CHAPTER - 7

MECHANOLUMINESCENCE STUDIES ON
M$_2$MgSi$_2$O$_7$ (M = Sr, Ca, Ba) DOPED WITH Eu$^{2+}$
AND Dy$^{3+}$ PHOSPHORS
MECHANOLUMINESCENCE STUDIES ON M$_2$MgSi$_2$O$_7$ (M = Sr, Ca, Ba) DOPED WITH Eu$^{2+}$ AND Dy$^{3+}$ PHOSPHORS

7.1 INTRODUCTION

In this chapter Mechanoluminescence studies on M$_2$MgSi$_2$O$_7$ (M = Sr, Ca, Ba) phosphors doped with Eu$^{2+}$ and Dy$^{3+}$ is done. These phosphors underwent an impulsive deformation with an impact of a load for Mechanoluminescence (ML) investigations. Temporal characteristics of Mechanoluminescence of the phosphors were observed, which expressed single sharp peak with a long decaying section. In order to investigate about the luminescence centre responsible for ML peak, Mechanoluminescence spectrum of the same phosphor was also observed. Mechanoluminescence spectrum recorded shown similarity in shape as well as peak wavelength with Photoluminescence (PL) spectrum that verifies the existence of single emission centre due to the transition of Eu$^{2+}$ ions due to transitions from any of the sublevels of 4f$^6$5d$^1$ configuration to $^8S_{7/2}$ level of the 4f$^7$ configuration. Decay rates for different impact velocities were also calculated using curve fitting technique. Time of ML peak and rate of decay did not change significantly with respect to increasing impact velocity of the load and peak ML intensity varied linearly. Increasing impact velocity causes more number of electrons will be ionized to reach to the conduction band so there will be more number of electrons available to be recombined at recombination or luminescence centre.

It is well known that ML is produced during deformation of crystal, a correlation between the ML intensity and the crystal deformation is expected. Various techniques have been used for deformation of the crystal for ML studies.\[1\]
ML Devices, which we have used, was designed by Chandra (1983), Chandra and Deshmukh (1985) to improve the performance of earlier designed devices. The ML intensity were measured at different impact velocities by dropping a load of particular mass and shape from different heights. The photomultiplier tube and its housing are put in the box through the lid. The box is perfectly dark for accurate ML measurements. A hollow cylindrical aluminium pipe of diameter 2.1 cm was mounted on the box by the clamps. At the top of hollow pipe a friction less pulley is fixed with the help of wooden cavity. For the measurement of different heights a scale parallel to guided hollow cylinder is fixed. The ML is excited impulsively by dropping a load of particular mass from different heights. The phosphor was placed on a transparent Lucite plate and was covered with aluminium foil with the help of adhesive taps. A RCA 931A photomultiplier tube was connected to an EHT supply of -700 V and output of the tube was supplied to a digital storage oscilloscope (Caddo 2025c). ML spectra were taken using different colored optical filters.
7.2 MECHANOLUMINESCENCE OF $\text{M}_2\text{MgSi}_2\text{O}_7$: Eu$^{2+}$, Dy$^{3+}$ (M= Sr, Ca, Ba) BY IMPULSIVE DEFORMATION

ML characteristics of the phosphors, induced impulsively by an impact of a moving load of weight 500 g were measured. This weight was dropped on the sample from different heights to maintain specific impact velocities. Impact velocity creates impulse on the sample, which deforms the sample resulting in emission of radiation in visible range. Temporal ML characteristics i.e. the curve between the time and ML signals were plotted.

7.2.1 Mechanoluminescence studies on $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu$^{2+}$, Dy$^{3+}$

The characteristics of ML of $\text{Sr}_2\text{MgSi}_2\text{O}_7$:Eu$^{2+}$, Dy$^{3+}$ phosphor induced by the impact of a moving load of weight 500g onto the phosphors were measured (Figure 7.2.1 (a)). Single peak is observed in ML intensity versus time curve. The presence of a single peak indicates some charge transfer process involved in ML emission. The luminescence intensity depends upon impact velocity. The experiment was carried out for different impact velocities i.e. same weight dropped with different heights.

In present study ML is excited impulsively, and ML emission is mostly due to deformation of the powder samples. In such cases only one peak is observed in the transient ML intensity curve. However in certain cases like colored alkali halides and in some phosphors of II-VI category, two peaks are observed in the transient ML intensity versus time curve of materials. The existence of second peak which is always less intense as compared to the first peak may be understood in the following manner. When such materials are mechanically deformed, the electric field
introduced during the deformation either ionizes the electrons from the defect centre or from the valence band. Electron thus obtained in conduction band may either recombine directly with the holes present in the luminescence centre or recombination centre, or they may be trapped for some time in the trapping levels present near the conduction band.

First peak in the transient ML intensity versus time curve is due to the recombination of electrons in the conduction band with the holes at the luminescence centre. However the delayed peak i.e. the second peak is due to the delayed de-trapping of the electrons and their subsequent recombination with the holes. Thus second peak in the ML intensity versus time will be observed only in those crystals or phosphors where there will be traps capable of trapping the electrons for considerable time. It has been found that when the deformation rate decreased (impact velocity decreased) then only one i.e. first peak is observed. In this case the time related to the first peak becomes comparable with the time needed for the de-trapping of the electrons from the traps.

In order to investigate the luminescence centres responsible for ML emission, Mechanoluminescence spectrum is also recorded.
Fig. 7.2.1 (a) Mechanoluminescence Signal intensity with time for different impact velocities of Sr$_2$MgSi$_2$O$_7$: Eu$^{2+}$, Dy$^{3+}$ (0.5, 1.5 mol %)
Fig. 7.2.1 (b) Mechanoluminescence Spectrum (c) Photoluminescence Spectrum of $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu$^{2+}$, Dy$^{3+}$ (0.5, 1.5 mol %)
In Mechanoluminescence spectra (Figure 7.2.1 (b)) a broaden single peak is found at about 480 nm which was compared with the Photoluminescence spectra (Figure 7.2.1 (c)) of the same sample and both the spectra found to be very similar in peak intensity as well as shape. This helped us in making estimation that there is an existence of a single emission centre which is because of the transition of Eu$^{2+}$ ions due to transitions from any of the sublevels of 4f$^5$5d$^1$ configuration to $^8S_{7/2}$ level of the 4f$^7$ configuration.\[4-7\]

Figure 7.2.1 (d) shows the dependency of ML intensity with increasing impact velocity and the graph implies that the relationship between Impact velocity and ML peak is linear i.e. ML peak increases with increasing impact velocity.

![Mechanoluminescence Signal peak with impact velocity of Sr$_2$MgSi$_2$O$_7$: Eu$^{2+}$, Dy$^{3+}$ (0.5, 1.5 mol %)](image-url)
It is predicted that increase in impact velocity, increases the piezoelectricity in the crystal which causes more number of electrons to get ionized and reach to the conduction band, so luminescence centres or recombination centre will get greater number of electrons to be recombined with the holes present in the centre. This may be one of the possible reasons for increase in peak ML intensity with impact velocity.\cite{3, 6-8}

![Graph showing the relationship between impact velocity and mechanoluminescence peak](image)

**Fig. 7.2.1 (e)** Mechanoluminescence Signal peak with impact velocity of $\text{Sr}_2\text{MgSi}_2\text{O}_7$: $\text{Eu}^{2+}$, $\text{Dy}^{3+}$ (0.5, 1.5 mol %)

It can easily be observed (Figure 7.2.1 (e)) that time for peak ML intensity doesn’t change significantly with increasing impact velocity.
When the load or load makes an impact on the crystal with an initial velocity $v_0$, the former decelerates and after a particular time its velocity becomes zero. The time dependence of the velocity of the load may be written as\(^{[9-12]}\):

$$v = v_0 \exp(-\beta v_0 t) \quad \text{............... (Eqn.7.1)}$$

Where $\beta$ is a constant, Equation (1) can be written as

$$\frac{dx}{dt} = v_0 \exp(-\beta v_0 t) \quad \text{............... (Eqn.7.2)}$$

Where $dx$ is the compression of the crystal during the time interval $dt$

Integrating above equation (2), we have

$$x = \frac{1}{\beta} \exp(-\beta v_0 t) + C \quad \text{............... (Eqn.7.3)}$$

The value of $x = 0$ for $t=0$, therefore, equation (3) may be written as

$$x = \frac{1}{\beta} [1 - \exp(-\beta v_0 t)] \quad \text{............... (Eqn.7.4)}$$

Sample is in powder form which is hard enough that, even greater impact velocities compress it up to a particular extent and doesn’t change significantly with increasing impact velocity. Equation 7.4 expresses that, impact time remain mostly unchanged with increasing impact velocity because there is not significant change in compression. This may be one of the possible reasons that the time corresponds to peak ML intensity doesn’t change significantly.

