 mol%) at different calcination temperature

3.5.3 Effect of Calcination Time

Figure 8 represents PL intensity spectra of the sample that we have made with the calcination time of 3 h -7 h. The pattern showed that the samples PL intensity continuously enhances with the increasing of calcination time. Conform that the crystal grow when insulation. But when the calcination time was too long, the phase over-burned and liquefaction phenomenon, leading the emission peaks PL intensity decrease. Therefore, the optimum calcination time is 5 h in this experiment.

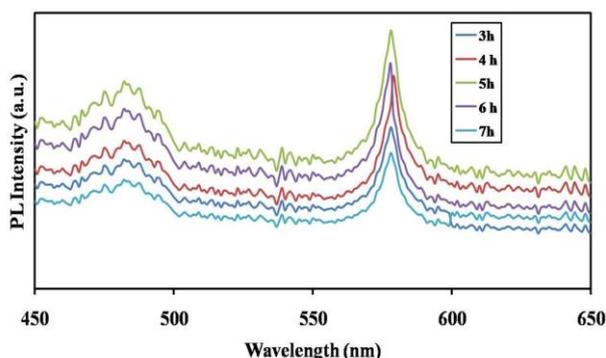


Fig. 8 PL emission spectra of CaMgSiO₄: Dy³⁺ (0.5 mol%) at different calcination time

3.5.4 Concentration Quenching

In order to explore the effect of doping concentration on PL luminescence properties, a series of CaMgSiO₄: Dy³⁺ (0.1, 0.2, 0.5, 1, 2 mol%) phosphors were prepared. Figure 9 shows the PL spectra of CaMgSiO₄: Dy³⁺ with different doping

concentration. The PL emission of the Dy³⁺ increases gradually and reaches a maximum at 0.5 mol%. With further increasing of Dy³⁺ 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 Dy³⁺ ions at the high concentration.

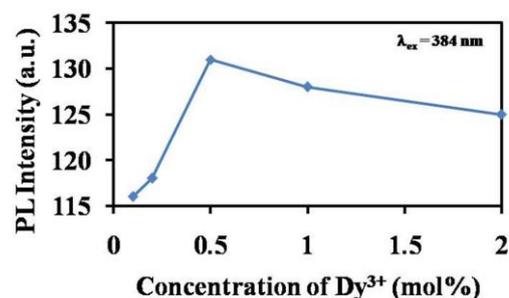


Fig. 9 PL intensity vs. concentration of Dy³⁺ doped in CaMgSiO₄: Dy³⁺ phosphors

4. CONCLUSIONS

The CaMgSiO₄: Dy³⁺ phosphors were synthesized via solid state reaction method. The XRD spectra showed that the phosphors was pure CaMgSiO₄ (ICSD code 202281) and the phosphor was nearly spherical morphology and uniformity better. From the results of SEM and photoluminescence intensity, the property of the light-emitting material was improved with the increasing of temperature. However, when the temperature was too high it will appear crushing grain and larger agglomeration. The optimum sintering temperature of this experiment was 1050 °C. The results of the PL study showed that the best holding time of this experiment was 5 h. The as-obtained CaMgSiO₄: Dy³⁺ phosphors showed higher PL emission intensity (at 484 and 578 nm). These peaks were attributed to electronic transition (⁴F_{9/2} → ⁶H_{15/2} and ⁴F_{9/2} → ⁶H_{13/2}) of Dy³⁺. The optimal doping concentration of Dy³⁺ was observed at 0.5 mol%. These results indicate that synthesized phosphor may be good promising candidate phosphors in the field of solid state lighting.

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