

Synthesis of $\text{Ca}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} activated and Ce^{3+} doped Phosphor for Energy Storage

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Abstract:

The Eu^{2+} activated and Ce^{3+} doped $\text{Ca}_2\text{MgSi}_2\text{O}_7$ phosphor is prepared via high temperature solid state reaction. The phase identification shows that the calcining temperature of this material is 1200°C . The photoluminescence analysis presents $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Ce}^{3+}\text{Eu}^{2+}$ phosphor exhibits a prominent emission band around 470nm . The Thermoluminescence (TL) analysis observed that it has been a single glow peak was occurred in all the TL glow curves of $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+},\text{Ce}^{3+}$ codoped phosphor . The single isolated peak due to the formation of only one type of luminescence centre which is created due to the UV irradiation So the application of this material can be extended.

Key Words: Photoluminescence , Thermoluminescence and kinetic parameters

Introduction:

Persistent luminescence is an optical process in which a material is excited with high energy radiation like ultraviolet light, beta rays can also be used and the resulting visible luminescent emission remains visible for an appreciable time – from seconds to many hours - after the excitation has stopped. The effect is also called phosphorescence, afterglow. A wide variety of host materials are used as luminescent compounds, but when it comes to persistent luminescence, the number of known hosts is relatively low. The majority of research on this phenomenon is concentrated around the aluminates, with SrAl_2O_4 as most famous representative, and the silicates, represented by $\text{Ca}_2\text{MgSi}_2\text{O}_7$. Alkaline earth akermanites family $\text{M}_2\text{MgSi}_2\text{O}_7$ ($\text{M} = \text{Ca},\text{Sr},\text{Ba}$) materials presenting afterglow mechanisms, and they are the most widely studied persistent luminescent silicates. But only few host crystals have been found to exhibit persistent luminescence with Eu^{2+} activators. $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+},\text{Ce}^{3+}$ has a much brighter and longer afterglow than their non-codoped variants. In this research paper, $\text{Ca}_2\text{MgSi}_2\text{O}_7$ phosphors with the various concentration ratio of dopant and co-dopant were prepared using the solid state reaction. The Photoluminescence (PL) studies were done to identify the long lasting phosphor. Thermoluminescence (TL) glow curve of the phosphor were observed. Charge carrier traps play a important role in persistent luminescence mechanisms. One of their main properties is their the activation energy required to release a captured charge carrier. Shallow traps (with a depth lower than around 0.4 eV are fully emptied at low temperatures, and do not dynamically take part in processes at room temperature. Very deep traps (around 2 eV or deeper, on the other hand, require more energy to be emptied than is available at room temperature. Therefore, charge carriers caught by these traps remain there until the material is sufficiently heated. To observe persistent luminescence at room temperature, the traps should have suitable activation energy somewhere between these two extremes (a trap depth around 0.65 eV is considered to be optimal . In this paper, we will also observed that the nature of the trapped charge carriers. (electrons or holes) is still subject of discussion.

Material and Method:

Synthesis of rare earth codoped sample ($\text{Ca}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}, \text{Ce}^{3+}$) was prepared by solid state diffusion reaction method. The phosphor $\text{Ca}_2\text{MgSi}_2\text{O}_7$ is prepared from the compounds calcium carbonate (CaCO_3) and magnesium oxide (MgO), SiO_2 and CeO_2 , Eu_2O_3 . The prepared phosphor $\text{Ca}_2\text{MgSi}_2\text{O}_7$ is weighed and grounded into a fine powder using agate mortar and pestle about an hour. The grounded mixture was placed in an alumina crucible and heated from room temperature to 1200°C in a muffle furnace with a heating rate of $5^\circ\text{C}/\text{min}$. After reaching 1200°C the phosphor heated for 3 hours and the furnace was allowed to cool to room temperature along with the samples. Photoluminescence was recorded by RF-5301 PC SHIMADZU Spectrofluorophotometer (RF 5301 PC). Emission and excitation were recorded using a 1.5 nm width of spectral slit. The thermoluminescence glow curve was recorded using a TL 10091, NUCLEONIX spectroscopy, which used a 254 nm UV lamp and had a heater that heated up to 600°C . The sample typically weighs around 30 milligrams.

