Thermally stimulated luminescence studies of undoped and doped CaB$_4$O$_7$ compounds

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Abstract. Thermoluminescence of undoped and doped CaB$_4$O$_7$ with activators such as Cu and Mn has been investigated. The polycrystalline samples of undoped and doped CaB$_4$O$_7$ are prepared by melting method. The formation of CaB$_4$O$_7$ compound is checked by X-ray diffraction study and the compound is found to have orthorhombic structure at room temperature. The TSL studies of undoped CaB$_4$O$_7$ sample shows two glow peaks at 150°C and 265°C and one shoulder at around 190°C. The TSL studies of Cu doped CaB$_4$O$_7$ sample also shows two glow peaks at 160°C and 270°C and a shoulder at around 230°C whereas the TSL glow curves of Mn doped CaB$_4$O$_7$ has only one single strong glow peak at 135°C. A comparative TSL studies of these compounds shows that CaB$_4$O$_7$ compound doped with Mn is the most sensitive and the TSL intensity is enhanced by about 40 times when compared with the TSL intensity of undoped CaB$_4$O$_7$ compound. The trap parameters namely order of kinetics (b), activation energy (E) and frequency factor (s) associated with the 135°C glow peak of CaB$_4$O$_7$: Mn phosphor are determined using isothermal decay and glow curve shape (Chen's) methods.

Keywords: Calcium borate, X-ray diffraction, thermally stimulated luminescence, trap parameters.

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1. Introduction

Phosphors prepared from inorganic compounds by doping with suitable activator and coactivator impurities are generally polycrystalline which are capable of converting one or more forms of energy into radiation in or close to the visible region of the electromagnetic spectrum. These phosphors find many industrial applications in the manufacture of TV/CRO screens, fluorescent lamps, EL panels, visible light emitting diodes, X-ray imaging, IR sensors, radiation dosimetry, luminescence paints etc. In recent years, significant progress has been made in the development of new materials for radiation dosimetry. These include alkali and alkaline earth tetra borates [1,2]. The following work is undertaken to study the TL mechanism in undoped and doped calcium borate compounds. Thermoluminescence in irradiated sintered CaB$_4$O$_7$ containing activators such as Cu, Pb, Eu or Dy has been first investigated by Fukuda et al [3,4,5]. As the TL glow curves often depend on the activators so it seems interesting to investigate further the effects of other activator such as Mn on the TSL output of polycrystalline CaB$_4$O$_7$ compound.

2. Experimental details

The polycrystalline samples of undoped and doped CaB$_4$O$_7$ were prepared by melting method [6]. The preparation of calcium borate sample has been made by mixing calcium carbonate (99%,Loba Chemie, Bombay) and boric acid (99.5%, s.d. fine-chem Ltd., Boisar) in stoichiometric ratio and the mixture is melted at 900°C in a platinum crucible for 4.5 hours and then cooled at a rate of about 60 K/min. The crystalline material was ground and sieved to a grain size of 200μm. Doped CaB$_4$O$_7$ samples are prepared in a similar manner by taking the starting material in stoichiometric ratio and adding 0.5 wt% of CuCl$_2$ (98%, Loba Chemie, Bombay) or MnCl$_2$ (99.5%, s.d. fine-chem Ltd.,Boisar) in the mixture.

The characterization of CaB$_4$O$_7$ is carried out by X-ray diffraction study. X-ray diffractogram of the compound is taken at room temperature in a wide range of Bragg angle 2θ ($10° \leq 2\theta \leq 80°$) using a X-ray diffractometer type PW 1710, Holland with Cu target and at a scanning rate of 3°/min.

