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TL Glow Curve Study, Kinetics, PL and XRD Analysis of Mn^{2+} Doped $CaAl_2O_4$ Phosphors

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ABSTRACT

The present paper reports Thermoluminescence (TL) Glow curve of Mn^{2+} doped $CaAl_2O_4$ phosphor with different UV exposure time. The Glow peak shows general order kinetics and evaluation of kinetic parameters was done by peak shape method. Calculations of Trap Depth were done with Chen's different methods and order of kinetics, activation energy and frequency factor are calculated. The recorded glow curve shifts towards higher temperature with increasing intensity as a function of UV exposure time until 30 minutes where it is seen that the peak shifts towards low temperature side and intensity also decreases. The peaks were found at 345˚C, 356.83˚C, 358˚C and 356.73˚C respectively using the heating rate 6.7˚C/s. The PL (photoluminescence) excitation spectra show peaks at 248 nm and 362 nm whereas emission spectra shows peaks between 364 nm and 551 nm. Sample was characterized by XRD technique.

Keywords: Phosphors; Photoluminescence; Thermoluminescence; Kinetic Parameters; Trap Depth

1. Introduction

Rare earth and non-rare earth doped inorganic phosphors are widely used in a variety of applications, such as lamp industry, radiation dosimetry, X-ray imaging, and color display [1]. Major applications of the phosphors are in fluorescent lamps and emission display devices such as Electroluminescence Panels (EL), Plasma Display Panels (PDP), Field Emission Displays (FED) and so on [2,3]. This has revived interest in the research on new methods of phosphor synthesis in recent years. Mn^{2+} luminescence can be useful in obtaining a low cost green or red emitting phosphor. Rare earth doped aluminate phosphors are of special interest, since they show long phosphorescence and a short-time decay depending on the differing conditions of preparation used [4,5]. In recent years, calcium aluminates ($CaAl_2O_4$) have been the subject of many investigations primarily due to the fact that this compound has several interesting technological applications. For example, $CaAl_2O_4$ is the main phase in Calcium Aluminate Cements. Crystalline Calcium Aluminate is being used in high strength and high toughness ceramic—polymer composite materials. For some years, new application for Calcium Aluminates has emerged in bioceramics, optical-ceramics, catalyst support and structural ceramics. As a part of our research on phosphor materials an attempt is made to prepare Mn^{2+} doped $CaAl_2O_4$ phosphor which shows a high TL intensity.

2. Experimental Method

By solid state reaction process, $CaCO_3$, Al_2O_3, $MnCO_3$ and CaF_2 were mixed in stoichiometric ratio by dry grinding in mortar and pestle for nearly 45 minutes. The mixture is taken in quartz boats and is fired in air at 1300˚C for 1 hour. The sample is then irradiated by UV radiation 365 nm source. The heating rate used for TL measurement is 6.7˚C/s. The glow curves were recorded by using TLD reader I1009 supplied by Nucleonix Sys. Pvt Ltd. Hyderabad [6,7]. The curves were analyzed by using computerized glow curve deconvolution program. The sample was characterized by XRD. The XRD measurements were carried out using Bruker D8 Advance X-ray diffractometer. The x-rays were produced using a sealed tube and the wavelength of x-ray was 0.154 nm (Cu K-alpha). The x-rays were detected using a fast counting detector based on Silicon strip technology (Bruker Lynx-Eye detector). The particle size was calculated using the Debye-Scherrer formula. The excitation and emission spectra were taken with the help of spectrofluorophotometer.