It is seen that decaying portions of the ML intensity with time suggest the following relation:-

$$I = I_0 \exp\left(-\frac{t}{\lambda}\right) \quad \text{............... (Eqn.7.5)}$$
Where \( I_0 \) is coefficient constant and \( \lambda \) is decaying constant.

After the impact of a load from a height onto the mechanoluminescent phosphor material, initially the elastico Mechanoluminescence (EML) intensity increases with time, attains a peak value and then it decreases with time exponentially. The decay of the decrease in the EML intensity is related to the time constant for rise of impact stress and the decay time of decay in EML is equal to the lifetime of electrons in the shallow traps lying in the normal piezoelectric region of the crystals, which get filled during the de-trapping of thermally stable traps at the time of the increase of pressure.

<table>
<thead>
<tr>
<th>Impact Velocity</th>
<th>342</th>
<th>313</th>
<th>280</th>
<th>242</th>
<th>198</th>
<th>140</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \tau ) Decay Constant (ms)</td>
<td>5.85</td>
<td>6.58</td>
<td>6.47</td>
<td>6.52</td>
<td>5.85</td>
<td>6.33</td>
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</table>

It can be seen that the intensity decreases exponentially with time (Figure 7.2.1 (a)). Semi log graph between Mechanoluminescence signal intensity “I” versus \((t-t_m)\) for \( \text{Sr}_2\text{MgSi}_2\text{O}_7: \text{Eu, Dy} \) phosphor is shown in Figure 7.2.1 (f). These are straight lines and, were fitted using following equation with Origin 8.0

\[
\tau = \frac{1}{\text{slo} \text{p of straight line}} \quad \text{............. (Eqn.7.6)}
\]

Yielding the value of decay constant. Curve fitting results show that decay constant varies from 5.85 ms to 6.58 ms (Table 7.2.1) which is fairly good decay rate.
Fig. 7.2.1 (f) Decay curve between $t - t_m$ and logarithm of ML signals ($\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu$^{2+}$, Dy$^{3+}$ (0.5, 1.5 mol %))
7.2.2 Mechanoluminescence studies on $\text{Ba}_2\text{MgSi}_2\text{O}_7$: Eu$^{2+}$, Dy$^{3+}$

As discussed earlier, the characteristics of ML of $\text{Ba}_2\text{MgSi}_2\text{O}_7$:Eu$^{2+}$, Dy$^{3+}$ phosphor induced by the impact of a moving load of weight 500 g onto the phosphors were measured (Figure 7.2.2 (a)). Again a single peak is observed in ML intensity versus time curve. The luminescence intensity depends upon impact velocity. The experiment was carried out for different impact velocities i.e. same weight dropped with different heights.

Figure 7.2.2 (a) expressed single peak which is indicative of existence of single emission centre and In this case the time related to the first peak becomes comparable with the time needed for the de-trapping of the electrons from the traps. In order to investigate the luminescence centres responsible for ML emission in $\text{Ba}_2\text{MgSi}_2\text{O}_7$: Eu$^{2+}$, Dy$^{3+}$, Mechanoluminescence spectrum has also been recorded (Figure 7.2.2 (b)).

A broaden single peak is found at about 504 nm which was compared with the Photoluminescence spectra (Figure 7.2.2 (c)) of the same sample and both the spectra found to be very similar in peak intensity as well as shape. This gives us estimation that there is an existence of a single emission centre and the Mechanoluminescence emission is because of the transition of Eu$^{2+}$ ions due to transitions from any of the sublevels of $4f^65d^1$ configuration to $^8S_{7/2}$ level of the $4f^7$ configuration. \cite{4-7}
**Fig. 7.2.2 (a)** Mechanoluminescence Signal intensity with time of Ba$_2$MgSi$_2$O$_7$: Eu$^{2+}$, Dy$^{3+}$ (0.5, 1.5 mol %)
Fig. 7.2.2 (b) Mechanoluminescence Spectrum (c) Photoluminescence Spectrum of Ba$_2$MgSi$_2$O$_7$: Eu$^{2+}$, Dy$^{3+}$ (0.5, 1.5 mol %)
Figure 7.2.2 (d) expressed that peak ML intensity increased with increasing impact velocity. Increase in impact velocity tends to increase the piezoelectricity near the activator consequently more number of electrons gets free to move in conduction band so there are more electrons to be recombined in recombination or trap level.

Figure 7.2.2 (e) elaborates that time corresponds to peak ML signal doesn’t change a lot with increasing impact velocity. The reason for which is already discussed for Sr₂MgSi₂O₇: Eu²⁺, Dy³⁺ phosphors should be applicable in this case also. Being very hard, these phosphors don’t compress a lot. Equation (7.4) shows that impact time will not be affected if there is small or ignorable compression, so we get the time corresponds to peak ML signal at almost same points.
**Fig. 7.2.2 (e)** Mechanoluminescence Signal peak with impact velocity of Ba$_2$MgSi$_2$O$_7$: Eu$^{2+}$, Dy$^{3+}$

(0.5, 1.5 mol %)

Figure 7.2.2 (a) shows comparative graphs of Time Versus ML intensity of Ba$_2$MgSi$_2$O$_7$: Eu, Dy phosphor for different impact velocities. It shown very similar characteristic as in the case of Sr$_2$MgSi$_2$O$_7$: Eu, Dy. Decaying portions of the ML intensity with time suggest the relation given in Equation 7.5.
Fig. 7.2.2 (f) Decay curve between $t - t_m$ and logarithm of ML signals ($\text{Ba}_2\text{MgSi}_2\text{O}_7$: Eu$^{2+}$, Dy$^{3+}$ (0.5, 1.5 mol %))
Table 7.2.2 Calculation of ML decay constant

<table>
<thead>
<tr>
<th>Impact Velocity</th>
<th>342</th>
<th>313</th>
<th>280</th>
<th>242</th>
<th>198</th>
</tr>
</thead>
<tbody>
<tr>
<td>τ Decay Constant (ms)</td>
<td>2.95</td>
<td>2.95</td>
<td>2.94</td>
<td>3.36</td>
<td>3.77</td>
</tr>
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</table>

It can be seen that the intensity decreases exponentially with time (7.2.2 (a)). Semi log graph between Mechanoluminescence signal intensity “I” versus (t-tₘ) for Ba₂MgSi₂O₇: Eu²⁺, Dy³⁺ phosphor is shown in Figure 7.2.2 (f). These are straight lines and, were fitted using Equation 7.6 with Origin ver. 8.0.

Curve fitting results show that decay constant (τ) varies from 2.95 ms to 3.77 ms (Table 7.2.2) which is fairly good decay rate.
7.2.3 Mechanoluminescence studies on Ca$_2$MgSi$_2$O$_7$: Eu$^{2+}$, Dy$^{3+}$

The characteristics of ML of Ca$_2$MgSi$_2$O$_7$:Eu$^{2+}$, Dy$^{3+}$ phosphor induced by the impact of a moving load of weight 500g onto the phosphors were measured (Figure 7.2.3 (a)). Very similar to the pattern observed for previous two cases, here also single peak is observed in ML intensity versus time curve. The luminescence intensity depends upon impact velocity. The experiment was carried out for different impact velocities i.e. same weight dropped with different heights.

Figure 7.2.3 (a) showed single peak which helps in predicting, an existence of single emission centre and in this case the time related to the first peak becomes comparable with the time needed for the de-trapping of the electrons from the traps. Mechanoluminescence Spectrum is recorded using different colour filters for investigating about the luminescence centre responsible for ML emission and is shown in Figure 7.2.3 (a). A broaden single peak is found at about 510 nm which was compared with the Photoluminescence spectra of the same sample and both the spectra found to be very similar in peak intensity as well as shape (Figure 7.2.3 (b)) . It indicates that there is an existence of a single emission centre created due to transition of Eu$^{2+}$ ions.
Fig. 7.2.3 (a) Mechanoluminescence Signal intensity with time of Ca$_2$MgSi$_2$O$_7$; Eu$^{2+}$, Dy$^{3+}$ (0.5, 1.5 mol %)
Fig. 7.2.3 (b) Mechanoluminescence Spectrum (c) Photoluminescence Spectrum of Ca$_2$MgSi$_2$O$_7$: Eu$^{2+}$, Dy$^{3+}$ (0.5, 1.5 mol %)
Figure 7.2.3 (d) shows the dependency of ML intensity with increasing impact velocity and the graph implies that the relationship between Impact velocity and ML peak is linear i.e. ML peak increases with increasing impact velocity. Increase in impact velocity tends to increase the piezoelectricity near the activator consequently more number of electrons gets free to move in conduction band so there are more electrons to be recombined in recombination or trap level. A detailed explanation can be given in very similar way as discussed in earlier two cases i.e. as discussed for (Sr$_2$MgSi$_2$O$_7$: Eu$^{2+}$, Dy$^{3+}$ and Ba$_2$MgSi$_2$O$_7$: Eu$^{2+}$, Dy$^{3+}$)