Result and Discussions:**Photoluminescence :**

Fig. shows the excitation and emission spectra of $\text{Ca}_2\text{MgSi}_2\text{O}_7: \text{Ce}^{3+}\text{Eu}^{2+}$ phosphor. From the figure $\text{Ca}_2\text{MgSi}_2\text{O}_7: \text{Ce}^{3+}\text{Eu}^{2+}$ phosphor exhibits a prominent emission band around 470 nm. The position and shape of the emission spectra of $\text{Ca}_2\text{MgSi}_2\text{O}_7: \text{Ce}^{3+}\text{Eu}^{2+}$ phosphor are approximately same with Eu^{2+} doped that phosphor. But from the fig. It can be also observed that Ce_2O_3 co-doping enhanced the luminescence intensity of Eu^{2+} doped host lattice ($\text{Ca}_2\text{MgSi}_2\text{O}_7: \text{Ce}^{3+}\text{Eu}^{2+}$) which implies that Ce^{3+} can efficiently transfer the absorbed energy to Eu^{2+} . From the above results, related to the enhancement in PL emissions on adding Ce^{3+} to $\text{Ca}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}$ phosphor, we could observe that some form of energy transfer taking place with Ce^{3+} ions acting as sensitizers and Eu^{2+} ions as activators. A method that can be used to demonstrate the occurrence of energy transfer is to measure the excitation spectrum of the emission from the activator. If the excitation spectrum of the activator emission shows the excitation bands of the sensitizer in addition to those of the activator, it indicates energy transfer from the sensitizer to the activator, since the excitation energy is absorbed by the sensitizer and emitted by the activator. However, in the present co-doped sample, the excitation spectrum of the emission of Eu^{2+} ion not only contains its excitation bands at 242 nm, 270 nm and 325 nm. Generally energy transfer occurs only when the emission band of sensitizer overlaps spectrally with the absorption band of activator.

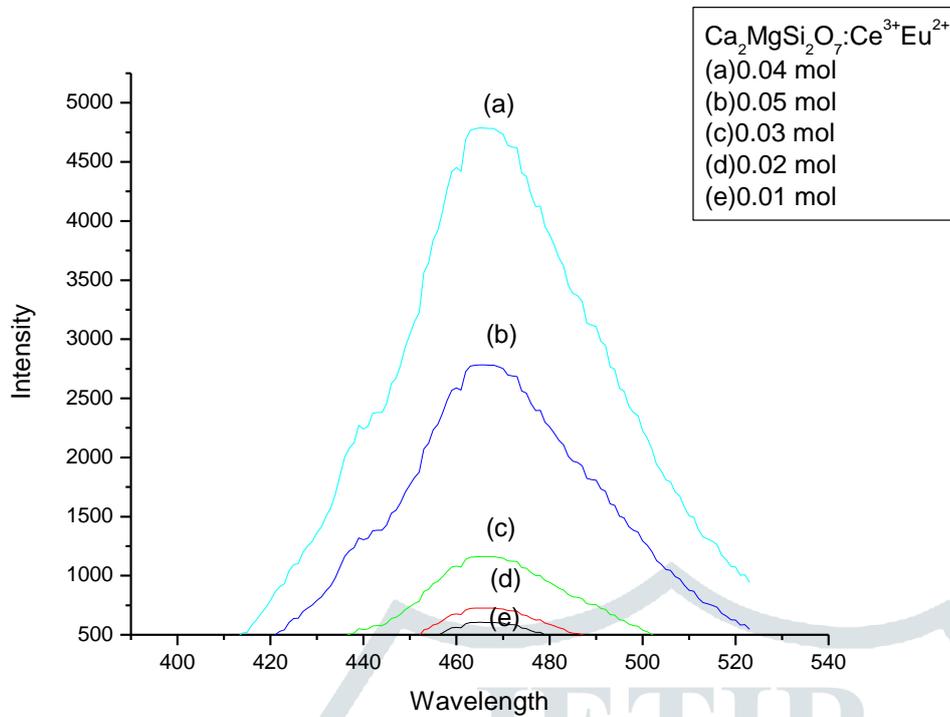


Fig: Emission spectra of Ca₂MgSi₂O₇:Ce³⁺Eu²⁺ sample.