All samples were heated to 400°C for 10 minutes and then quenched to room temperature before X-irradiating

them. The powder samples were irradiated by X-rays obtained from Cu target of Machlett tube operated at 20 kV and 15 mA. The TSL studies were made by using Personal Computer Based Thermoluminescence Analyzer System (type 1007) supplied by Nucleonix Systems Private Limited, Hyderabad, India. The glow curves were recorded by heating the samples at a uniform rate of 4ºC/s with the help of a temperature controller (type 575) made by Nucleonix Systems Private Limited, Hyderabad, India and the luminescence emission was detected by a photo-multiplier tube (type 9924 B) imported from U.K. The photo-current from PM tube is amplified by a DC amplifier (type 552) made by Nucleonix Systems Private Limited, Hyderabad, India which is interfaced to a personal computer. The T S L out put is finally recorded by a printer connected to the personal computer.

3. Results and discussion

3.1 Structural study

In order to ascertain the structure of prepared CaB_4O_7 compound, X-ray diffraction pattern of powder sample CaB_4O_7 is recorded (Fig. 1). The sharp and single diffraction peaks of the XRD pattern suggested the formation of new compound. From the 2θ values of the diffraction lines, interplanar spacing (d) of the peaks was calculated. The diffraction lines were indexed using a computer program package "Powdmult" [7,8]. Out of those a suitable orthorhombic unit cell was selected for which $\Sigma\Delta d (= d_{obs} - d_{cal})$ was found to be minimum. The lattice parameters of the unit cell were refined using least-squares method and were found to be: $a = 27.9159$Å, $b = 3.4790$Å, $c = 6.4198$Å. A good agreement between the observed and calculated d-values (Table 1) suggests the suitability of the crystal structure and unit cell parameters.

3.2 TSL study

Under this study, glow curves of undoped, Cu and Mn doped CaB_4O_7 samples are recorded for the different time of X-irradiation.

The TSL glow curves of CaB_4O_7 powder samples are recorded by X-irradiating at room temperature for 1, 2, 4 and 10 minutes (Fig. 2). The room temperature X-irradiated CaB_4O_7 sample exhibit two glow peaks at temperatures 150 and 265ºC and one shoulder at around 190ºC and the intensity of 150ºC glow peak is the stronger. Moreover the intensities of the glow peaks are found to increase with increase of the X-ray dose. The TSL glow curves of Cu-doped CaB_4O_7 powder sample are recorded by X-irradiating at room temperature for 1, 3 and 5 minutes (Fig. 3). The T S L glow curves of X-irradiated CaB_4O_7 : Cu exhibit two glow peaks at 160 and 270ºC and one shoulder at around 230ºC and the intensity of 160ºC glow peak is the higher. In this case also the intensities of glow peaks are found to increase with the increase of X-ray dose. The TSL glow curves of Mn doped CaB_4O_7 powder sample are recorded by X-irradiating at room temperature for 10,20,30,45 and 60 seconds (Fig. 4). The TSL glow curves of X-irradiated CaB_4O_7 : Mn exhibit only one strong TL glow peak at the temperature of 135ºC. It is observed that in this case also, the glow peaks grow in intensities with the increase of X-ray dose.

The TL glow curves of both undoped and Cu doped CaB_4O_7 compounds shows two glow peaks indicating that two different species of traps are being activated within the particular temperature range each with its own value
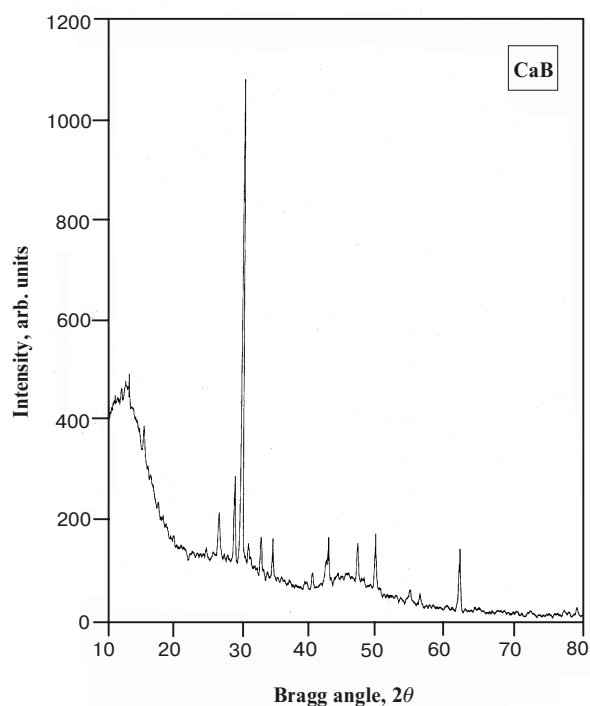
Table 1. Comparison of observed and calculated d-values (Å) of some reflections of CaB_4O_7 sample at room temperature.