![Graph showing the dependency of ML intensity with increasing impact velocity.](image)

**Fig.** 7.2.3 (d) Me chanoluminescence Signal peak intensity with impact velocity of Ca$_2$MgSi$_2$O$_7$: Eu$^{2+}$, Dy$^{3+}$ (0.5, 1.5 mol %)
Fig. 7.2.3 (e) Time corresponds to ML Signal peak with impact velocity of Ca$_2$MgSi$_2$O$_7$: Eu$^{2+}$, Dy$^{3+}$ (0.5, 1.5 mol %)

Figure 7.2.3 (a) shows comparative graphs of Time Versus ML intensity for different impact velocities of Ca$_2$MgSi$_2$O$_7$: Eu$^{2+}$, Dy$^{3+}$ phosphor. It is seen that the rising and decaying portions of the ML intensity with time suggest the following relations:-
Fig. 7.2.3 (f) Decay curve between $t - t_m$ and logarithm of ML signals ($\text{Ca}_2\text{MgSi}_2\text{O}_7$: Eu$^{2+}$, Dy$^{3+}$ (0.5, 1.5 mol %))
Table 7.2.3 Calculation of ML decay constant

<table>
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<th>Impact Velocity</th>
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<th>313</th>
<th>280</th>
<th>242</th>
<th>198</th>
<th>177</th>
</tr>
</thead>
<tbody>
<tr>
<td>τ Decay Constant (ms)</td>
<td>2.45</td>
<td>2.78</td>
<td>2.84</td>
<td>3.24</td>
<td>3.82</td>
<td>4.12</td>
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</table>

Figure 7.2.3 (f) shows the graph between Mechanoluminescence signal intensity “I” versus (t-t_m) for Ca_2MgSi_2O_7: Eu^{2+}, Dy^{3+} phosphor. It can be seen that the intensity decreases exponentially with time.

Result similar to previously discussed, can again be seen that the intensity decreases exponentially with time (Figure 7.2.3 (a)). Semi log graph between Mechanoluminescence signal intensity “I” versus (t-t_m) for Ca_2MgSi_2O_7: Eu^{2+}, Dy^{3+} phosphor is shown in Figure 7.2.3 (f). These are straight lines and, were fitted using Equation 7.6 with Origin ver. 8.0.

Curve fitting results show that decay constant (τ) varies from 2.45ms to 4.12ms (Table 7.2.3) which is again a fairly good decay rate.

7.3 ML PROPERTIES COMPARISON OF M_2MgSi_2O_7: Eu^{2+}, Dy^{3+} (M = Sr, Ba, Ca) PHOSPHORS

ML properties are compared for different M_2MgSi_2O_7:Eu^{2+}, Dy^{3+} phosphors is shown in Table 7.3.1. ML signal emission intensity is found to be 58 a.u., 39.38 a.u. and 91.58 a.u. for Sr_2MgSi_2O_7:Eu^{2+}, Dy^{3+}, Ba_2MgSi_2O_7:Eu^{2+}, Dy^{3+} and Ca_2MgSi_2O_7:Eu^{2+}, Dy^{3+} phosphor, respectively. It may be noted that Ca_2MgSi_2O_7:Eu^{2+}, Dy^{3+} phosphor provided maximum luminescence intensity. As far as time corresponds to the ML peak intensity are 5.80, 12.60, 5.70 ms for the respective phosphors. This signifies that at the beginning Ca_2MgSi_2O_7:Eu^{2+}, Dy^{3+} provide the high emission. The decay constants range values of 5.85 - 6.58 ms, 2.94 - 3.77 ms and 2.45 - 4.12 ms, for the
hosts \( \text{Sr}_2\text{MgSi}_2\text{O}_7 \), \( \text{Ba}_2\text{MgSi}_2\text{O}_7 \) and \( \text{Ca}_2\text{MgSi}_2\text{O}_7 \), respectively. ML spectrum of \( \text{Sr}_2\text{MgSi}_2\text{O}_7 \), \( \text{Ba}_2\text{MgSi}_2\text{O}_7 \) and \( \text{Ca}_2\text{MgSi}_2\text{O}_7 \) exhibited 480, 505 and 510 nm respectively, corresponds to peak ML intensity.

Table 7.3.1 Comparison of ML properties of \( \text{M}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}, \text{Dy}^{3+} \) phosphors

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Parameters/Factors</th>
<th>Phosphors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( \text{Sr}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}, \text{Dy}^{3+} )</td>
</tr>
<tr>
<td>1</td>
<td>ML intensity with impact velocity 343 cm/s</td>
<td>58 a.u.</td>
</tr>
<tr>
<td>2</td>
<td>Time Corresponds to Peak ML signal intensity</td>
<td>5.80 ms</td>
</tr>
<tr>
<td>3</td>
<td>Range of Decay constant</td>
<td>5.85 ms - 6.58 ms</td>
</tr>
<tr>
<td>4</td>
<td>Wavelength corresponds to peak ML signal intensity</td>
<td>480 nm</td>
</tr>
</tbody>
</table>

It can be concluded that \( \text{Ca}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}, \text{Dy}^{3+} \) is the best phosphor among all these phosphor considering the ML properties, specifically for sensor device because it gives high ML signal intensity with a very little duration of impact.

7.4 MECHANISM INVOLVED IN ML EMISSION

Mechanism involved in the process of Mechanoluminescence of these materials can be understood using the following steps [1]:

During the impact of a load onto the sample the crystallite gets fractured and new surfaces are created. Due to the bulk piezoelectricity or local piezoelectricity one surface of the fractured crystallite is positively charged and the other surface is negatively charged. It has been shown that very high electric field of the order of \( 10^6 \) volt/cm, is produced during the fracture of crystallites. In such order of electric field
the electrons ejected from negatively charged surfaces may get accelerated and subsequently excite the Eu$^{2+}$ ions lying on the surface of positively charged surfaces. Thus the de-excitation of excited Eu$^{2+}$ may give rise to the light emission characteristics of 4f$^6$5d$^1$ configuration to $^8S_{7/2}$ level of the 4f$^7$ configuration. The symmetry between PL and ML spectra supports these facts. It is to be noted that in the present case, the sample was not excited with Ultra Violet light, and therefore, the ML emission may not be related to the trapping and de-trapping of electrons.

### 7.5 CONCLUSIONS

Following common conclusions can be made after studying Mechanoluminescence characteristics of M$_2$MgSi$_2$O$_7$:Eu$^{2+}$, Dy$^{3+}$ (M = Sr, Ba, Ca)

1. Single sharp peak was observed in temporal characteristics which gives an indication of presence of single emission centre

2. Photoluminescence Spectrum was compared with Mechanoluminescence Spectrum of the same sample. It was found that both spectrum exhibited single emission peak, which confirms the existence of single emission peak in ML temporal characteristics curve arising due to transitions from any of the sublevels of 4f$^6$5d$^1$ configuration to $^8S_{7/2}$ level of the 4f$^7$ configuration.

3. The value of time for peak intensity ($t_m$) doesn’t change significantly with increasing value of impact velocity.

4. The peak ML intensity increases linearly with respect to impact velocity because of piezoelectricity in the sample increases with increasing impact velocity that causes more number of electrons to get ionized and reach to
the conduction band, so luminescence centres or recombination centre will get greater number of electrons to be recombined with the holes present in the centre.

(5) When a fixed mass of the sample is put under impact of a moving load, ML intensity increases almost linearly and then decreases exponentially with fair decay time.

(6) Decay rates of exponentially decaying section of the temporal characteristics curve doesn’t change largely with impact velocity.
REFERENCES

Future Scope

Besides the work presented in this Ph. D. thesis, there is still a lot of scope for future to extend the investigation further viz.

(a) Effect of doping different rare earth materials to identify best possible dopant / dopant-co dopant combination to check suitability of $\text{M}_2\text{MgSi}_2\text{O}_7$ ($\text{M} = \text{Sr, Ba, Ca}$) phosphor for
   - Lamp phosphors
   - Paint pigments

(b) Impact of varying concentration of $\text{Eu}^{2+}$ and $\text{Dy}^{3+}$ in Mechanoluminescence properties

(c) Studies on thermoluminescence with varying concentration of $\text{Eu}^{2+}$ and $\text{Dy}^{3+}$.

(d) Studies on thermoluminescence with varying dose source i.e. Beta or Gama sources.

