



UV Emission In $\text{Li}_2\text{CaMg}(\text{SO}_4)_3:\text{Ce}$ Phosphor For Phototherapy

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ABSTRACT

A series of $\text{Li}_2\text{Ca}(\text{SO}_4)_2$ and $\text{Li}_2\text{CaMg}(\text{SO}_4)_3$ phosphors doped with Ce^{3+} ions were prepared using the wet chemical method. X-Ray diffraction and SEM micrographs studies were used to determine their phase formation, purity and morphology. The photoluminescence (PL) excitation spectra indicate that the $\text{Li}_2\text{CaMg}(\text{SO}_4)_3:\text{Ce}^{3+}$ phosphors can be effectively excited by ultraviolet (293nm) light. The photoluminescence (PL) properties of the as-prepared phosphors were investigated. Two strong resolved peaks in emission spectra are observed at 309 and 329 nm in the UV range, which are assigned to the 5d-4f transition of Ce^{3+} ions. The concentration quenching effect for Ce^{3+} was found at the optimum doping concentration of 2 mol%. The presence of Mg in the host affects the photoluminescence characteristics of $\text{Li}_2\text{Ca}_{(2-x)}\text{Mg}_x(\text{SO}_4)_3:\text{Ce}_{(2\text{m}\%)}$ were observed.

Keywords: $\text{Li}_2\text{CaMg}(\text{SO}_4)_3$; XRD; SEM; Photoluminescence; Wet chemical method.

I. INTRODUCTION

Rare earth-doped luminescent materials play an integral role in modern life, due to their tremendous range of applications in scintillations, colour displays, fluorescent lamps, intensifying screens, dosimetry of ionizing radiations, etc. [1–3]. Their chemical composition, degree of structural disorder, defects and the presence of dopants/impurities have notable influence on the electronic and optical properties of luminescent materials. The luminescent properties of Ce^{3+} doped compounds have been of considerable interest in recent years [4–6]. Ce^{3+} has a very simple electron configuration, there is only one electron in the 4f shell and it is an excellent system for studying the behaviour of one-electron 4f and 5d states in different environments [7]. Ce^{3+} exhibits host dependent 4f–5d absorption and 5d–4f emission due to the strong interaction between its 5d states and the crystal lattice. The ground 4f1 electronic configuration of Ce^{3+} is split by a spin–orbit interaction into two sublevels, $2F_{5/2}$ and $2F_{7/2}$, with an energy interval of $\sim 2000\text{ cm}^{-1}$ [8,9]. The 4f–5d transitions are electric dipole allowed transitions and, because there is only one single electron in the 5d configuration, repulsion between 5d electrons is

absent [10]. As an important family of luminescent materials, sulfates have attracted intense attention. In particular, researchers have concentrated on the sulfate series of phosphors with an ABSO_4 structure, where A is a monovalent cation (Li^+ , Na^+ , K^+ , Rb^+ , and Cs^+) and B is a divalent cation (Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+}) due to their large band gap, along with the high absorption of SO_4^{3-} in UV region. The role of rare earths is very important considering the wide variety of prospective applications. In this regard, studies have reported on the luminescence of Ce^{3+} in mix sulfate phosphors [11]. In most cases, cerium-activated phosphors emit in the UV or blue spectral range and a broad band is usually observed. However, the crystal field of the host lattice shifts the Ce^{3+} emission to longer wavelengths. One of the applications of Ce^{3+} emission is in phototherapy, wherein the UV or blue part of the light spectrum is used in the treatment of several skin diseases [12, 13].

In the present work, synthesis and photoluminescence characterization of Ce doped $\text{Li}_2\text{Ca}(\text{SO}_4)_2$ and $\text{Li}_2\text{CaMg}(\text{SO}_4)_3$ are reported. These materials are prepared by wet chemical synthesis method. The XRD

technique shows the crystalline nature of the prepared material. The photoluminescence properties of the as-prepared phosphors were investigated and the Ce^{3+} ions in these hosts were found to give broadband emission in the UV range. The presence of Mg in the host affects the photoluminescence characteristics of $\text{Li}_2\text{CaMg}(\text{SO}_4)_2$:Ce.