h	k	l	d_{obs}	d_{cal}	I/I_0*100
1	1	0	3.4531	3.4522	44
0	2	0	1.7399	1.7395	19
0	0	4	1.6053	1.6050	25
8	2	0	1.5559	1.5568	100
3	2	2	1.5100	1.5091	14
19	0	1	1.4308	1.4302	16
7	1	4	1.3680	1.3688	15
11	2	3	1.1919	1.1971	9
0	3	1	1.1411	1.1412	14
4	0	6	1.0575	1.0576	15
14	2	4	1.0153	1.0151	15
27	1	2	0.9469	0.9470	6
30	1	0	0.8989	0.8989	5
28	1	3	0.8747	0.8747	12

Fig. 1. XRD pattern of CaB_4O_7 sample at room temperature.

of activation energy (E) and frequency factor (s). Comparison of intensities of glow peaks (Fig. 5) shows that addition of Cu impurity to undoped CaB_4O_7 enhance the TL intensity by a very small amount.

The Mn doped CaB_4O_7 compound shows only one single strong TL glow peak indicating that only one species of traps are being activated at a particular temperature with its activation energy (E) and frequency factor (s). Moreover this glow peak is observed at some low temperature compared to undoped and Cu doped CaB_4O_7 compounds. Comparison of intensity of glow peak (Fig. 5)

in Mn doped CaB_4O_7 compound shows that addition of Mn impurity to undoped CaB_4O_7 compound enhances the TL intensity by about 40 times.

It has been suggested that glow peak observed at 135ºC in CaB_4O_7 : Mn is peculiar to Mn activator and is related to the relaxation of the excited Mn^{++} ions. Upon irradiation, Mn^{++} ions capture one or two electrons to become Mn^+ or Mn^0.
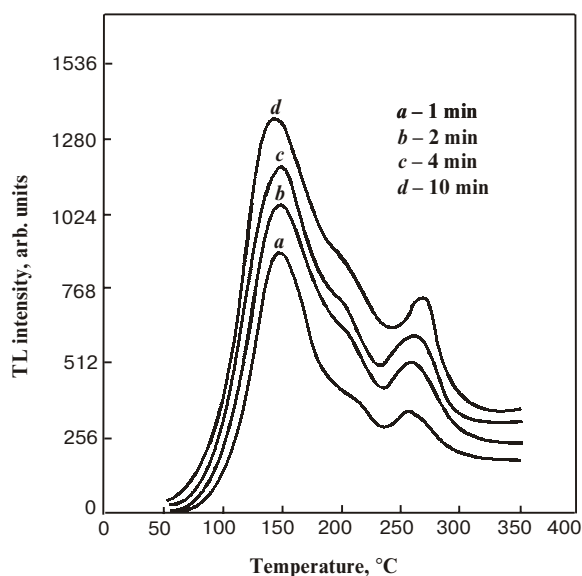
$$Mn^{++} + electron \rightarrow Mn^+$$
$$Mn^{++} + 2\,electron \rightarrow Mn^0$$