3. Result and Discussion

3.1. XRD Pattern of $CaAl_2O_4$: Mn^{2+} Doped Phosphor

The XRD pattern of the sample is shown in **Figure 1**,

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which confirms that the sample is $CaAl_2O_4$: Mn^{2+} doped phosphor. It shows the monoclinic structure match with JCPDS card no. 88-2477. Eleven different peaks are obtained at 2θ values of 23.42˚, 27.85˚, 29.8˚, 33.43˚, 35.1˚, 36.73˚, 41.24˚, 46.74˚, 55.27˚, 57.58˚ and 67.22˚. This shows that the sample have monoclinic structure. The XRD peaks correspond to Bragg diffraction at (111), (200), (210), (211), (221/300), (311), (400), (322/410) and (332) planes of Monoclinic. The sharp peaks indicate microcrystalline behavior of the $CaAl_2O_4$: Mn^{2+} sample. **Table 1** gives various Bragg reflections that are indexed using JCPDS Files card 88-2477 and the calculated unit cell dimensions of $CaAl_2O_4$: Mn^{2+}. Inter-planar distance "d" calculated by Debye-Scherrer formula:

$$d = \frac{0.9\lambda}{\beta\cos\theta}$$

Here λ is wavelength of X-ray source, β is FWHM (Full width half maximum) of XRD pattern and θ is angle of diffraction. The value of inter-planar distance was found to be 8.09 nm.

3.2. PL Studies of $CaAl_2O_4$: Mn^{2+} Doped Phosphor

Figure 2 shows the excitation spectrum having the peak at 248 nm and 362 nm when given 400 excitation wavelengths. **Figure 3** shows the emission spectra which has the peak at 364 nm, 397 nm, 450 nm, 466 nm, 491 nm and 551 nm when given excitation 254 nm.

3.3. TL Glow Curve and Kinetic Parameter of $CaAl_2O_4$: Mn^{2+} Doped Phosphor

The kinetic parameters of Mn^{2+} doped $CaAl_2O_4$ phosphor with different UV exposure time were calculated. The TL glow curve of Mn^{2+} doped $CaAl_2O_4$ shows general order kinetics. The UV irradiation of 365 nm is given to the phosphor. Every time 5 mg of irradiated sample was taken for TL measurements. **Figure 4** shows the comparative study of TL glow curve of Mn^{2+} doped $CaAl_2O_4$ phosphor as a function of UV exposure time. It is seen that TL glow curve shifts towards higher temperature with increased intensity, when the irradiation exposure time is increased. The peak were found at 345˚C, 356.83˚C, 358˚C and 356.73˚C respectively. **Table 2** shows the various parameters like shape factor (μ), activation energy, and frequency factor of different UV exposure time. **Table 3** shows the trap depth calculations obtained from General order kinetics.

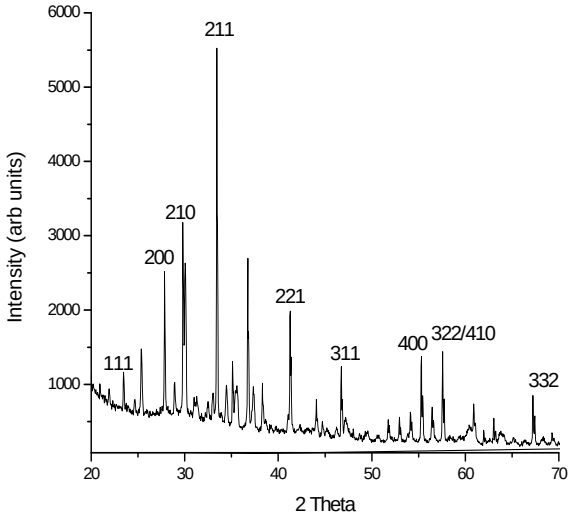

Figure 1. XRD pattern of $CaAl_2O_4$: Mn^{2+} doped Phosphor.

Table 1. Indexing of X-Ray Diffraction Pattern (Monoclinic Structure).

