

Photoluminescence, trap states and thermoluminescence decay process study of $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ phosphor

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Abstract. Europium and dysprosium-doped calcium magnesium silicate powder with different concentrations of dysprosium were synthesized using solid-state reaction. The Fourier transform infrared (FT-IR) spectra confirmed the proper preparation of the sample. The prepared phosphors were characterized using photoluminescence excitation and emission spectra. Prominent green colour emission was obtained under ultraviolet excitation. The thermoluminescence glow curves of the samples were measured at various delay times. With increased delay time, the intensity of the thermoluminescence peak decays and the position of the thermoluminescence peak shifts towards higher temperature, indicating the considerable retrapping associated with general order kinetics.

Keywords. Photoluminescence; thermoluminescence; kinetic data; persistence luminescence.

1. Introduction

$\text{M}_2\text{MgSi}_2\text{O}_7$ (Sr, Ca) doped with Eu^{2+} and Dy^{3+} phosphor has shown quite good long lasting behaviour. Silicate phosphors have few advantages over previously developed aluminate long lasting phosphors on chemical stability, heat stability, lower cost and varied luminescence colour from blue to yellow (Shi *et al* 2007). It is clear that the Eu^{2+} ion acts as the luminescent centre and it is known that some rare earth (R^{3+}) co-dopants enhance the persistent luminescence obtained with Eu^{2+} doping alone. The exact role of the co-dopants and that of other lattice defects is uncertain, but the R^{3+} ions have been suggested to trap holes or electrons or just to create/modify defects due to charge compensation. The development and tailoring of new persistent luminescence (PLUM) materials would be greatly facilitated, if the mechanisms were known (Carlson *et al* 2009; Wu *et al* 2011a). Alkali earth silicates are useful luminescent hosts with high physical and chemical (Jiang *et al* 2004). $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ is known as an efficient phosphor with good stability, which also shows green emission with great stability and persistency (Yen and Weber 2004). In this paper, $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ phosphors with the different concentration ratios of dopant and co-dopant were prepared using high temperature solid-state reaction. The photoluminescence (PL) studies were done to identify the long lasting phosphor. Thermoluminescence (TL) glow curve of the phosphor were measured after various delay times to estimate the persistency of the phosphor.

2. Materials and method

Phosphor $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ powder of different concentration ratios of Eu/Dy was prepared by solid-state reaction. All the materials like SiO_2 , CaCO_3 , MgO , Dy_2O_3 and Eu_2O_3 were thoroughly ground for ~1 h in a mortar, pre-sintered at 900 °C and fired at 1200 °C for ~2 h, with H_3BO_3 (1.6 mol%) used as flux (Yen and Weber 2004). Phosphor was irradiated with a 365 nm UV source for thermoluminescence (TL) measurements. By the use of a Nucleonix (Hyderabad, India) I1009 TLD reader thermoluminescence glow curves were recorded at room temperature. Spectrofluorophotometer (Shimadzu, RF-5301 PC) using the xenon lamp as excitation source was used for the measurement of photoluminescence (PL) excitation and emission spectra. FT-IR studies were done at IIT Mumbai using instrument of Make: Bruker, Germany.

3. Results and discussion

3.1 FT-IR analysis

Figure 1 shows FT-IR spectra of the sample. In the presented spectrum, the absorption bands of silicate groups were clearly evident. The intense band centred at 977 cm^{-1} was assigned to the Si-O-Si asymmetric stretch, the bands at 940 and 848 cm^{-1} to the Si-O symmetric stretch and the bands at 582, 512 and 484 cm^{-1} to the Si-O-Si vibrational mode of bending. The band, centred at 582, 512, 636 and 1016 cm^{-1} can be assigned to the presence