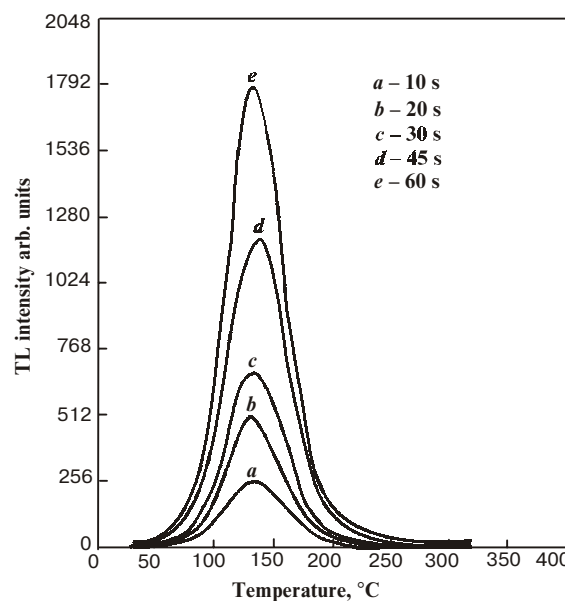**Fig. 2.** TSL glow curves of CaB_4O_7 sample for different times of X-irradiation.

Fig. 4. TSL glow curves of CaB_4O_7:Mn sample for different times of X-irradiation.

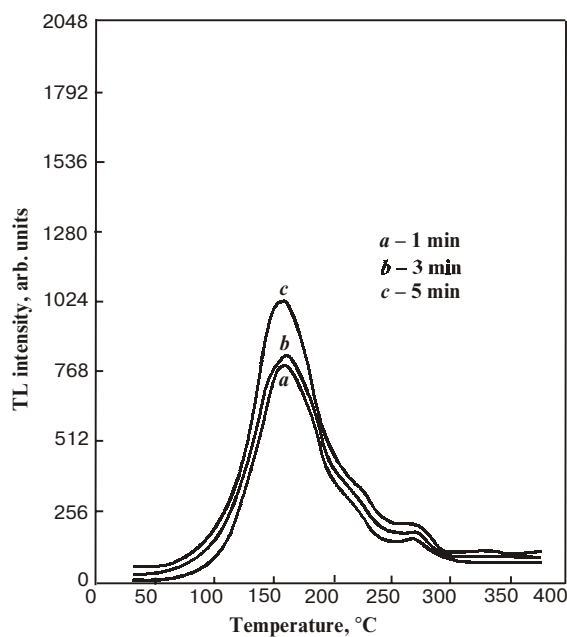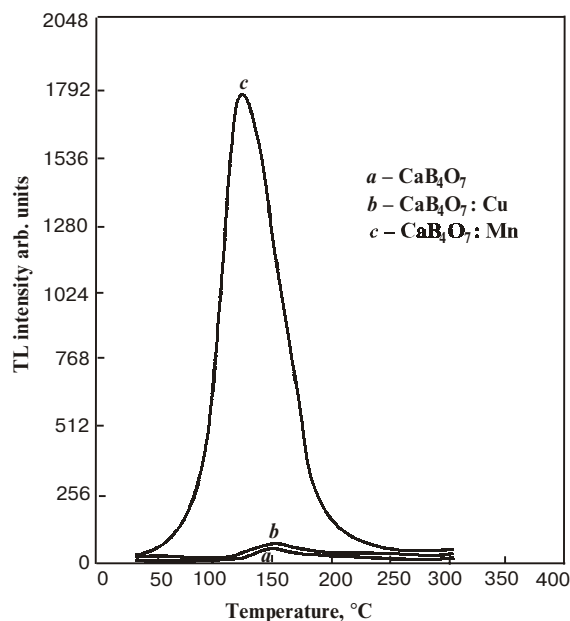**Fig. 3.** TSL Glow curves of CaB_4O_7: Cu sample for different times of X-irradiation.
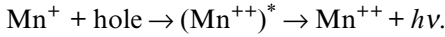

Fig. 5. Comparative TSL glow curves of undoped Cu and Mn doped culcium borate samples.

