



Luminescence in $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2 : \text{Eu}^{2+}$

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ABSTRACT

In this paper $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Eu}^{2+}$ prepared through solid state reaction. Obtained compound characterized by photoluminescence emission and excitation and to confirm the crystal structure X ray diffraction pattern is recorded

Keywords : Photoluminescence, Chlorosilicate, Eu^{2+}

I. INTRODUCTION

During recent years, scientists have turned their attention towards chlorosilicates to get good chemical, physical and thermal stability. Silicate based phosphors are widely used in display devices. There are some problems with synthesis and long term use of silicates. Silicates need temperatures higher than 1000 C, even up to 1400 C for synthesis. . They may get converted to glassy form. At high synthesis temperatures they can also react with low cost crucible materials such as porcelain and china clay.

For tuning the emission and excitation spectra, several substitutions have been tried. E.g. the substitution of Ca by Sr and Cl by F enhanced the green emission [1] in $\text{Ca}_8\text{SiO}_4\text{Cl}_2:\text{Eu}^{2+}$. In the same host Zhao et al [2] used sulfur co-doping for obtaining red emission. In $\text{Sr}_4\text{Si}_3\text{O}_8\text{Cl}_4$, the emission bands of the phosphors on uv excitation at room temperature shifted to longer wavelength with increasing Ca^{2+} content[3]. Some intermediate phases have been explored in more details as a result of such efforts.

In this paper $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2$ is prepared and photoluminescence characteristic are studied.

Though this compound was known for quite some time, it attracted attention of phosphor researchers as late as 1987ⁱ when Ye et al noted its good chemical and thermal stability. In 1992, PL of Eu^{2+} was reportedⁱⁱ. Lin et studied emission of Ce^{3+} which could also act as a sensitizer for Eu^{2+} ^{iii iv}. 427 nm emission of Ce^{3+} shows good overlap with Eu^{2+} excitation. Owing to green emission and near UV/blue excitation.

$\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Eu}^{2+}$ in solid-state lighting (SSL) was also proposed^v. Luminescence of several rare earths such as Ce^{3+} ^{vi}, Eu^{2+} ^{vii viii}, Dy^{3+} ^{ix x} was studied with the objective of finding phosphors for solid state lighting.

Long lasting luminescence in $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2 : \text{Eu}^{2+}, \text{Nd}^{3+}$ was first reported by Wang et al^{xi} and due to better stability of this phosphor compared to the commercial $\text{SrAl}_2\text{O}_4:\text{Eu}$, the interest continues to date^{xii}.

Preparation

$\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Eu}^{2+}$ is prepared through solid state reaction. Ingredients used were CaCO_3 , MgO , CaCl_2 ,

Eu_2O_3 and silicic acid ($\text{SiO}_2 \cdot 1.5 \text{H}_2\text{O}$). The mixtures of corresponding raw materials with a mole ratio of $\text{CaCO}_3 : \text{MgO} : \text{SiO}_2 : \text{CaCl}_2 = 7 : 1 : 4 : 1.5$. All constituents in the required proportions were mixed together. The mixture on thoroughly grinding was transferred to furnace for heating at 700 C for 4 hrs. The powder so obtained was reduced at 900 C in a covered crucible under burning atmosphere provided by burning charcoal to convert Eu^{3+} to Eu^{2+} .

II. RESULT AND DISCUSSION

Fig 1 shows XRD pattern of $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2$. It shows an excellent match with ICDD file 41-0248. $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2$ has a cubic crystal structure with space group of Fd-3m .

PL spectra of Eu^{2+} activated $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2$ are shown in Fig. 2. Various Eu^{2+} concentrations ranging between 0.1-2.0 mol % were tried. Maximum emission was obtained for 1 mol.%. These results only are shown. Earlier, Guo et al [viii] also observed maximum emission for 0.9 mol.%. We observed an emission band around 505 nm. In the excitation spectrum three broad overlapping bands can be seen around 275, 332 and 367 nm, besides a shoulder around 430 nm. The positions of these bands are in good agreement with those reported earlier [xi]. In earlier works, a weak emission band had been observed around 426 nm [xi].