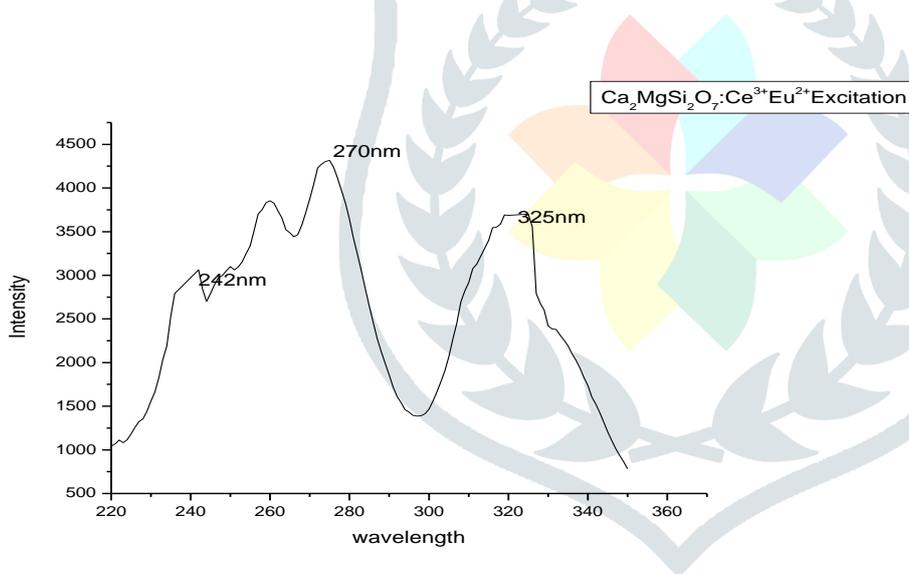


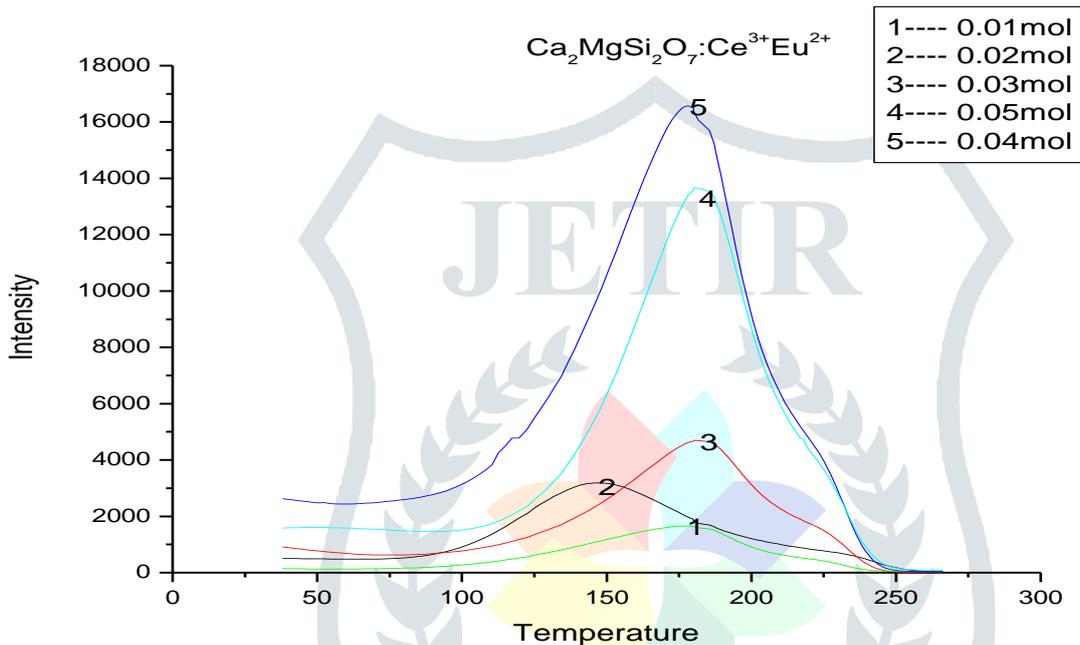
Fig : Excitation Spectra of Ca₂MgSi₂O₇:Ce³⁺Eu²⁺ doped phosphor

Thermoluminescence:

The thermo-luminescence (TL) glow curve of Ce³⁺Eu²⁺ co-doped Ca₂MgSi₂O₇ phosphors with different concentration were recorded and are shown in fig. In the fig, all the TL glow curve were first irradiated for 5min using UV source, then after radiation source was switch off and the irradiated sample were heated at a linear heating rate of 5⁰C/S , from room temperature to 250⁰C. From the fig, initially the TL intensity increases with the temperature, attains a peak value for a particular temperature and then decreases with further increase in temperature. All the TL glow curves recorded exhibit rich structure and substantial

intensity in the range from 50 °C to 250°C. The depth of traps of prepared sample was calculated using glow peak method and half width method.