On thermal stimulation, Mn^+ ions give rise to TSL emission according to the following mechanism:

$$Mn^+ + hole \rightarrow (Mn^{++})^* \rightarrow Mn^{++} + h\nu.$$

Whereas in case of Mn^0 atoms, thermal stimulation gives rise to TSL emission according to the following mechanism:

$$Mn^0 + 2\,hole \rightarrow (Mn^{++})^* \rightarrow Mn^{++} + h\nu$$

The increase in the intensities of the glow curves with increase of irradiation dose can be understood by the fact that more and more traps responsible for these glow peaks were getting filled with the increase of irradiation dose and subsequently these traps release the charge carriers on thermal stimulation to finally recombine with their counterparts, thus giving rise to different glow peaks.

3.3 Trap parameters

Trap parameters such as order of kinetics (b), activation energy (E) and frequency factor (s) are calculated for the 135°C glow peak of $CaB_4O_7 : Mn$ phosphor using the isothermal luminescence decay method (ILDM). The theory and experimental details of the method is described elsewhere [9]. As a check the trap parameters are also calculated by the glow curve shape (Chen's) method.

3.3.1. Isothermal luminescence decay method

The isothermal luminescence decay method is based on recording the decay of luminescence intensity with respect to time at a constant temperature. Three temperatures are chosen on the rising side of the glow peak whose trapping parameters are to be determined. After irradiating the sample by X-ray or γ-ray of suitable dose, it is heated to one of the chosen temperatures and decay of luminescence intensity is recorded at a constant temperature. This procedure is repeated for other two temperatures. The experimental data is tested for finding the order of kinetics.

First order kinetics

TL intensity equation for the first order kinetics is [9]:

$$I = -\left(\frac{dn}{dt}\right) = ns \exp\left(-\frac{E}{kT}\right).$$

The solution of intensity equation for the isothermal case :

$$I(t) = n_0 s \exp\left(-\frac{E}{kT}\right)\exp\left[-st \exp\left(-\frac{E}{kT}\right)\right]$$

or,

$$\ln[I(t)] = -\left[s\exp\left(-\frac{E}{kT}\right)\right]t + \left[\ln(n_0 s) - \frac{E}{kT}\right] \quad (1)$$

So for the first order case, plot of $\ln[I(t)]$ vs time should yield a straight line.

The slope of this straight line is:

$$m = s\exp\left(-\frac{E}{kT}\right)$$

or,

$$\ln[m(T)] = -\frac{E}{kT} + \ln(s) \quad (2)$$

The slope (m) of straight line plots of $\ln[I(t)]$ vs time at different temperatures are noted and again $\ln[m(T)]$ vs $1/T$ are plotted which is a straight line (equ.2). The slope $m' = -E/k$ of this straight line give thermal activation energy (E) where k is the Boltzman's constant and intercept part $\ln(s)$ of equation (2) gives the value of frequency factor (s).

General order kinetics

TL intensity equation for the general order kinetics is:

$$I = -\left(\frac{dn}{dt}\right) = s'\, n^b \exp\left(-\frac{E}{kT}\right),$$

where $s' = \dfrac{s}{n_0^{b-1}}$ is the pre-exponential factor.

The solution of intensity equation for the isothermal case [10]:

$$\left(\frac{I_0}{I}\right)^{\frac{b-1}{b}} - 1 = s\exp\left[-\frac{E}{kT}\right](b-1)t, \quad (3)$$

so for the general order case, plot of $(I_0/I)^{(b-1)/b} - 1$ vs time should yield a straight line where b is the order of kinetics ($1 < b \leq 2$), I_0 is the intensity at $t = 0$ and I is the intensity at any instant t. The experimental data is tested by choosing different test values of b, among which the value of b that gives the best fit as straight line gives the order of kinetics (b).

The slope of this straight line equation (3) is:

$$m = (b-1)s\exp\left(-\frac{E}{kT}\right). \quad (4)$$

The determination of slope (m) of straight line plots of $(I_0/I)^{(b-1)/b} - 1$ vs time at different temperatures will give the value of frequency factor according to the relation :

$$s = \frac{(m_2)^{\frac{T_2}{T_2 - T_1}}}{(b-1)(m_1)^{\frac{T_1}{T_2 - T_1}}}, \quad (5)$$

where m_1 and m_2 are the slopes corresponding to the temperatures T_1 and T_2 respectively.