(e) The best afterglow phosphor known till now is $\text{SrAl}_2\text{O}_4$: $\text{Eu}^{2+}$, $\text{Dy}^{3+}$, unfortunately, exposition to water may affect the luminescence properties of these materials which limit their use e.g. in the paints as a pigment. $\text{M}_2\text{MgSi}_2\text{O}_7$: $\text{Eu}^{2+}$, $\text{Dy}^{3+}$ phosphors have been reported to be retaining their luminescence properties even in liquids. Considering this point, studies of phosphorescence decay of these silicate based phosphors after dissolving it in a solvent.
Photoluminescence and Thermoluminescence Investigation of Europium- and Dysprosium-Doped Dibarium Magnesium Silicate Phosphor

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Europium- and dysprosium-doped barium magnesium silicate powder with different concentrations of dysprosium was synthesized using solid state reactions. The prepared phosphors were characterized using photoluminescence. Prominent green color emissions were obtained under ultraviolet excitation. The thermoluminescence glow curves of the samples were measured after various delay times. With increased delay time, the intensity of the thermoluminescence peak decays, and the position of the thermoluminescence peak shifts to higher temperatures, indicating the considerable retrapping associated with general order kinetics. Refined lattice parameters of monoclinic phosphor were calculated.

Keywords: kinetic data, persistence luminescence, photoluminescence, thermoluminescence

Introduction

The best afterglow phosphor known till now is SrAl2O4: Eu2+, Dy3+, which is a commercial phosphor and may have afterglow for more than 20 hr.[1,2] Unfortunately, exposition to water may impair the luminescence properties of these materials, which limits their use, for example, in the paints as a pigment. Silicates are very good luminescent materials mainly because of their rigid and stable crystal structure. Many of the silicate-based phosphors doped with divalent or trivalent rare earth materials have been preferred for use as commercial phosphor in fluorescent lamp, scintillators, and so forth.[3,4] Recently Eu2+-doped dibarium earth magnesium disilicates have been found to show persistent luminescence probably strong and long enough to attract commercial interest. The Eu2+-doped dibarium magnesium disilicates with luminescence spectrum (λmax = 505 nm) are ideal for the human eye, making the materials very suitable for practical applications.[5] In this work, dibarium magnesium disilicates (Ba2MgSi2O7) doped with Eu2+ and co-doped with Dy3+ were prepared with solid state reaction. Different luminescent properties of the sample were studied in detail and XRD characterization was also done to confirm the nature of the sample.

Materials and Method

Phosphor powders of composition Ba2MgSi2O7:Eu2+, Dy3+ powder of different concentrations Dy3+ (0.5, 1.0, and 1.5 mol% of Dy3+ with 0.5 mol% of Eu2+), were prepared by solid state reaction. The starting materials SiO2, BaCO3, MgO, Dy2O3, and Eu2O3 were thoroughly ground for approximately 1 hr in a mortar, pre-sintered at 900°C, then fired at 1200°C for approximately 2 hr, with H3BO3 (1.6 mol%) used as flux.[6] The phosphor was irradiated with a 365-nm UV source and then heated at 5°C/min for thermoluminescence (TL) measurements. TL glow curves were recorded at room temperature with a Nucleonix (Hyderabad, India) 11009 TLD reader. The photoluminescence (PL) excitation and emission spectra were measured by a spectrofluorophotometer (SHIMADZU, RF-5301 PC, Kyoto, Japan) using a Xenon lamp of power 150 watt as excitation source. To confirm the nature of phosphor, X-ray diffraction (XRD) characterization of the sample is done using Panalytical Xpert PRO MPD (Singapore) with copper k alpha anode of wavelength 1.5405 Å.

Results and Discussion

XRD Analysis

In order to obtain the crystallographic parameter of the sample the powder, XRD spectra were analyzed by Rietveld fitting method.[8,9] Background, scale factor, and lattice parameters were refined until to obtain a fairly good agreement between observed and calculated XRD spectra (Fig. 1).

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Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/lstl.
Table 1 presents refined lattice parameters of the phosphor Ba$_2$MgSi$_2$O$_7$ with Eu, Dy (0.5 mol%). The values of lattice parameters of the phosphor reported by Aitasalo et al.[8] were used to fit the observed spectra. Refinement is done using Celref version 3 (Collaborative Computational Project No. 14 [CCP14] for Single Crystal and Powder Diffraction Birkbeck University of London and Daresbury Laboratory, London, UK). The calculated spectra confirmed the presence of monoclinic Ba$_2$MgSi$_2$O$_7$. The calculated lattice parameters are shown in Table 1 and are slightly greater than values obtained by Aitasalo et al.[8] This may be due to the presence of Eu$^{2+}$ (dopant) and Dy$^{3+}$ (co-dopant) ions having greater ionic radii than Ba$^{2+}$ ions.

There are a few extra peaks in observed XRD pattern, which could be due a great number of stacking faults induced by the presence of the doping ions and also due to secondary phases and impurities formed during the elaboration process.

**Photoluminescence**

The excitation and emission spectra of Ba$_2$MgSi$_2$O$_7$: Eu, Dy phosphors prepared are shown in Fig. 2. The excitation spectrum for an emission wavelength of 505 nm shows a prominent band at 392 nm. The emission spectra are identical in shape and the bands differ only in intensities. The broadband emission spectra centered at 505 nm (blue-green region) observed under the ultraviolet excitation of 395 nm correspond to the Eu$^{2+}$ emission due to transitions from sublevels of 4f$^5$5d$^1$ configuration to $^8$S$_7/2$ level of the 4f$^7$ configuration. The emission spectra cover from 400 to 600 nm which is a sign of a good phosphor. Since the crystal field can perfectly affect the 4f$^5$5d$^1$ electron states of Eu$^{2+}$, there is no modification in the shape of the emission spectrum; therefore, it is concluded that the crystal field is not changed much with the compositional variation.[10,11] Eu$^{2+}$ ions are expected to occupy [BaO$_8$] sites because the coordination number of Ba$^{2+}$ ion is eight and four for both Mg$^{2+}$ and Si$^{4+}$ ions. It is difficult for Eu$^{2+}$ ions to incorporate the tetrahedral [MgO$_4$] or [SiO$_4$] symmetry but can easily incorporate octahedral [BaO$_6$].[12] Another fact that supports only Ba$^{2+}$ site can be occupied by Eu$^{2+}$ is the ionic radii of eightfold coordinated Eu$^{2+}$ and Ba$^{2+}$ are closer, Ba$^{2+}$: 0.142 and Eu$^{2+}$: 0.125 nm. Co-dopant Dy$^{3+}$ ion acts to introduce the trap levels that increase the decay time of the phosphor.[13] The PL excitation spectra and comparison of PL emission spectra shown displays maximum intensity when Eu:Dy is 1:3 after that concentration quenching of Dy$^{3+}$ occurs, which results in decrease in PL intensity. The pairing or coagulation of activator ions may have created quenching centers, and seems to be the reason for decrease in intensity after a specific concentration of Dy$^{3+}$ions.[14]

**Thermoluminescence Kinetic Parameters**

TL is one of the possible ways to estimate the trap states of the material. Shape factor is calculated using peak shape method.[15–18] The afterglow of any phosphor is generated by the detrapped carriers that recombine with the opposite carrier in the luminescent center with a transition resulting in visible region. Ba$_2$MgSi$_2$O$_7$ doped with Eu, Dy with concentration ratio 0.5 and 1.5 mol%, respectively, was used to undertake the TL measurements because we observed maximum PL signal strength at this ratio.

Peak shape method is used for determining the order of kinetics of TL glow curves so as to determine suitability of the phosphor for long afterglow.

In Fig. 1(a), $\omega = \tau + \delta$; $\delta$ is the high temperature half width, $\tau$ is the low temperature half width $\mu = \delta/\omega$, is shape factor, $T_m$ is the peak temperature at the maximum, and $T_1$ and $T_2$ are, respectively, the temperatures on either sides of $T_m$, corresponding to half intensity.

The TL glow curves exhibit a broad peak because of the transition between ground and excited energy levels of the dopant Eu$^{2+}$. Figure 3 (Table 2) shows TL glow curve of the above-mentioned sample with different UV exposure time that expresses TL glow curve peak intensity increases with increasing UV exposure time till 20 min of exposure, then it starts decreasing. It is predicted that with increasing UV exposure, greater number of charge carriers are released, which increases the trap density results with increase of TL.
intensity, but after a specific exposure traps starts to destroy results in decrease in TL intensity (referring to Table 2).[19,20]

The peak temperature of the TL glow curves is clearly affected by the UV exposure (Table 2). To estimate the order of kinetics, shape factor is calculated Table 2.[19,21,22] In present work, shape factor ($\mu$) is in the range 0.41–0.50, which indicates the presence of general order kinetics[19] and there are possibilities of retrapping of charge carriers before its recombination results a long decay process.[22]

**The Decay Process**

According to several studies[23–25] the decay of phosphors exhibiting long-lived afterglow contains a rapid decay and

---

**Table 1.** Refined lattice parameters and indexing of XRD pattern. Final values: (standard errors on the second line)

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<th>$b$ (Å)</th>
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<th>$k$</th>
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---

Fig. 2. Excitation and emission spectra of $\text{Ba}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}, \text{Dy}^{3+}$.