II. METHODS AND MATERIAL

The wet chemical method seems to be the simplest and most effective synthesis route compared with all the other traditional methods commonly adopted, to prepare Ce^{3+} doped $\text{Li}_2\text{Ca}(\text{SO}_4)_2$ and $\text{Li}_2\text{CaMg}(\text{SO}_4)_3$ sulfate phosphors. The starting materials were weighed in a stoichiometric ratio using an analytical balance with an accuracy of 0.0001 g. In this method lithium sulfate, calcium sulfate and magnesium sulfate (AR grade of 99.99% purity) were taken in separate beakers and dissolved in double distilled de-ionized water. Similarly dopant material $\text{Ce}_2(\text{SO}_4)_3$ (AR grade of 99.99% purity – E. Merck) was also dissolved in double distilled de-ionized water in a separate beaker. Then all the transparent solutions were added together to obtain a homogeneous solution of $\text{Li}_2\text{CaMg}(\text{SO}_4)_2$:Ce. The resultant solution was stirred using a magnetic stirrer for >30 min. It was confirmed that no undissolved constituents were left behind in the solution and all the salts were completely dissolved in water. A series of Ce^{3+} doped phosphors was prepared in different concentrations (1, 2, 3 and 5 mol %) in the host matrix. The sample in its powder form was obtained by evaporating at 80 °C for 8 h. The dried sample was then quenched at 700°C for 1 hr in carbon atmosphere, where the redox reaction occurs. The resultant powder was crushed to fine particles using an agate pestle and mortar. This powder was used as a phosphor in further study. By using the above same procedure $\text{Li}_2\text{Ca}(\text{SO}_4)_3$:Ce phosphors were prepared.

The XRD technique was used in order to identify the product and check their crystallinity. The phase composition and phase structure were measured by X-ray diffraction (XRD) pattern using a PAN-analytical diffractometer with Cu K α radiation ($\lambda=1.5405$ AU) operating at 40Kv, 30mA. The XRD data were collected in a 2θ range from 10 to 80°, with the continuous scan mode. The morphology and microstructure were characterized with JEOL, JSM-6360LV SEM

environmental scanning electron microscope (SEM). The PL excitation and emission spectra were recorded using a RF-5301PC spectrofluorophotometer fitted with a sensitive photomultiplier tube with a 150W ‘xenon flash lamp’ as an excitation source. The excitation and emission spectra were recorded using a spectral slit width of 1.5nm with high sensitivity. All the measurements were carried out at room temperature.

III. RESULTS AND DISCUSSION

A. Phase identification and morphology

The X-ray diffraction pattern of $\text{Li}_2\text{CaMg}(\text{SO}_4)_3$ phosphor is shown in Figure 1. The XRD pattern did not show the presence of the any constituent's or traces of ammonium phosphates, which is indirect evidence of the formation of the desired compound. The results showed the final product was in homogeneous and crystalline form. All the peaks are due to $\text{Li}_2\text{CaMg}(\text{SO}_4)_3$ single phase and no impurity peaks were observed. However, some new diffraction peaks also emerge, which are characteristic diffraction peaks for the prepared samples, but cannot be attributed to any known compounds. The slow scan was performed in the 2θ range from 10–70°. Figure 2(A and B) shows the SEM images of $\text{Li}_2\text{CaMg}(\text{SO}_4)_3$ phosphor calcined at 700°C. It shows that all the samples have solid rectangular morphology and micro level size. Moreover, the phosphor particles with smooth surface were observed. The SEM images show crystallites of nearly uniform size of about 1 μm (Figure 2A).