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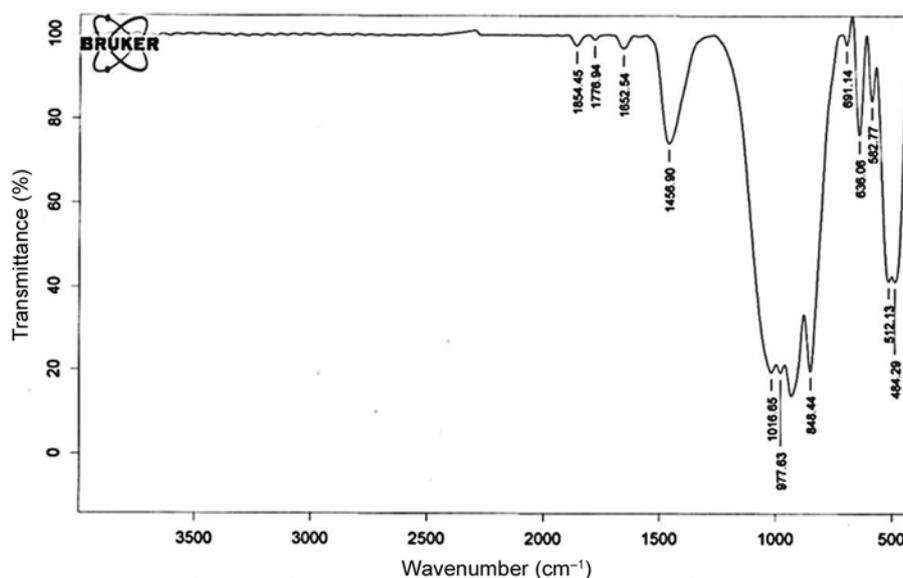


Figure 1. FT-IR spectra of $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$.

of SiO_4 group. In the prepared sample at around 691 cm^{-1} there is the band due to Si-O bending vibrations. Furthermore, in keeping with Gou *et al* (2005), the absorption bands positioned at 1016, 977 and 512 cm^{-1} , respectively, could be ascribed to the presence of SiO_4 group. The band centred at 1777 and 1854 cm^{-1} can be attributed to the presence of small amount of calcite. The free CO_3^{2-} ion has a $D3h$ symmetry (trigonal planar) and its spectrum is dominated by the band (asymmetric stretching) at 1456 cm^{-1} . The presence of carbonate bands is attributed to a carbonation process of the material as a consequence of the high calcite content in the prepared sample. The obtained results are in a good correspondence with those, published by Martinez *et al* (2000) for CaO-SiO₂ sol-gel glasses. According to Jiang *et al* (2003) Ca^{2+} is preferred for tetrahedral sites rather than Mg^{2+} , because of the larger radius of Ca^{2+} than Mg^{2+} . When Ca^{2+} is located in tetrahedral sites, Ca-O bonds are highly covalent in character and dopant Eu^{2+} occupies the site created by Ca^{2+} , because of similar ionic radii. This might create distortion in the lattice, resulting in 1456 and 1652 cm^{-1} vibration modes assigned to vibration in Ca^{2+} and Mg^{2+} ions, respectively (Salim *et al* 2009).

3.2 Photoluminescence

Photoluminescence excitation and emission spectra of $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Eu}, \text{Dy}$ phosphors prepared are shown in figure 2. Excitation spectra was monitored at a wavelength of 515 nm , which shows prominent peaks at 395 nm . Emission spectra were identical in shape and the bands differ only in intensities. Broad emission spectra centered at 510 nm (green region) observed under the ultraviolet excitation of 395 nm correspond to the Eu^{2+}

emission, arising due to transitions from sublevels of $4f^65d^1$ configuration to $^8S_{7/2}$ level of the $4f^7$ configuration, but with Eu^{2+} occupying different lattice sites. Since, the crystal field can greatly affect the $4f^65d^1$ electron states of Eu^{2+} , it suggests that the crystal field is not changed much with the compositional variation (Pawde *et al* 2012; Pawade and Dhoble 2013).

Jiang *et al* (2003) reported that the possible sites for incorporating Eu^{2+} in $\text{Ca}_2\text{MgSi}_2\text{O}_7$ lattice are Ca^{2+} sites, or the Mg^{2+} sites or the Si^{4+} sites. Mg^{2+} (0.58 \AA), and Si^{4+} sites (0.26 \AA) are small, but Ca^{2+} (1.12 \AA) is equal to the size of Eu^{2+} (1.12 \AA). So, Eu^{2+} ions hardly incorporate into tetrahedral $[\text{MgO}_4]$ and $[\text{SiO}_4]$, and only incorporate into $[\text{CaO}_8]$ anions complexes in $\text{Ca}_2\text{MgSi}_2\text{O}_7$. From figure 2, it can be seen that only an emission band is observed at 510 nm in the emission spectra of $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}/\text{Dy}^{3+}$ phosphor. Co-dopant Dy^{3+} ion assists in electron trapping and supplies more trap levels, which increases the decay time of the phosphor (Aitasalo *et al* 2006). PL emission spectra shown displays maximum intensity when $\text{Eu}:\text{Dy}$ was $1:3$, after it starts decreasing in PL intensity. The pairing or coagulation of activator ions may have created quenching centres, which seems to be the reason for decrease in intensity after a specific concentration of Dy^{3+} ions (Tabei and Shionoya 1975).