Fig. 3. TL glow curves of $\text{Ba}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}, \text{Dy}^{3+}$ measured for different UV exposure time.
a slow decay corresponding to the afterglow phosphorescence. With increasing delay time, the intensity of the glow peak decreases and the position of glow peak shifts progressively to higher temperatures (Fig. 4). There may be two reasons for the shift in the TL peak maximum. Many closely spaced trapping levels may form a trapping center, creating a broad TL glow curve. The lower temperature components will decay relatively faster and the shape of the curve will change, showing a shift of the TL peak to higher temperatures. If these were the case, the half width band of the TL glow curve should decrease with increased delay time.\textsuperscript{[26,27]} However, the half width band is nearly constant with delay time (half width band $\omega$ in Table 3). Consequently a model involving many trapping levels is not appropriate. The other possible reason is the retrapping of charge carriers (i.e., kinetic order $>1$). In this case, the position of the TL peak is associated with the initial concentration of trapped carriers, and the change in initial concentration necessarily changes $T_m$. The released carriers are re-trapped before they recombine, giving rise to a delay in the luminescence emission and a spreading of the emission over a wider temperature range.\textsuperscript{[26,27]}

For investigation of decay process of Ba$_2$MgSi$_2$O$_7$:Eu$^{2+}$, Dy$^{3+}$ phosphor, it was given 25 min of UV exposure, then TL glow curves were measured with different delay time; 0, 10, 15, 20, 25, 30, 60, and 75 min, respectively (Fig. 4). Figure 5 represents decay in TL glow curve peak of Ba$_2$MgSi$_2$O$_7$:Eu$^{2+}$, Dy$^{3+}$, which consists of an exponential nature, but the exposure remains even after 75 min.

The existence of single peak in TL glow curve suggests there is a possibility of single trap only, which encouraged us to stick to the single exponential term model.

### Table 2. Estimation of shape factors of TL glow curve under different UV exposure

<table>
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<tr>
<th>UV (min)</th>
<th>$T_1$ ($^\circ$C)</th>
<th>$T_m$ ($^\circ$C)</th>
<th>$T_2$ ($^\circ$C)</th>
<th>$\tau$ ($^\circ$C)</th>
<th>$\delta$ ($^\circ$C)</th>
<th>$\omega$ ($^\circ$C)</th>
<th>$\mu = \delta/\omega$</th>
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<tr>
<td>5</td>
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<td>32.57</td>
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<td>74.62</td>
<td>100.74</td>
<td>126.80</td>
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<td>25</td>
<td>66.83</td>
<td>98.1</td>
<td>127.49</td>
<td>31.27</td>
<td>29.39</td>
<td>60.66</td>
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### Table 3. Estimation of shape factors of TL glow curves plotted after different decay time

<table>
<thead>
<tr>
<th>Decay time (min)</th>
<th>$T_1$ ($^\circ$C)</th>
<th>$T_m$ ($^\circ$C)</th>
<th>$T_2$ ($^\circ$C)</th>
<th>$\tau$ ($^\circ$C)</th>
<th>$\delta$ ($^\circ$C)</th>
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<tr>
<td>Immediately</td>
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<td>98.10</td>
<td>127.49</td>
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<tr>
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<tr>
<td>60</td>
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<td>124.42</td>
<td>156.09</td>
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<td>37.12</td>
<td>31.67</td>
<td>68.79</td>
<td>0.46</td>
</tr>
</tbody>
</table>
The TL temperature maximums in Fig. 5 were fitted using a mono-exponential decay function (Eq. (1)):

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

(1)

Yielding the value of decay constant \( \rho \) and \( I_0 \) is a constant.

The decay constant was found to be 6.39 min. In most of the useful long afterglow material, the decay constant is much more than the value we got in this case; for \( \text{Sr}_3\text{MgSi}_2\text{O}_7: \text{Eu}, \text{Dy} \), it is of the order of few hours, which expressed, in this case, that trap is not so deep for being extremely large lasting, but still there is a possibility of retrapping of released trap charge carriers, resulting a long decay process.\(^{19,20,26}\)

Conclusion

The XRD pattern of the prepared sample has shown agreement with the pattern reported by Aitasalo in 2006 and refined lattice parameters of the pattern were calculated, which confirms the formation of \( \text{Ba}_2\text{MgSi}_2\text{O}_7 \) Eu\(^{2+}\), Dy\(^{3+}\). TL glow curve for the phosphor results a general order kinetics and has shown maximum TL intensity when exposed to UV for 20 min. The TL intensity decreases and peak position temperature shifts toward higher side with increasing decay time that is indicative of strong retrapping associated with non-first-order kinetics. PL emission peaks exhibited more intensity when the Eu:Dy is 1:3 with a prominent peak at 503 nm. This is because Eu\(^{2+}\) ions are expected to occupy [BaO\(_8\)] sites created due to the crystal defects to form an emission center responsible for green color emission. The decay curve shows characteristics of a single exponential equation with decay constant of 6.39 min, which expressed that the phosphor is a considerable persistent luminescent material.

Acknowledgment

We are thankful to TIFR (Tata Institute of Fundamental Research) for proving us the facility of XRD instrumentation, we also acknowledge the same.

References

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

M$_2$MgSi$_2$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 aluminates 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). Ca$_2$MgSi$_2$O$_7$: Eu$^{2+}$, 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, Ca$_2$MgSi$_2$O$_7$: Eu$^{2+}$, 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 Ca$_2$MgSi$_2$O$_7$: Eu$^{2+}$, 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$_2$O$_3$ and Eu$_2$O$_3$ were thoroughly ground for ~ 1 h in a mortar, pre-sintered at 900 °C and fired at 1200 °C for ~ 2 h, with H$_3$BO$_3$ (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) 11009 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.*Author for correspondence (ravishrivastava95@gmail.com)
of SiO$_2$ 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$_3^-$ ion has a $D_3h$ 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–SiO$_2$ 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 Ca$_2$MgSi$_2$O$_7$: Eu, 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 Dhole 2013).

Jiang et al. (2003) reported that the possible sites for incorporating Eu$^{2+}$ in Ca$_2$MgSi$_2$O$_7$ lattice are Ca$^{2+}$ sites, or the Mg$^{2+}$ sites or the Si$^{4+}$ sites. Mg$^{2+}$ (0.58 Å), and Si$^{4+}$ sites (0.26 Å) are small, but Ca$^{2+}$ (1.12 Å) is equal to the size of Eu$^{2+}$ (1.12 Å). So, Eu$^{2+}$ ions hardly incorporate into tetrahedral [MgO$_4$] and [SiO$_4$], and only incorporate into [CaO$_4$] anions complexes in Ca$_2$MgSi$_2$O$_7$. From figure 2, it can be seen that only an emission band is observed at 510 nm in the emission spectra of Ca$_2$MgSi$_2$O$_7$: Eu$^{2+}$/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 Eu : 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 \( \text{Ca}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}, \text{Dy}^{3+} \) (Eu/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):

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

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 \( \beta \) the linear heating rate. In this work:

\[ \beta = 6.7 \text{°C s}^{-1}, \]

\[ \omega = \tau + \delta, \]

where \( \delta \) is the high temperature half width and \( \tau \) the low temperature half width. The shape factor

\[ \mu = \frac{\delta}{\omega}. \]

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 Ca$_2$MgSi$_2$O$_7$: Eu, Dy after different UV exposure times.

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

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

<table>
<thead>
<tr>
<th>Delay time (min)</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>35</th>
</tr>
</thead>
<tbody>
<tr>
<td>TL peak intensity (arb. unit)</td>
<td>115.7</td>
<td>55.6</td>
<td>31.67</td>
<td>28.61</td>
<td>25.86</td>
<td>17.66</td>
</tr>
</tbody>
</table>

Figure 4. Thermoluminescence glow curve at different delay times.

Figure 5. Peak intensity of different delayed TL glow curves against 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 Ca$_2$MgSi$_2$O$_7$: Eu$^{2+}$, 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 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 Ca$_2$MgSi$_2$O$_7$: Eu$^{2+}$, 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:

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

yielding the value of decay constant $\rho$ 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

Eu$^{2+}$ : Dy$^{3+}$ co-doped Ca$_2$MgSi$_2$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 Eu : Dy is 1 : 3. TL glow curve for Ca$_2$MgSi$_2$O$_7$ : Eu$^{2+}$, 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. Ca$_2$MgSi$_2$O$_7$ : Eu$^{2+}$, Dy$^{3+}$ phosphors show afterglow properties and also efficient emission colour in green, which is the most sensitive to the human eyes.