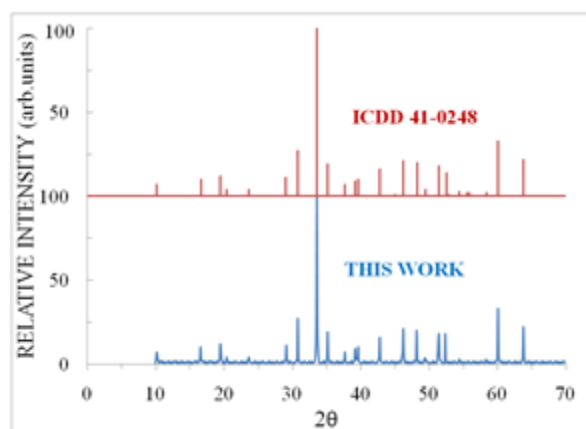


Figure 1: XRD pattern for $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2$ compared with ICDD data

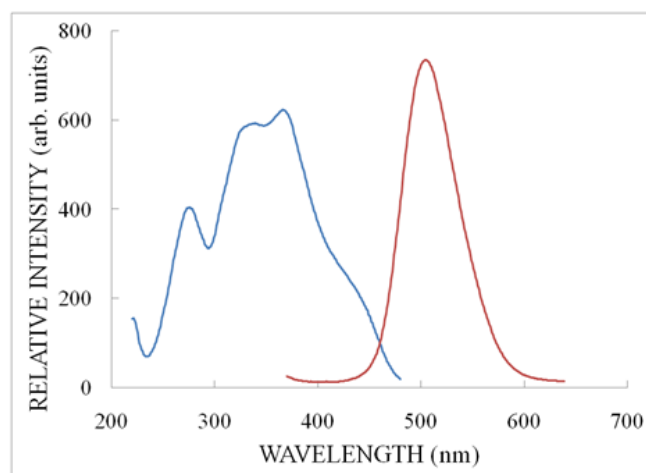


Figure 2: Photoluminescence spectra of $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Eu}^{2+}$

- a> Emission for 387 nm excitation
- b> Excitation for 500 nm emission

It is therefore expected that Eu^{2+} ions occupy the Ca sites. Eu^{2+} ions at Ca2 sites are responsible for emission at 505 nm, while those at Ca1 sites lead to blue emission peaking around 426 nm. Among other things, the site occupancy will also depend on the method of preparation and thermal treatments received during the synthesis. Apparently, in the procedure we have followed, all the Eu^{2+} ions are occupying Ca2 sites.

that for Ca (CN = 6 and 8) are 1.14 and 1.26, respectively. It is therefore expected that Eu^{2+} ions occupy the Ca sites. Eu^{2+} ions at Ca2 sites are responsible for emission at 505 nm, while those at Ca1 sites lead to blue emission peaking around 426 nm. Among other things, the site occupancy will also depend on the method of preparation and thermal treatments received during the synthesis. Apparently, in the procedure we have followed, all the Eu^{2+} ions are occupying Ca2 sites.

Fig 3 shows TL emission spectrum for $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Eu}^{2+}$ exposed to UV radiations. The sample was held at 100 C and the emission spectra

were recorded using Ocean Optics model USB 2000 spectrometer. As it employs CCD array as a detector, the spectra could be recorded in a fraction of second. PL is recorded at room temperature while TL emission spectrum at 100 C therefore the emission maximum is at slightly longer wavelengths (510 nm) and the peak is somewhat broader. Also, the resolution of USB 2000 spectrometer (10 nm) is not as good as that of spectrofluorimeter (1 nm).

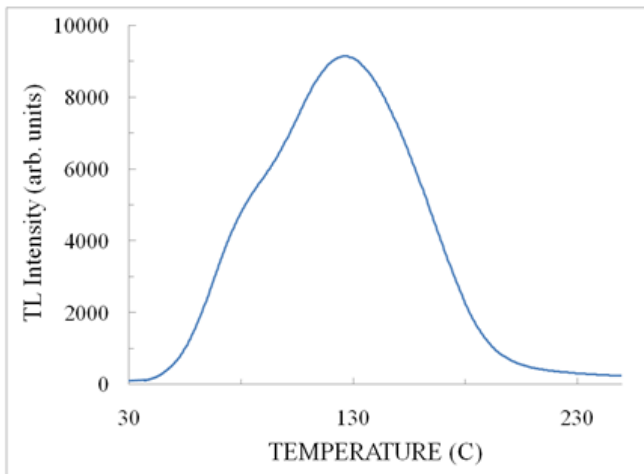


Figure 1: TL Glow Curve of $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Eu}^{2+}$

III. CONCLUSION

$\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Eu}^{2+}$ prepared through solid state reaction. XRD pattern of obtained compound is good agreement with ICDD data. Single emission band observed at visible range at 505nm. with excitation around 270 and 330 nm. Our results are in good agreement with reported work. First time we have recorded glow curve and the compound exhibited glow peak at 100C.

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