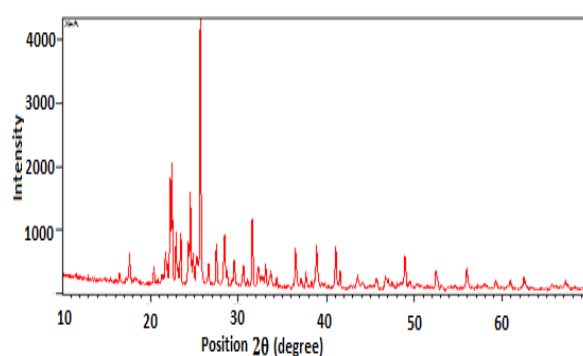


Figure 1. X- ray diffraction patterns of $\text{Li}_2\text{CaMg}(\text{SO}_4)_3$

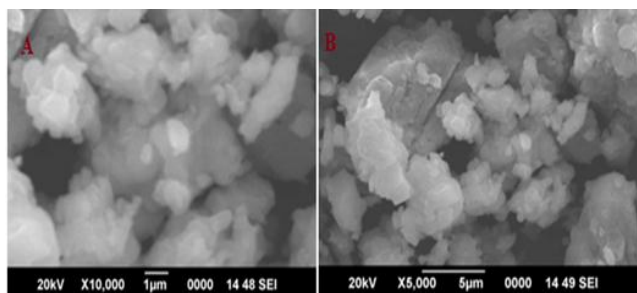


Figure 2. SEM images of $\text{Li}_2\text{CaMg}(\text{SO}_4)_3$

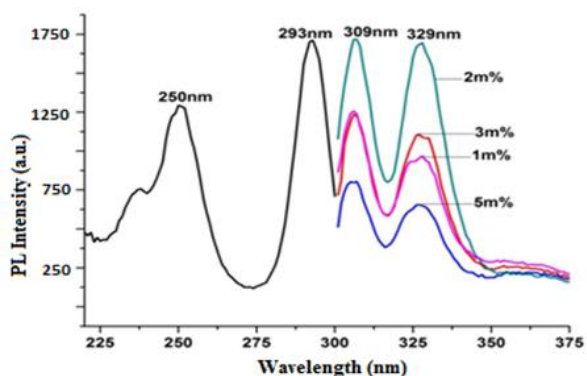


Figure 3. PL emission spectra of $\text{Li}_2\text{Ca}_2(\text{SO}_4)_3:\text{xCe}$ phosphor monitored at 293nm excitation.

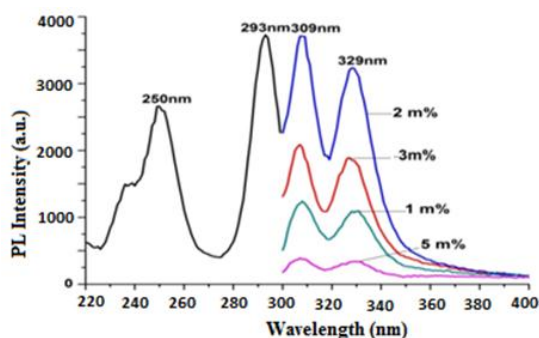


Figure 4. PL emission spectra of $\text{Li}_2\text{CaMg}(\text{SO}_4)_3:\text{xCe}$ phosphor monitored at 293nm excitation.

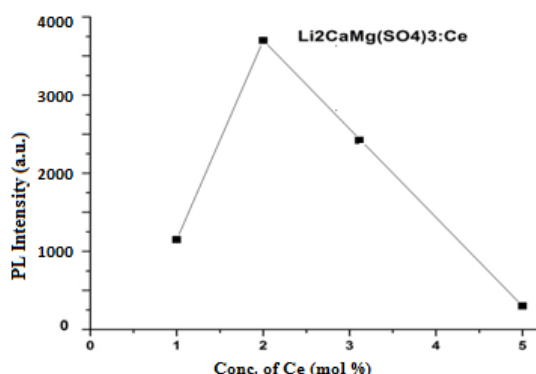


Figure 5. Variation in PL intensity with the conc. of

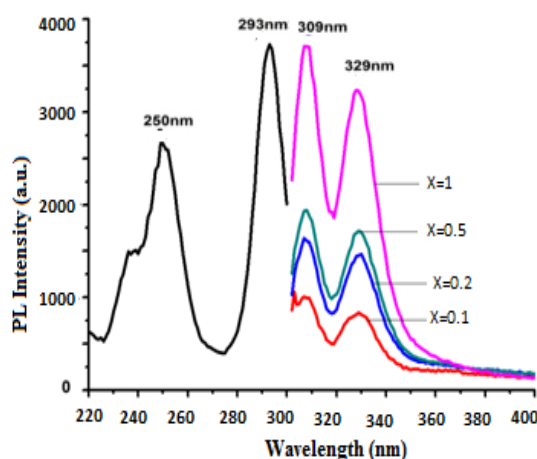


Figure 6. PL spectra of $\text{Li}_2\text{Ca}_{(2-x)}\text{Mg}_x(\text{SO}_4)_3:\text{Ce}_{(2\text{m}\%)}$
 Ce^{3+} ions in $\text{Li}_2\text{CaMg}(\text{SO}_4)_3:\text{Ce}$