Acknowledgement

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Luminescence studies on europium- and dysprosium-doped di-strontium magnesium silicate phosphor

Ravi Shrivastava · Jagjeet Kaur · Vikas Dubey · Beena Jaykumar

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Abstract Europium- and dysprosium-doped strontium magnesium silicate powder with different concentration ratios of dysprosium were synthesized using solid-state reaction. The XRD pattern confirmed the proper preparation of the sample. The prepared phosphors were characterized using photoluminescence excitation and emission spectra. Prominent blue color emission was obtained under ultraviolet excitation. The thermoluminescence (TL) glow curves of the sample were measured at various delay times. With increased delay time, the intensity of the TL peak decays and the position of the TL peak shifts towards a higher temperature, indicating the considerable retrapping associated with general order kinetics.

Keywords Thermoluminescence decay · Photoluminescence · Rare earth-doped

Introduction

The best afterglow phosphor known until now is SrAl$_2$O$_4$: Eu$^{2+}$, Dy$^{3+}$ which is a commercial phosphor and may have afterglow for more than 20 h. Unfortunately, exposure to water may impair the luminescence properties of these materials which limits their use, e.g., in paints as a pigment. A new kind of long-lasting phosphors, Eu$^{2+}$, Dy$^{3+}$ co-doped silicates M$_2$MgSi$_2$O$_7$ (M = Ca, Sr) with an afterglow time longer than 20 h has been developed that show better afterglow even in liquids [1]. Eu$^{2+}$ ion acts as the luminescent center, 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 [2, 3]. In this paper, Sr$_2$MgSi$_2$O$_7$: Eu$^{2+}$, Dy$^{3+}$ phosphors with different concentration ratios of dopant and co-dopant were prepared using high temperature for the solid state reaction. The photoluminescence (PL) studies were done to identify the phosphor with best PL intensity. The thermoluminescence (TL) glow curves of the phosphor, whose PL results were found best, were measured with different decay times for 20 min of UV exposure. TL glow curves of the same phosphor were measured after various delay times to estimate the persistency of the phosphor.

Materials and methods

The phosphor of Sr$_2$MgSi$_2$O$_7$: Eu$^{2+}$, Dy$^{3+}$ powder of different concentration ratios of Eu/Dy was prepared by solid state reaction. The starting materials SiO$_2$, SrCO$_3$, MgO, Dy$_2$O$_3$ and Eu$_2$O$_3$ were thoroughly ground for approximately 1 h in a mortar, pre-sintered at 900 °C, then fired at 1,300 °C for approximately 2 h, with H$_3$BO$_3$ (1.6 mol%) used as flux [4]. The phosphor was irradiated with a 365-nm UV source then heated at 6.7°C s$^{-1}$ for TL measurements. Thermally stimulated luminescence glow curves were recorded at room temperature by the use of a Nucleonix (Hyderabad, India) 11009 TLD reader. The PL excitation and emission spectra were measured by a spectrofluorophotometer (SHIMADZU, RF-5301 PC) using the xenon lamp as excitation source.

Results and discussion

XRD analysis of the sample

For confirmation of the prepared sample X-ray diffraction (XRD) characterization of the sample is done using Panalytical Xpert PRO MPD with a copper k alpha anode of wavelength 1.5405 Å. The pattern found is as follows:

Figure 1 gives the comparison between the XRD pattern of Sr$_2$MgSi$_2$O$_7$ (Eu/Dy = 0.5/1.5) as prepared, and the standard XRD pattern (COD card No. 96-431-7124). Figure of merit while matching these was 0.9194 which illustrates that the phase of the prepared sample agrees with the standard pattern COD card No. 96-431-7124. The pattern is characterized by a few prominent peaks found at different glancing angles.

The indexing and refinement of lattice parameters are calculated using software Celref v.3. The refined values of trigonal di-strontium magnesium silicate were found as: $a = 8.0009$ Å, $b = 8.0099$ Å, $c = 5.1579$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, and cell volume = 330.2 (Å$^3$), which again signify the proper preparation of the discussed sample and are shown in Table 1.

Photoluminescence

The excitation and emission spectra of the prepared Sr$_2$MgSi$_2$O$_7$: Eu, Dy phosphors are shown in Fig. 2. The excitation spectrum was monitored at a wavelength of
490 nm which shows prominent peaks at 371 and 393 nm. The emission spectra are identical in shape and the bands differ only in intensities. The broadband emission spectra centered at 480 nm (blue region) observed under the ultraviolet excitation of 365 nm correspond to the Eu$^{2+}$ emission arising due to transitions from sub levels of the 4$f^6$ 5$d^1$ configuration to 8$S^{7/2}$ level of the 4$f^7$ configuration but with Eu$^{2+}$ occupying different lattice sites. Since the crystal field can greatly affect the 4$f^6$ 5$d^1$ electron states of Eu$^{2+}$, this suggests that the crystal field is not changed much with the compositional variation [5, 6].

Eu$^{2+}$ ion is expected to replace the Sr$^{2+}$ site in the tetragonal Sr$_2$MgSi$_2$O$_7$ structure since the ionic radii of the eight fold coordinated species are almost the same: Sr$^{2+}$: 0.126 and Eu$^{2+}$: 0.125 nm [7]. The co-dopant Dy$^{3+}$ ion acts to introduce the trap levels which increases the decay time of the phosphor [8]. The PL excitation spectra and comparison of PL emission spectra shown display maximum intensity when Eu:Dy was 1:3 then the intensity decreases because of the concentration quenching of Dy$^{3+}$ ions.

**Evaluation of thermoluminescence kinetic data**

Thermoluminescence is one of the possible ways to estimate the trap states of the material. The TL parameter of the thermal activation energy $E$ which is related to the trap depth is obtained using the peak shape method [9–12].

The relationship between the frequency factor ‘$s$’ and the depth of the trap ‘$E$’ is given by the following equation [13]:

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

where $k$ is Boltzmann constant, $E$ is trap depth, $b$ is order of kinetics, $T_m$ is temperature of peak position, and $\beta$ is the linear heating rate. In this work, $\beta = 6.7°Cs^{-1}$. 

![Fig. 1 XRD pattern of Sr$_2$MgSi$_2$O$_7$ (Eu/Dy = 0.5/1.5)](image-url)
Trap depth for second order kinetics is calculated using the following equation [13]:

$$E = 2kT_m \left( 1.76 \frac{T_m}{\omega} - 1 \right)$$  \hspace{1cm} (2)

$\omega = \tau + \delta$; $\delta$ is the high temperature half-width and $\tau$ is the low temperature half-width. The shape factor $\mu = \delta/\omega$.

Figure 3 shows the TL glow curve of the sample for different UV exposures and demonstrates that the TL signals increase with increasing UV exposure. TL signals are maximum for 20 min of UV exposure, after that they start to decrease. The charge carrier density may have been increasing with increasing UV exposure, but, after 20 min of UV exposure, the trap level may have started to be destroyed resulting in a decrease in thermoluminescence signals.

<table>
<thead>
<tr>
<th>Table 1 Indexing and lattice parameters of Sr₂MgSi₂O₇ : Eu, Dy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero Lambda a b c Alpha Beta Gamma Vol.</td>
</tr>
<tr>
<td>---------------------------------</td>
</tr>
<tr>
<td>Standard values</td>
</tr>
<tr>
<td>0 1.5418 8.0107 8.0107 5.1636 90 90 90 331.4</td>
</tr>
<tr>
<td>0 0 1 0 1 0 0 0</td>
</tr>
<tr>
<td>Final values : (Standard errors on 2nd line)</td>
</tr>
<tr>
<td>0 1.5418 8.0009 8.0009 5.1579 90 90 90 330.2</td>
</tr>
<tr>
<td>0 0 0.0061 0 0.0008 0 0 0</td>
</tr>
<tr>
<td>h k l 2$\theta$ (Obs) 2$\theta$ (Cal) Dif</td>
</tr>
<tr>
<td>---------------------------------</td>
</tr>
<tr>
<td>1 1 1 23.406 23.3375 0.0685</td>
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<td>1 2 1 30.457 30.4032 0.0538</td>
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<td>0 0 2 34.84 34.7859 0.0541</td>
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<td>2 1 3 59.639 59.6643 −0.0253</td>
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<td>2 5 1 65.321 65.3632 −0.0422</td>
</tr>
<tr>
<td>4 1 3 73.506 73.6051 −0.0991</td>
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</table>
Shape factors range between 0.45 and 0.51, which indicates that it is a case of non-first order kinetics, approaching towards second order, responsible for deeper trap depth resulting in the long afterglow.

The value of trap depth of the phosphor was calculated with different methods (Table 2, 3), and ranges between 0.514 and 0.751 eV which again is a sign of a good PLUM material.