Ce ³⁺ concentration	Eu ²⁺ concentration	T ₁ (°C)	T _M (°C)	T ₂ (°C)	τ (K)	δ(K)	ω (K)	μ	E(e V)	E (e V)
0.01 mol		114.98	122.5	188.16	7.52	65.66	73.18	0.89	0.58	0.56
0.02 mol		136.43	176.45	202.1	40.02	25.65	65.67	0.40	0.58	0.59
0.03 mol		145.93	180.25	209.18	34.32	28.93	63.25	0.46	0.91	1.2
0.04 mol		141.2	178.1	202.1	36.9	24	60.9	0.39	0.65	0.64
0.05 mol		150.62	180.25	205.68	29.63	25.43	8.23	0.46	1.1	1.3



Conclusion: Ce³⁺Eu²⁺ co-doped Ca₂MgSi₂O₇ phosphors Eu were successfully prepared by using the solid state reaction. A study of thermoluminescence properties of Eu²⁺,Ce³⁺ codoped Ca₂MgSi₂O₇ phosphors , it has been observed that , a single glow peak was occurred in all the TL glow curves of Ca₂MgSi₂O₇: Eu²⁺,Ce³⁺ codoped phosphor . The single isolated peak due to the formation of only one type of luminescence centre which is created due to the UV irradiation. Calculated activation energy of the phosphor shows that the phosphor is a quite good persistent luminescent material. Ce³⁺Eu²⁺ co-doped Ca₂MgSi₂O₇ phosphors show afterglow properties. The PL spectra of Ce³⁺ Eu²⁺ co- doped sample it has been observed that, emission spectra of the prepared samples is (in the shape and position) approximately same with the single doped rare earth ions in host lattice . But this case, enhanced the emission intensity by Ce³⁺ can transfer absorbed energy to Eu²⁺ ion respectively.

References:

- 1.. Hoogenstraaten W., Klasens H.A. Some properties of zinc sulfide activated with copper and cobalt. J. Electrochem. Soc. 1953;100:366–375. doi: 10.1149/1.2781134. [[CrossRef](#)] [[Google Scholar](#)]
2. Yen W.M., Shionoya S., Yamamoto H. Phosphor Handbook. 2nd ed. CRC Press/Taylor and Francis; Boca Raton, FL, USA: 2007. [[Google Scholar](#)]