3.3 Thermoluminescence kinetic parameters

Thermoluminescence is one of the possible ways to estimate the trap states of the material. TL parameter of the thermal activation energy, E which is related to the trap depth is obtained using peak shape method (Chen 1969; Chen 1983; Yuan 2004; Wang and Wang 2007; Gökçe *et al* 2009).

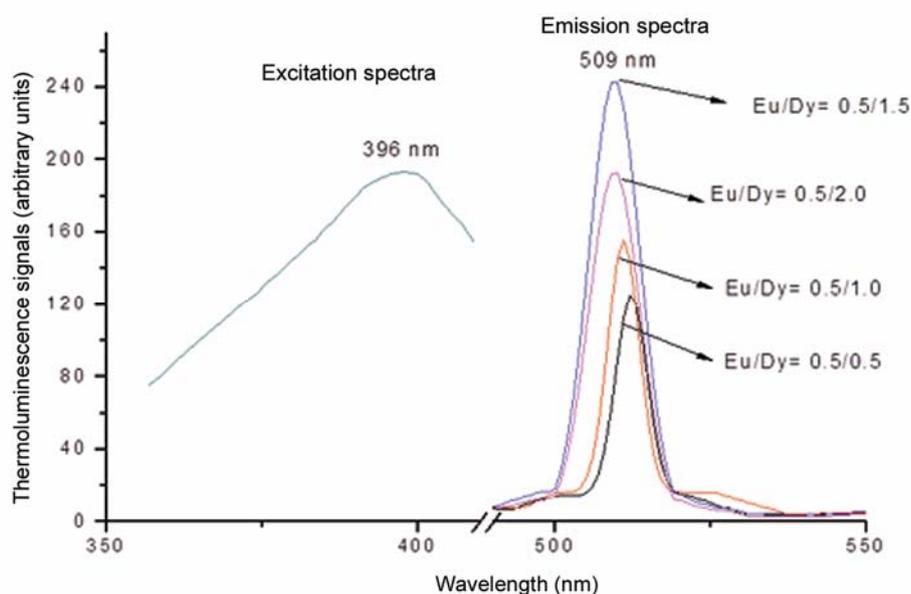


Figure 2. Excitation and emission spectra of $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ ($\text{Eu}/\text{Dy} = 0.5/1.5$).

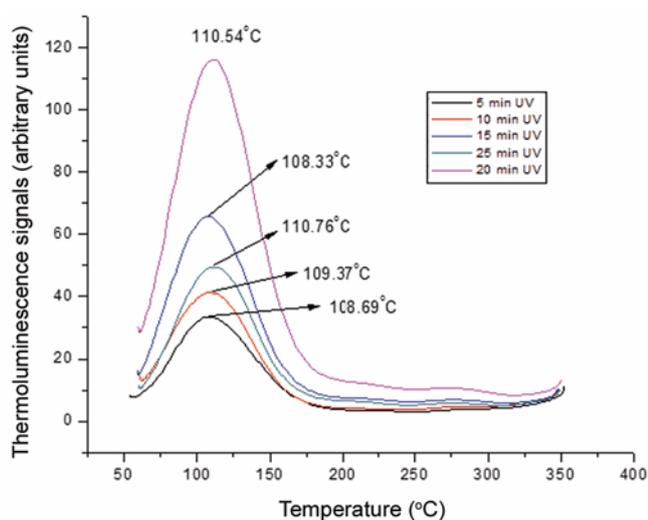


Figure 3. TL glow curve of $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ after different UV exposures.