![Excitation and emission spectra of Sr₂MgSi₂O₇:Eu²⁺, Dy³⁺](image)

**Fig. 2** Excitation and emission spectra of Sr₂MgSi₂O₇:Eu²⁺, Dy³⁺

![TL glow curves measured for various delay times](image)

**Fig. 3** TL glow curves measured for various delay times

Shape factors range between 0.45 and 0.51, which indicates that it is a case of non-first order kinetics, approaching towards second order, responsible for deeper trap depth resulting in the long afterglow.

The value of trap depth of the phosphor was calculated with different methods (Table 2, 3), and ranges between 0.514 and 0.751 eV which again is a sign of a good PLUM material.
<table>
<thead>
<tr>
<th>UV mins</th>
<th>Heating rate (°C/s)</th>
<th>( T_1 ) (°C)</th>
<th>( T_m ) (°C)</th>
<th>( T_2 ) (°C)</th>
<th>( \beta )</th>
<th>( \alpha )</th>
<th>( \phi )</th>
<th>( \delta )</th>
<th>( \rho )</th>
<th>( \delta_d )</th>
<th>Frequency factor</th>
<th>Lifetime of charge in the trap (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>6.7</td>
<td>75.8</td>
<td>100.93</td>
<td>127.35</td>
<td>25.13</td>
<td>6.5</td>
<td>10^{-10}</td>
<td>0.51</td>
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<td>70.65</td>
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<td>125.29</td>
<td>30.23</td>
<td>1.5</td>
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<td>6.7</td>
<td>68.59</td>
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<td>69.62</td>
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<td>140.75</td>
<td>31.08</td>
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<td>0.56</td>
<td>3.7</td>
<td>3.7 x 10^3</td>
<td>220.40</td>
<td>2.20</td>
</tr>
</tbody>
</table>
The decay process

From Table 4, the effect of different decay times at peak temperature and intensity in a phosphor is readily apparent; the shape factor and activation energy are also shown in the same table [13–15]. The shape factors are indicative of mixed order kinetics. The TL glow curves exhibit a broad peak because of the transition between ground and excited energy levels of the dopant Eu$^{2+}$. With increasing delay time, the intensity of the glow peak decreases and the position of the glow peak shifts progressively toward higher temperatures (Fig. 4).

There may be two reasons for the shift in the TL peak maximum. According to Liu et al., many closely spaced trapping levels may form a trapping center, creating a broad TL glow curve. The lower temperature components will decay relatively faster and the shape of the curve will change, showing a shift of the TL peak to higher temperatures [16]. If these were the case, the half-width band of the TL glow curve should decrease with increased delay time [3].

The other possible reason is the retrapping of charge carriers (i.e., kinetic order >1). The released 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 [3].

According to several studies, the decay of phosphors exhibiting long-lived afterglows contains a rapid decay and a slow decay corresponding to the afterglow phosphorescence [10–12]. For investigation of the decay process of Sr$_2$MgSi$_2$O$_7$: Eu$^{2+}$, Dy$^{3+}$ phosphor, it was given 20 min of UV exposure and then the TL glow curves were measured with different delay times: immediately, and at 15, 30, 45, 60, 75, 90, 105, 120, and 135 min, respectively (Fig. 4).

Figure 5 presents the decay curve of Sr$_2$MgSi$_2$O$_7$: Eu$^{2+}$, Dy$^{3+}$ that consists of an exponential decay, but the exposure remains even after 135 min. The TL glow curve plotted against time in Fig. 4 was expressed using the single exponential equation:

$$ I = I_0 \exp \left[ -\frac{t}{\tau} \right] $$

Yielding the value of decay constant $\tau$ and $I_0$ is a constant.

We tried to get the equation of the best fit curve of intensity versus time graph to discover the value of the decay constant which was found to be 25.81 min and the value of $I_0$ was 3,095.77. Origin Pro v.8.0 was used to calculate these values which indicate that the trap is quite deep and that there is a possibility of retrapping released charge carriers, resulting in a long decay process [3, 17].

Table 3  Trap depth of Sr$_2$MgSi$_2$O$_7$: Eu, Dy with different methods

<table>
<thead>
<tr>
<th>Methods</th>
<th>5 min UV</th>
<th>10 min UV</th>
<th>15 min UV</th>
<th>25 min UV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_c = c_c \left(\frac{\tau_e^2}{\sigma}\right) - b_c(2kT_m)$</td>
<td>0.733</td>
<td>0.532</td>
<td>0.514</td>
<td>0.613</td>
</tr>
<tr>
<td>$E_{oa} = c_{oa} \left(\frac{\tau_a^2}{\sigma}\right) - b_{oa}(2kT_m)$</td>
<td>0.745</td>
<td>0.563</td>
<td>0.548</td>
<td>0.609</td>
</tr>
<tr>
<td>$E_{d} = c_{d} \left(\frac{\tau_d^2}{\sigma}\right) - b_{d}(2kT_m)$</td>
<td>0.751</td>
<td>0.595</td>
<td>0.582</td>
<td>0.605</td>
</tr>
</tbody>
</table>
Table 4  Variation in TL peak intensity with increasing delay time

<table>
<thead>
<tr>
<th>Delay time (min)</th>
<th>0</th>
<th>15</th>
<th>30</th>
<th>45</th>
<th>60</th>
<th>75</th>
<th>90</th>
<th>105</th>
<th>120</th>
<th>135</th>
</tr>
</thead>
<tbody>
<tr>
<td>TL peak intensity (arb unit)</td>
<td>38,539.48</td>
<td>21,470.04</td>
<td>15,751.36</td>
<td>12,439.33</td>
<td>8,718.52</td>
<td>4,936.23</td>
<td>3,785.79</td>
<td>3,146.99</td>
<td>2,783.68</td>
<td>2,077.74</td>
</tr>
</tbody>
</table>
Conclusion

The TL glow curve for Sr$_2$MgSi$_2$O$_7$: Eu$^{2+}$, Dy$^{3+}$ expressed general order kinetics. The TL intensity decreases and the peak position temperature shifts towards the higher side with increasing decay time, which is indicative of strong retrapping.
associated with non-first order kinetics. The decay curve shows characteristics of a single exponential equation and the decay constant was found to be 25.81 min. The calculated trap depth of the phosphor indicates that the phosphor is a very good PLUM material. PL emission peaks exhibited more intensity when the Eu:Dy ratio is 1:3 with a prominent peak at 480 nm. This is because Eu$^{2+}$ replaces the Sr$^{3+}$ site location created due to the crystal defects to form an emission center responsible for blue color emission.

Acknowledgment We are grateful to TIFR (Tata institute of fundamental research), Mumbai for providing us with the XRD pattern of our sample for its crystallographic study.

References

Kinetics and thermoluminescence glow curve study
of Ba$_2$MgSi$_2$O$_7$:Eu$^{3+}$, Dy$^{3+}$

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Beena Jaykumar

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Abstract This paper reports thermoluminescence glow curves of Eu$^{3+}$, Dy$^{3+}$-doped Ba$_2$MgSi$_2$O$_7$ phosphor for different UV exposure times. Kinetic data were evaluated by the peak-shape method. The glow curves shift toward higher intensity with increasing exposure time to UV at 365 nm. When the heating rate was 5 °C s$^{-1}$, peaks were observed at 101.76, 109.69, 102.67, and 104.05 °C, respectively, after UV exposure for 5, 10, 15, and 20 min. The glow peaks are indicative of second-order kinetics. Different kinetic data, i.e. trap depth, order of kinetics, activation energy, and frequency factor were also calculated. To evaluate the persistence characteristics of the luminescence of the phosphor, the lifetime of the charge in the trap was calculated; it was 348, 660, 368, and 428 s for UV exposure of 5, 10, 15, and 20 min, which indicates the luminescence of the phosphor is persistent.

Keywords Silicate phosphors · Kinetic data · Thermoluminescence (TL) · Exposure time · Order of kinetics · Trap depth

Introduction

Use of rare-earth luminescence in persistent luminescence (PLUM) materials is one of the latest applications of rare earth elements. Since the mid-1990s a completely new generation of PLUM phosphors has been developed. Strontium aluminate phosphors activated by Eu$^{2+}$ and Dy$^{3+}$ ions have recently attracted much attention because of their excellent properties, for example high quantum efficiency, long persistence of phosphorescence, and good stability [1].

In recent times, Eu$^{3+}$-doped akermanites (Ba, Ca, Sr)$_2$MgSi$_2$O$_7$ have been extensively investigated as red phosphors, because of their chemical stability. The
intensities of Eu$^{3+}$ excitation lines at approximately 394 and 465 nm are clearly enhanced in these materials compared with most other Eu$^{3+}$-doped phosphors [2].