Material	$CaAl_2O_4$ (Calcium Aluminate)				Wave Length	1.54	FWHM	0.159
Peak	**2θ(observed)**	**2θ(Standard)**	**2θ(difference)**	**$h^2 + k^2 + l^2$**	**hkl**	**d spacing (Observed) (A˚)**	**d spacing (Calculated) (A˚)**	**Difference (d spacing) (A˚)**
1	23.42	23.97	–0.55	3	111	8.525	8.516	0.009
2	27.85	27.93	–0.08	4	200	8.450	8.449	0.001
3	29.8	30.06	–0.26	5	210	8.413	8.408	0.005
4	33.43	30.1	3.33	6	211	8.338	8.407	–0.069
5	35.1	35.46	–0.36	7	-	8.301	8.293	0.008
6	36.73	37.21	–0.48	7	-	8.263	8.251	0.012
7	41.24	41.04	0.2	9	221/300	8.148	8.154	–0.005
8	46.74	46.37	0.37	11	311	7.992	8.003	–0.011
9	55.27	54.55	0.72	16	400	7.713	7.738	–0.025
10	57.58	57.43	0.15	17	322/410	7.630	7.635	–0.005
11	67.22	68.27	–1.05	22	332	7.251	7.206	0.044

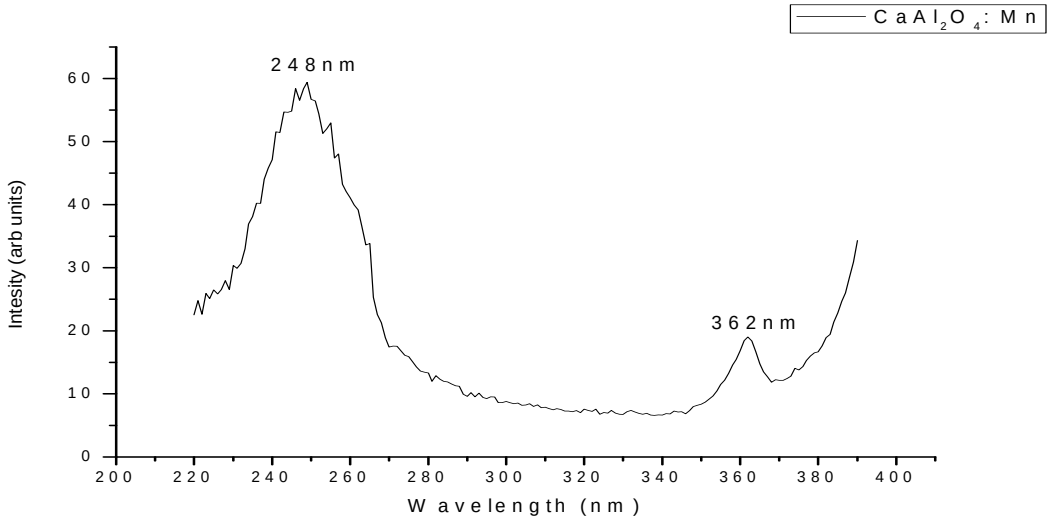

Figure 2. PL excitation spectra of Mn^{2+} doped $CaAl_2O_4$ phosphor with 400 nm excitation.

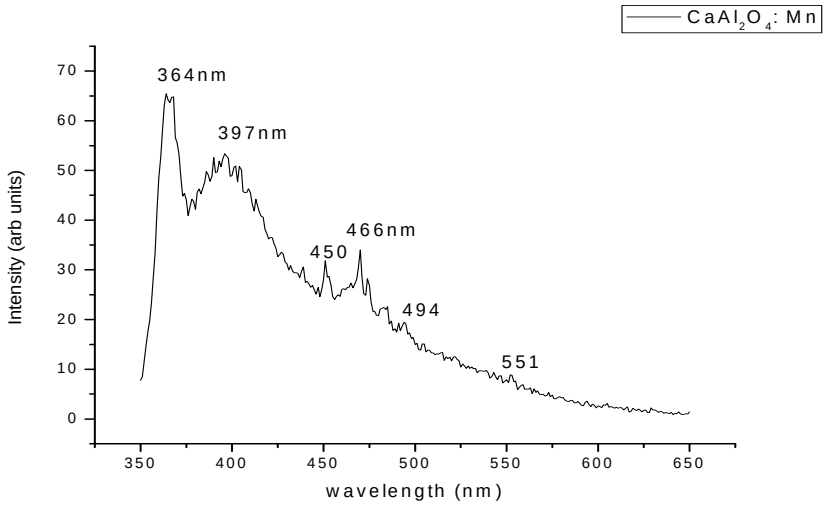

Figure 3. PL emission spectra of Mn^{2+} doped $CaAl_2O_4$ phosphor with 254 nm excitation.