Figure 3 shows TL glow curve of the sample for different UV exposures and it is shown that the thermoluminescence signals increases with increasing UV exposure. Thermoluminescence signals are maximum for 20 min of UV exposure, after that it starts to decrease. The charge carrier density may have been increasing with increasing UV exposure, but after 20 min of UV exposure. Trap level may have started to destroy, resulting in decrease in thermoluminescence signals.

The TL glow curves (figures 3 and 4) exhibit a broad peak because of the transition between ground and excited energy levels of the dopant Eu^{2+} . The relationship

between the frequency factor 's' and the depth of the trap 'E' is given by the following equation (Pagonis *et al* 2006):

$$\frac{\beta E}{kT_m^2} = s \left[1 + (b-1) \frac{2kT_m}{E} \right] \exp(E/kT_m), \quad (1)$$

where k is the Boltzmann constant, E the trap depth, b the order of kinetics, T_m the temperature of peak position, b the order of kinetics and β the linear heating rate. In this work:

$$\beta = 6.7 \text{ } ^\circ\text{C s}^{-1},$$

$$\omega = \tau + \delta,$$

where δ is the high temperature half width and τ the low temperature half width. The shape factor

$$\mu = \delta/\omega.$$

The value of shape factor varied from 0.49 to 0.54, which indicate the second order kinetics that support the probability of retrapping released charge carriers before recombination. The afterglow of any phosphor is generated by the detrapped carriers which recombine with the opposite carriers in the luminescent centre with a transition, resulting in visible region (Chen and McKeever 1997; Kaur *et al* 2012).

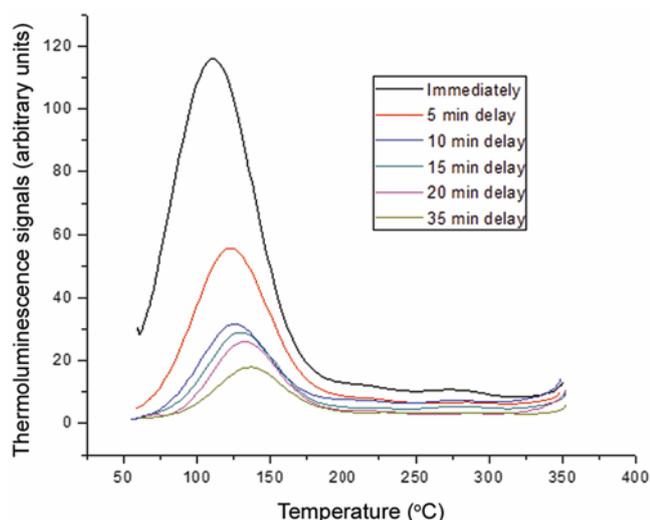
From table 1, it is readily apparent that the effect of different UV exposures in peak temperature and intensity in a phosphor. The shape factor, activation energy and frequency factor are also shown in table 1 (Chen and McKeever 1997; Pagonis *et al* 2006; Kaur *et al* 2012). Activation energy was in the range of 0.56–0.61 eV,

Table 1. Kinetic parameters of $\text{Ca}_2\text{MgSi}_2\text{O}_7 : \text{Eu, Dy}$ after different UV exposure times.

UV (min)	Heating rate ($^{\circ}\text{C s}^{-1}$)	T_1 ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)	T_2 ($^{\circ}\text{C}$)	τ	δ	ω	$\mu = \delta/\omega$	Activation energy (eV)	Frequency factor
5	6.7	73.35	108.69	144.13	35.34	35.44	70.78	0.50	0.56	4.7×10^6
10	6.7	74.64	109.37	142.84	34.73	33.47	68.20	0.49	0.58	1.05×10^7
15	6.7	78.51	110.76	147.99	32.25	37.23	69.48	0.54	0.58	7.6×10^6
20	6.7	75.93	110.54	145.41	34.61	34.87	69.48	0.50	0.58	7.5×10^6
25	6.7	74.64	108.33	140.24	33.69	31.91	65.60	0.49	0.61	2.2×10^7

Table 2. Variation in TL peak intensity with increasing delay time ($\text{Ca}_2\text{MgSi}_2\text{O}_7 : \text{Eu, Dy}$).