B. PL study of $\text{Li}_2\text{CaMg}(\text{SO}_4)_3:\text{Ce}^{3+}$

The ultraviolet (UV) excitation spectrum for LCMS: Ce at 300 K, shown in Figure 3, Two principal centers in excitation spectra are observed one of them is at around 250 nm and another at around 293 nm in Ce^{3+} ion. This could be assigned to the $4f \rightarrow 5d$ transition of Ce^{3+} ions in solids is parity allowed electric dipole transition ($f - d$) and has large oscillator strength and produces efficient broadband luminescence. Where $4f$ is the lowest excited charge transfer state of the Ce^{3+} ion and $5d$ is the molecular orbital of the surrounding ligand. The emission spectra of Ce^{3+} doped LCMS for different concentrations of Ce^{3+} excited at 293 nm is shown in Figure 4. Two strong resolved peaks in emission spectra are observed at 309 and 329 nm, which are assigned to the $5d-4f$ transition of Ce^{3+} ions. The double humped emission spectrum is characteristic of Ce^{3+} and could be attributed to $5d-4f$ ($^2F_{5/2}$, $^2F_{5/2}$) transitions. The centre of gravity of the crystal-field split $5d$ configuration is influenced by the host lattice anion. The excitation to this band is observed around 293nm. The emission of the Ce^{3+} doped sample is dominated by the $^4f_0 \rightarrow ^4f_1(^2F_{5/2})$ transition of Ce^{3+} (329 nm). The PL emission intensity gradually increases with increasing Ce^{3+} concentration in the range from 1 to 5mol %. Optimum PL intensity was observed for a Ce^{3+} ion concentration of 2 mol%, beyond which, the fluorescence intensity tends to quench. It is also noticed that the peak positions of the emission bands have not changed. These phosphors are emitting in the UV region. It is observed that the peak positions of the emission bands having same profile in $\text{Li}_2\text{Ca}(\text{SO}_4)_3:\text{Ce}$ also (Figure 3), but with Lower PL intensity as compared to $\text{Li}_2\text{CaMg}(\text{SO}_4)_3:\text{Ce}$.

Figure5 shows the variation in the PL intensity of $\text{Li}_2\text{CaMg}(\text{SO}_4)_3:\text{xCe}$ phosphors with Ce^{3+} doping concentration. In Figure6, PL of a series of NCMS: Ce^{3+} (0.5m %) sample with varying values of Mg^{2+} ($x = 0.1 \leq x \leq 1$) is shown and effect of doped Dy^{3+} concentration on the emission intensity was investigated. With increasing (x) content of Mg, the intensity peak increased and maximum intensity was observed for $x = 1$. No quenching could be observed in Mg content range. It shows that the PL characteristics of the material is better for $x = 1$ than other values of x in the sample. The results suggest that NCMS: Ce^{3+} may serve as a promising material for use as a UV emitting lamp phosphor.

IV. CONCLUSION

Polycrystalline Ce^{3+} doped $\text{Li}_2\text{CaMg}(\text{SO}_4)_3$ sulfate phosphors were successfully prepared via wet chemical synthesis method. The luminescence properties of these sulfate phosphors are being reported for the first time. The structural properties of these phosphors were investigated by XRD. PL emission spectra for the as-prepared phosphors were observed in the UV region. Under 293 nm UV excitation, $\text{Li}_2\text{CaMg}(\text{SO}_4)_3:\text{Ce}$ phosphors displayed efficient broadband emission in the UV region with maximum intensity at 309 nm. The optical properties of these phosphors led to the conclusion that they may serve as promising materials for use as lamp phosphors in the UV region and may be useful for UV emitting lamp phosphor in the application of phototherapy.

V. ACKNOWLEDGEMENT

Author SPP is thankful to management of the Institution KNM, Nagpur and SAIF, Punjab University, Chandigarh for providing useful facilities of the instrumentation, SHIMADZU Spectrofluorophotometer (RF-5301PC) and PAN-analytical diffractometer; JEOL, JSM-6360LV SEM respectively.

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