It is well known that Eu$^{3+}$ is a excellent activator, with a good emission spectrum in the red region; it is, therefore, necessary to choose a good host material for synthesis of a red phosphor for use in white LEDs excited by ultraviolet light [8]. Silicate is an excellent matrix for phosphors because of its low cost, stable crystal structure, high physical and chemical stability, and strong water persistence compared with other matrixes [8].

In this work, dibarium magnesium disilicate (Ba$_2$MgSi$_2$O$_7$) doped with Eu$^{3+}$ and Dy$^{3+}$ was prepared by use of a solid-state reaction. The effect of the rare-earth ion doping on the luminescence properties of this material was studied by measurement of kinetic data and the lifetime of the charge in the trap.

**Materials and methods**

Solid state reaction was used for preparation of Ba$_2$MgSi$_2$O$_7$:Eu$^{3+}$, Dy$^{3+}$. Appropriate oxides and carbonates (BaCO$_3$, Eu$_2$O$_3$, Dy$_2$O$_3$, SiO$_2$, MgO, and H$_3$BO$_3$) were thoroughly ground for approximately 1 h in a mortar, pre-sintered at 900 °C, then fired at 1,300 °C for approximately 3 h, with H$_3$BO$_3$ (1.6 mol%) used as flux [3, 4]. Solid state reaction is widely used to prepare phosphors because samples prepared using this method have good luminescence and very good morphology also. The phosphor was irradiated with a 365-nm UV source then heated at 5 °C s$^{-1}$ for thermoluminescence (TL) measurements. Thermally stimulated luminescence glow curves were recorded at room temperature by use of a Nucleonix (Hyderabad, India) I1009 TLD reader.

The peak shape method was used to determine kinetic data [7]. If the TL glow curve is as illustrated in Fig 1:

Then $T_M$ is the temperature at the peak maximum, $T_1$ and $T_2$ are, respectively, the temperatures on either side of $T_M$, corresponding to half intensity, $\tau = T_M - T_1$ is the half-width at the low temperature side of the glow peak, $\delta = T_2 - T_M$ is the half-width at the fall-off side of the glow peak, $\omega = T_2 - T_1$ is the total half-width, and $\mu = \delta/\omega$ is the so-called geometrical shape or symmetry factor.

The Lushchik formula for second order kinetics is:

![Fig. 1 Peak shape method for evaluating kinetic data](image-url)
\[ E(eV) = \frac{(2kT_m^2)}{\delta} \] (1)

Chen’s method [7] does not make use of any iterative procedures and does not require knowledge of the kinetic order, which is found from the peak shape by using the symmetry factor \( \mu \). The equations can be combined as:

\[ E_x = c_x \left( \frac{kT_m^2}{x} \right) - b_x(2kT_m) \] (2)

where \( x \) is \( \tau, \delta, \) or \( \omega \). The values of \( c_x \) and \( b_x \) are summarized as below:

\[
\begin{align*}
   c_{\tau} &= 1.510 + 3.0(\mu - 0.42) \\
   b_{\tau} &= 1.58 + 4.2(\mu - 0.42) \\
   c_{\delta} &= 0.976 + 7.3(\mu - 0.42) \\
   b_{\delta} &= 0 \\
   c_{\omega} &= 2.52 + 10.2(\mu - 0.42) \\
   b_{\omega} &= 1
\end{align*}
\]

where \( \mu = 0.42 \) for first-order TL glow peaks and \( \mu = 0.52 \) for second-order peaks.

The relationship between frequency factor, \( s \), and the depth of the trap, \( E \), is given by the equation:

\[ \beta E/kT_m^2 = s[1 + (b - 1) \times 2kT_m/E] \exp(E/kT_m) \] (3)

The afterglow of PLUM material is of the order of few minutes/hours, a fact that can be easily demonstrated by use of Eq. (4) [10]:

\[ \tau = s^{-1} \exp\left( \frac{E}{kT} \right) \] (4)

where, \( \tau \) is the lifetime of the charge in the trap, \( T \) is the storage temperature = 300 K (approx.), and \( k \) is the Boltzmann constant.

---

Fig. 2 Glow curves of Ba\(_2\)MgSi\(_2\)O\(_7\):Eu\(^{3+}\), Dy\(^{3+}\) for different UV exposure times
<table>
<thead>
<tr>
<th>UV exposure time (min)</th>
<th>Heating rate ($\beta$) (K s$^{-1}$)</th>
<th>$T_1$ (K)</th>
<th>$T_m$ (K)</th>
<th>$T_2$ (K)</th>
<th>$\tau$</th>
<th>$\delta$</th>
<th>$\omega$</th>
<th>Shape factor $\mu = \delta/\omega$</th>
<th>Activation energy ($E$)</th>
<th>Frequency factor ($s$)</th>
<th>Lifetime of charge in the trap ($\tau$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>5</td>
<td>349.67</td>
<td>374.76</td>
<td>418.67</td>
<td>25.09</td>
<td>43.91</td>
<td>69.00</td>
<td>0.64</td>
<td>0.55</td>
<td>$5.5 \times 10^6$</td>
<td>348.30</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>355.64</td>
<td>382.69</td>
<td>423.32</td>
<td>27.05</td>
<td>40.63</td>
<td>67.68</td>
<td>0.60</td>
<td>0.59</td>
<td>$1.2 \times 10^7$</td>
<td>660.83</td>
</tr>
<tr>
<td>15</td>
<td>5</td>
<td>349.67</td>
<td>375.67</td>
<td>418.78</td>
<td>26.00</td>
<td>43.11</td>
<td>69.11</td>
<td>0.62</td>
<td>0.55</td>
<td>$5.6 \times 10^6$</td>
<td>368.85</td>
</tr>
<tr>
<td>20</td>
<td>5</td>
<td>350.64</td>
<td>377.05</td>
<td>418.75</td>
<td>26.41</td>
<td>41.70</td>
<td>68.11</td>
<td>0.61</td>
<td>0.57</td>
<td>$8.1 \times 10^6$</td>
<td>428.76</td>
</tr>
</tbody>
</table>
Results and discussion

Determination of kinetic data

Trapping properties, for example trap depth ($E$), frequency factor ($s$), and order of kinetics ($b$), for the glow peaks were obtained under ultraviolet excitation. TL glow curves of Ba$_2$MgSi$_2$O$_7$:Eu$^{3+}$, Dy$^{3+}$ phosphor are indicative of second-order kinetics. Figure 2 illustrates TL glow curves obtained after UV irradiation of the phosphor for different exposure times.

All the glow curves contained two peaks, with the peak formed at lower temperature being more prominent. The presence of two emission centers can be assumed and the high-temperature peak should be regarded as extrinsic, because of introduction of the Dy$^{3+}$ co-dopant into the basic Sr$_2$MgSi$_2$O$_7$:Eu material [9]. The low-temperature peak arises because of transition between the ground and excited energy levels of the dopant ion Eu$^{3+}$. We used the prominent peak to calculate kinetic data.

At a heating rate 5 °C s$^{-1}$ dominant peaks in the glow curves are observed at approximately 101.76, 109.69, 102.67, and 104.05 °C, respectively, after UV exposure for 5, 10, 15 and 20 min. It is seen that intensity increases with increasing UV exposure time.

From Table 1 it is readily apparent how peak temperature varies with UV exposure; the shape factor, activation energy, and frequency factor are also shown in the same table [5, 6]. Trap depth of the phosphor was also calculated, by use of different methods (Table 2) [7].
Evaluation of the material for persistent luminescence

If the afterglow is to be strong, it is obvious trap density must be high. The trap depth estimated for most PLUM materials is in the range 0.50–1.25 eV, as reported by Mashangva et al. [10] and shown in Table 3.

The calculated activation energy varied from 0.55 to 0.89 eV. This indicates that Ba₂MgSi₂O₇:Eu, Dy is a good PLUM phosphor.

We also calculated the lifetime (τ) of charge in the trapping level by use of Eq. (4). It was found to be in the range of a few minutes, i.e. 348.30, 660.83, 368.85, and 428.76 s for 5, 10, 15, and 20 min of UV exposure, respectively, which is one characteristic of long-lasting phosphors (LLP).

**Conclusion**

1 Glow curves for Ba₂MgSi₂O₇:Eu⁺³, Dy³⁺ were indicative of second-order kinetics.
2 Intensity increases with increasing UV exposure time.
3 Trap depths were in the range 0.557 to 0.893 eV.
4 The frequency factor varied from $5.5 \times 10^6$ to $1.2 \times 10^7$ s⁻¹.
5 Lifetime of charges in the trap were in the range 348 to 660 s.
6 The material can be regarded as a PLUM because:
   a. Trap density is high.
   b. Trap depth is in the range 0.50 to 1.2 eV, as is observed in practice for most long-lasting phosphors.
   c. Lifetime of charges in the trap is of the order of few minutes/hours.

**Reference**