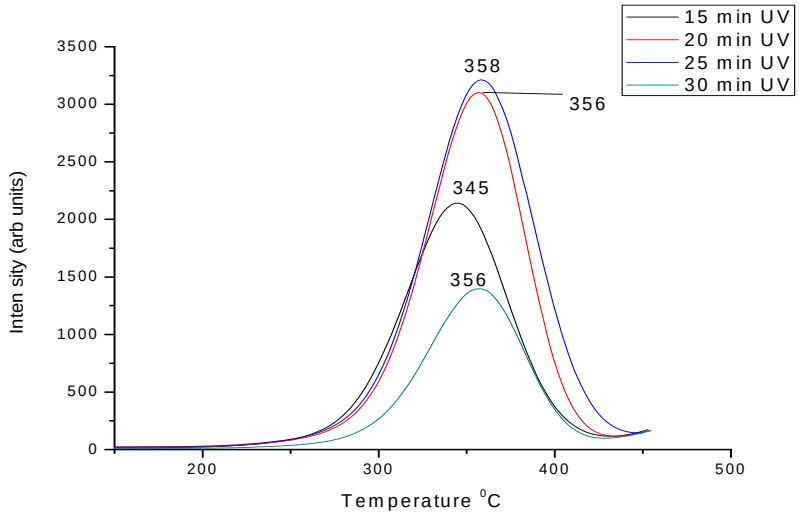

Figure 4. Comparative study of TL glow curve of $CaAl_2O_4$ Mn^{2+} doped with different UV exposure time.

Table 2. Evaluation of kinetic parameters such as activation energy (E), frequency factor S and shape factor (μ) $CaAl_2O_4$: Mn^{2+} doped phosphor.

UV in min	T_1(˚C)	T_m(˚C)	T_2(˚C)	τ	δ	ω	$\mu = \delta/\omega$	Activation energy E in (eV)	Frequency factor S in sec^{-1}
15	309.5	345.6	379.02	36.12	33.4	69.52	0.48	1.36	1.60×10^{12}
20	323	356.8	387.76	33.8	30.93	64.73	0.47	1.51	1.65×10^{13}
25	322.3	358.1	392.57	35.82	34.46	70.28	0.49	1.43	3.60×10^{12}
30	323	356.7	387.09	33.77	30.36	64.13	0.47	1.51	1.65×10^{13}

Table 3. Calculation of Trap Depth using Chen's different Methods.

Methods	15 min UV	20 min UV	25 min UV	30 min UV
$E_\tau = c_\tau\left(\frac{kT_m^2}{\alpha}\right) - b_\tau\left(2kT_m\right)$	1.35	1.36	1.45	1.49
$E_\omega = c_\omega\left(\frac{kT_m^2}{\alpha}\right) - b_\omega\left(2kT_m\right)$	1.39	1.40	1.48	1.51
$E_\delta = c_\delta\left(\frac{kT_m^2}{\alpha}\right) - b_\delta\left(2kT_m\right)$	1.40	1.43	1.49	1.52

4. Conclusion

It has been concluded that the Mn^{2+} doped $CaAl_2O_4$ phosphor is monoclinic in structure, with light emitting in blue-green region of electromagnetic spectrum. The value of inter-planar distance was found to be 8.09 nm. The activation energy was calculated to be in the range of 1.36 to 1.51 eV for different UV exposure time. The frequency factor was found to be 1.60×10^{12} to 1.65×10^{13} sec^{-1}.

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