Band Gap Analysis of Ca$_3$MgSi$_2$O$_8$:Dy$^{3+}$ Nanorod Arrays By A Solid State Reaction Method

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Abstract

Present study throws light on solid state synthesis, phase and band properties of a Dy\(^{3+}\) doped Ca\(_3\)MgSi\(_2\)O\(_8\). Crystal phase of the phosphor was characterized by X-ray diffraction (XRD) and surface morphology was crystal size was determined by using scanning electron microscopy (SEM), and transmission electron microscopy (TEM) respectively. To determine the band gap behaviour of the crystal absorption spectra was used, which was further analyzed by using Tauc plot. The band gap is calculated \(\approx 4.5\) eV, which decreases on increasing doping concentration of Dy\(^{3+}\).

Introduction

The versatile structure, physical and chemical properties of calcium magnesium orthosilicate made it very useful for wide range of applications as phosphor applications, biomedical applications, and application in cement industries etc. [1–3]. These compounds are also present in the earth mantle as mineral inclusions [4–6]. It has been reported that the Ca\(_3\)MgSi\(_2\)O\(_8\) crystallizes as merwinite phase with P21/a space group with coordination 4. This structure is more closely packed than that of other possible phases olivine [7]. Merwinite structure was explained as the more stable phase in the upper earth mantle. Stability of merwinite phase of calcium magnesium orthosilicate was explained by Liu. He confirmed that the phase is stable at 1273 K and 20GPa [8]. The merwinite crystal structure consists alternate layer of octahedral MgO\(_6\) and tetrahedral double layer of SiO\(_4\) like an ideal cubic perovskite structure [9].

In this work, Ca\(_3\)MgSi\(_2\)O\(_8\):Dy\(^{3+}\) nanorod arrays have been synthesized by using a solid state reaction method. The crystallographic detail was confirmed by powder X-ray diffraction analysis. Surface morphology and particle size was confirmed by SEM and TEM analysis. FTIR analysis was done to confirm the bonding nature of the crystal. Band structure of the nano rod array was determined by recording the UV-Vis absorption spectra.

Experimental

The Ca\(_3\)MgSi\(_2\)O\(_8\) phosphor with fixed Dy\(^{3+}\) concentration was synthesized by previous described method [7]. It was synthesized by using oxides of each elements magnesium, silicon and dysprosium and carbonate of calcium. All the chemicals were purchased from Sigma-Aldrich and with 99.9% purity. Stoichiometric ratio of all the chemicals were weighed and mixed thoroughly with agate mortar and pestle. The mixture was transferred to a corundum crucible followed by heating at 1250\(^\circ\)C for 5 h. After cooling to room temperature obtained a powdered phosphor sample. (Scheme 1)

Results And Discussion

3.1 Structural and morphological studies:
Prepared phosphor was characterized for its phase, bonding behaviour, morphology by XRD, FTIR, SEM and TEM analysis. Figure 1 shows the XRD pattern of Ca₃MgSi₂O₈:Dy³⁺ phosphors recorded by Bruker D8 advanced X-ray powder diffractomete. The analysis revealed that the prepared sample is single merwinite phase. The peaks of XRD pattern are well matched with JCPDS card No 25–0161 XRD pattern of the prepared crystal reveals that it has merwinite phase with C2/c space group with the unit cell parameters having values a = 9.344 Å, b = 5.308Å and c = 13.290 Å edge length, bond angles α = 90°, β = 92.072(7)°, γ = 90°, and unit cell volume V = 658.7Å³. The crystal has two sites for Ca²⁺ ion, four sites for O ion and one site for Mg²⁺ and Si ion. The intense charateristic peaks confirms that the sample is crystalline in nature. The average crystal size was calculated by using classical Debye Scherrer formula $D = \frac{k\lambda}{\beta \cos \theta}$ and average particle size was obtained around 56 nm.

Figure 2 shows the surface morphology of the phosphor. The close observation reveals that the phosphor has smooth surface morphology with irregular arrangement of particles. The phosphor has heavy growth of grains. The large grain size in the micrograph is attributed due to the higher temerature profile invloved during the synthesis process, which corresponses the diffusion mechanism responsible for large grain size.

Figure 3 shows the TEM image of the phosphor, which shows proper array of nano rod formation of the particle and the particle size obtained is well matched with the particle size obtained by XRD data.

Figure 4 shows the FTIR spectra of the sample. The band observed at 3455 cm⁻¹ was due to the stretching mode of the hydrogen-bonded OH⁻ ions; the band at 1680 cm⁻¹ arises from intercalated H₂O. The asymmetric stretching of (CO₃²⁻) carbonates can be observed in the range of 1920–1625 cm.

**Band Structure of the sample:**

The band gap estimation is one of the important characterization of a material. The band structure of the prepared phosphor with variable dopent concentration was studied by recording the absorption spectra of the sample with variable Dy³⁺ concentration. It was observed that the absorption wavelength shifts towards the higher wavelength side with increasing the Dy³⁺ concentration. The absorption wavelength was obtained at 250 nm, 254 nm, 258 nm and 263 nm for 0.5 mol% to 1.25 mol% of Dy³⁺ concentration respectively (Fig. 5). The absorption edge of the sample represents the band gap of the crystal which was determined by using Tauc plot (Fig. 6) [10]. The extra plotted straight line along the sharp edge of the curve intecepts the energy axis at a point which gives the estimation of the band gap and the value of optical band gap. The bad gap energy values were found 4.6 eV, 4.43 eV and 4.35 eV and 4.25 eV for 0.5 mol% − 1.25 mol% Dy³⁺ respectively (Fig. 6). It was obsevres that the band gap value decreases with increasing the Dy³⁺ concenration. The decrease in band gap is due to the increase in carrier concentration with increasing dopent concentration [11].

**Conclusion**
In conclusion the Ca$_3$MgSi$_2$O$_8$: Dy$^{3+}$ phosphor was successfully synthesized by solid state reaction process. The synthesized phosphor were nonuniform and had array like structure with two different symmetry sites of Ca$^{2+}$. The optical properties show a significant change in band gap of the Ca$_3$MgSi$_2$O$_8$: Dy$^{3+}$ phosphor. The band gap of Ca$_3$MgSi$_2$O$_8$: Dy$^{3+}$ is obtained $\approx$ 4.6eV, which decreases on increasing doping concentration of Dy$^{3+}$ into Ca$_3$MgSi$_2$O$_8$ upto 4.25 eV.

**Declarations**

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**Figures**
Figure 1

X-ray diffraction pattern of Ca$_3$MgSi$_2$O$_8$:Dy$^{3+}$ phosphors
Figure 2

Scanning electron microscope Ca3MgSi2O8:Dy3+ phosphors
Figure 3

Transmission electron microscope image of Ca3MgSi2O8:Dy3+ phosphors
Figure 4

FTIR pattern of Ca$_3$MgSi$_2$O$_8$:Dy$^3+$ phosphors
Figure 5

Absorption spectra of Dy3+ doped Ca3MgSi2O8 phosphor (A) Dy3+ = 0.5 (B) Dy3+ = 1.0 mol % (C) Dy3+ = 0.75 mol% (D) Dy3+ = 1.25 mol%
Figure 6

Tauc plot of Dy3+ (0.5%-1.25%) doped Ca3MgSi2O8 phosphor

Supplementary Files

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- Scheme1.png