Delay time (min)	0	5	10	15	20	35
TL peak intensity (arb. unit)	115.7	55.6	31.67	28.61	25.86	17.66

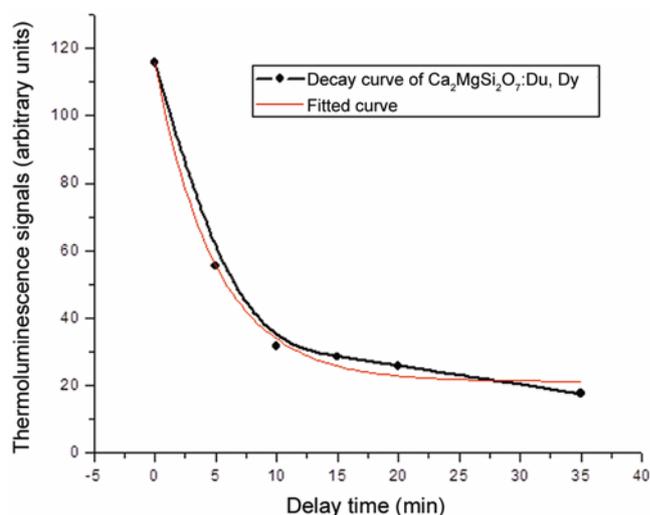
**Figure 4.** Thermoluminescence glow curve at different delay times.

which supports the fact that the sample show considerable amount of persistency in its luminescence property (Mashangva *et al* 2011).

3.4 Decay process

According to several studies (Kubo *et al* 2005; Lin *et al* 2005; Wu *et al* 2011b), the decay of phosphors exhibiting a long-lived afterglow includes both rapid and slow decays corresponding to the afterglow phosphorescence. For an investigation of the decay process of $\text{Ca}_2\text{MgSi}_2\text{O}_7 : \text{Eu}^{2+}, \text{Dy}^{3+}$ phosphor, it was exposed to UV for 20 min and TL glow curves were then measured with different delay times: 2, 5, 10, 15, 20 and 35 min (figure 4).

With increasing delay time, the intensity of the glow peak decreases and the position of the glow peak shifts progressively to higher temperatures (figure 4). The

**Figure 5.** Peak intensity of different delayed TL glow curves against delay times.

possible reason for shifting of peak temperature is retrapping of charge carriers (i.e. kinetic order > 1). The released charge carriers are retrapped before they recombine, giving rise to a delay in the luminescence emission and a spreading of the emission over a wider temperature range. If trap is deeper; more energy is required to release the trapped carriers that implies long afterglow (Lin *et al* 2005; Sharma *et al* 2009; Wu *et al* 2011a).

Figure 4 presents the TL glow curves of $\text{Ca}_2\text{MgSi}_2\text{O}_7 : \text{Eu}^{2+}, \text{Dy}^{3+}$ at different delay time (table 2). The decay is exponential but the exposure remains even after 35 min. TL glow curve temperature peak plotted against delay time (figure 5) using the single exponential equation:

$$I = I_0 \exp \left[-\frac{t}{\rho} \right] + C, \quad (2)$$

yielding the value of decay constant ρ and I_0 is a constant.

The existence of a single peak in the TL glow curve suggests that there is a possibility of only a single trap which encouraged us to continue to work with the single exponential term model. The decay constant was found to be 4.960 min, which indicates that the trap is quite deep and there is a possibility of retrapping released charge carriers, resulting in a long decay process (Martinez *et al* 2000; Wu *et al* 2011a).

4. Conclusions

$\text{Eu}^{2+}:\text{Dy}^{3+}$ co-doped $\text{Ca}_2\text{MgSi}_2\text{O}_7$ phosphors were successfully synthesized via the solid-state reaction. PL emission peaks exhibited maximum intensity of photoluminescence signals at 510 nm, when the $\text{Eu}:\text{Dy}$ is 1:3. TL glow curve for $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ expressed general order kinetics. Intensity of thermoluminescence signals decreases and peak position temperature shifts towards higher side with increasing delay time which is indicative of reasonable retrapping associated with non-first order kinetics. The decay curve shows characteristics of a single exponential equation with decay constant 4.960 min. Calculated trap depth of the phosphor indicates that the phosphor is a quite good persistent luminescent material. $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ phosphors show afterglow properties and also efficient emission colour in green, which is the most sensitive to the human eyes.

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