3. Wang D., Yin Q., Li Y., Wang M. Concentration quenching of Eu^{2+} in $\text{SrO}\cdot\text{Al}_2\text{O}_3\text{:Eu}^{2+}$ phosphor. *J. Lumines.* 2002;97:1–6. doi: 10.1016/S0022-2313(01)00413-6. [[CrossRef](#)] [[Google Scholar](#)]
5. Matsuzawa T., Aoki Y., Takeuchi N., Murayama Y. A new long phosphorescent phosphor with high brightness, $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+},\text{Dy}^{3+}$. *J. Electrochem. Soc.* 1996;143:2670–2673. doi: 10.1149/1.1837067. [[CrossRef](#)] [[Google Scholar](#)]
6. Abbruscato V. Optical and electrical properties of $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}$. *J. Electrochem. Soc.* 1971;118:930–933. doi: 10.1149/1.2408226. [[CrossRef](#)] [[Google Scholar](#)]
7. Takasaki H., Tanabe S., Hanada T. Long-lasting afterglow characteristics of Eu, Dy codoped $\text{SrO}\cdot\text{Al}_2\text{O}_3$ phosphor. *J. Ceram. Soc. Jpn.* 1996;104:322–326. doi: 10.2109/jcersj.104.322. [[CrossRef](#)] [[Google Scholar](#)]
8. Lin Y., Tang Z., Zhang Z., Wang X., Zhang J. Preparation of a new long afterglow blue-emitting $\text{Sr}_2\text{MgSi}_2\text{O}_7$ -based photoluminescent phosphor. *J. Mater. Sci. Lett.* 2001;20:1505–1506. doi: 10.1023/A:1017930630889. [[CrossRef](#)] [[Google Scholar](#)]
9. Aitasalo T., Hölsä J., Jungner H., Lastusaari M., Niittykoski J. Mechanisms of persistent luminescence in Eu^{2+} , RE^{3+} doped alkaline earth aluminates. *J. Lumines.* 2001;94–95:59–63. doi: 10.1016/S0022-2313(01)00279-4. [[CrossRef](#)] [[Google Scholar](#)]
10. Dorenbos P. Mechanism of persistent luminescence in Eu^{2+} and Dy^{3+} codoped aluminate and silicate compounds. *J. Electrochem. Soc.* 2005;152:H107–H110. doi: 10.1149/1.1926652. [[CrossRef](#)] [[Google Scholar](#)]
11. Blasse G., Grabmaier B.C. *Luminescent Materials*. Springer-Verlag; Berlin, Germany: 1994. [[Google Scholar](#)]
12. Poelman D., Avci N., Smet P.F. Measured luminance and visual appearance of multi-color persistent phosphors. *Opt. Express.* 2009;17:358–364. doi: 10.1364/OE.17.000358. [[PubMed](#)] [[CrossRef](#)] [[Google Scholar](#)]
13. Clabau F., Rocquefelte X., Jobic S., Deniard P., Whangbo M.H., Garcia A., Le Mercier T. On the phosphorescence mechanism in $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}$ and its codoped derivatives. *Solid State Sci.* 2007;9:608–612. doi: 10.1016/j.solidstatesciences.2007.03.020. [[CrossRef](#)] [[Google Scholar](#)]
14. Schulze A.R., Buschbaum H.M. Zur Verbindungsbildung von $\text{MeO}:\text{M}_2\text{O}_3$. IV. Zur Struktur von monoklinem SrAl_2O_4 . *Z. Anorg. Allg. Chem.* 1981;475:205–210. doi: 10.1002/zaac.19814750423. [[CrossRef](#)] [[Google Scholar](#)]
15. Lange H. Luminescent Europium Activated Strontium Aluminate. 3,294,699. US patent. 1966
16. Blasse G., Bril A. Fluorescence of Eu^{2+} -activated alkaline-earth aluminates. *Philips Res. Rep.* 1968;23:201–206. [[Google Scholar](#)]
17. Katsumata T., Nabae T., Sasajima K., Komuro S., Morikawa T. Effects of composition on the long phosphorescent $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+},\text{Dy}^{3+}$ phosphor crystals. *J. Electrochem. Soc.* 1997;144:L243–L245. doi: 10.1149/1.1837931. [[CrossRef](#)] [[Google Scholar](#)]
18. Hölsä J., Jungner H., Lastusaari M., Niittykoski J. Persistent luminescence of Eu^{2+} doped alkaline earth aluminates, $\text{MAl}_2\text{O}_4\text{:Eu}^{2+}$. *J. Alloy. Compd.* 2001;323–324:326–330. doi: 10.1016/S0925-8388(01)01084-2. [[CrossRef](#)] [[Google Scholar](#)]

19. Katsumata T., Nabae T., Sasajima K., Matsuzawa T. Growth and characteristics of long persistent SrAl₂O₄- and CaAl₂O₄-based phosphor crystals by a floating zone technique. *J. Cryst. Growth.* 1998;183:361–365. doi: 10.1016/S0022-0248(97)00308-4. [[CrossRef](#)] [[Google Scholar](#)]
20. Lin Y., Tang Z., Zhang Z., Nan C. Influence of co-doping different rare earth ions on the luminescence of CaAl₂O₄-based phosphors. *J. Eur. Ceram. Soc.* 2003;23:175–178. doi: 10.1016/S0955-2219(02)00080-8. [[CrossRef](#)] [[Google Scholar](#)]
21. Lin Y., Zhang Z., Tang Z., Zhang J., Zheng Z., Lu X. The characterization and mechanism of long afterglow in alkaline earth aluminates phosphors co-doped by Eu₂O₃ and Dy₂O₃. *Mater. Chem. Phys.* 2001;70:156–159. doi: 10.1016/S0254-0584(00)00500-9. [[CrossRef](#)] [[Google Scholar](#)]
22. Sakai R., Katsumata T., Komuro S., Morikawa T. Effect of composition on the phosphorescence from BaAl₂O₄: Eu²⁺, Dy³⁺ crystals. *J. Lumines.* 1999;85:149–154. doi: 10.1016/S0022-2313(99)00061-7. [[CrossRef](#)] [[Google Scholar](#)]