From equation (4) :

$$\ln[m(T)] = -\frac{E}{kT} + \ln[s(b-1)]. \quad (6)$$

Now to find the thermal activation energy (E) a graph $\ln[m(T)]$ vs $1/T$ is plotted, which is a straight line (equation 6). The slope $m' = -E/k$ of this straight line graph will give the value of thermal activation energy (E).

In order to calculate the trapping parameters corresponding to 135°C glow peak, three temperatures namely 120, 125 and 130°C were chosen and decay of luminescence intensity with time at these temperatures were recorded by X-irradiating the sample for 1 minute. The plots of $\ln I$ vs time were drawn at these temperatures which do not fit into the straight line nature which establish that the glow peak at 135°C does not obey first order kinetics. This indicates that TSL mechanism at this temperature is not associated with first order kinetics. Then plots of $(I_0/I)^{(b-1)/b} - 1$ vs time were drawn for different values of b ($1 < b \leq 2$). The best straight line fitting is obtained for $b = 2$ as shown in Fig. 6. This established that 135°C glow peak is associated with second order kinetics. The value of frequency factor (s) is found from the slope of these straight lines at 120 and 125°C by using the equation (5) and is found to be 4.68×10^9 sec^{-1}. To find the thermal activation energy (E), the slope (m) of these straight lines for the temperatures 120, 125 and 130°C were noted and were plotted as $\ln(m)$ vs $1/T$ as shown in Fig. 7 which is a straight line as expected. The activa-
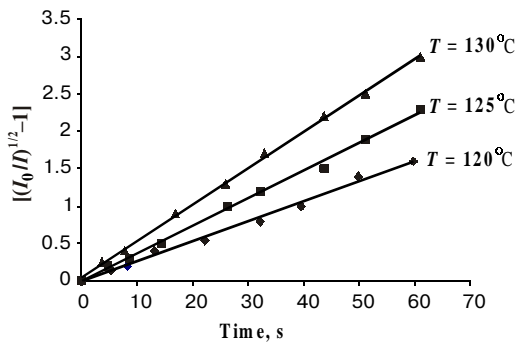

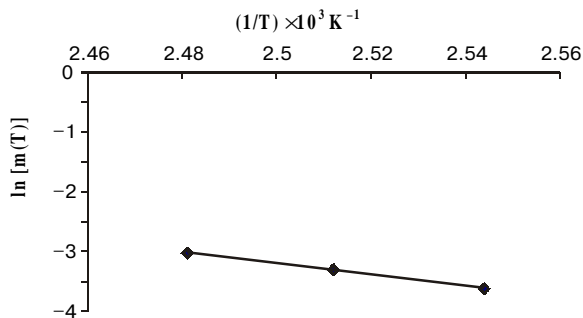**Fig. 6.** Isothermal luminescence decay curves of CaB$_4$O$_7$:Mn sample for 135°C glow peak.

Fig. 7. Plot of $\ln[m(T)]$ vs $1/T$ for 135°C glow peak of CaB$_4$O$_7$: Mn sample.

tion energy (E) is calculated from the slope ($m' = -E/k$) of this straight line and is found to be 0.82 eV.

3.3.2 Glow curve shape method

The method based on the shape of glow curve proposed by Chen was used to verify the above calculated trapping parameters. To determine these parameters the following shape parameters are determined: the total half intensity width ($\omega = T_2 - T_1$), the high temp. half width ($\delta = T_2 - T_m$), the low temp. half width ($\tau = T_m - T_1$), where T_m is the peak temperature and T_1 and T_2 are temp. on either side of T_m corresponding to half peak intensity.

Order of kinetics :

Order of kinetics (b) is determined by calculating the symmetry factor (μ_g) of the glow peak from the known values of shape parameters :

$$\mu_g = \frac{\delta}{\omega} = \frac{T_2 - T_m}{T_2 - T_1} . \tag{7}$$

The shape factor (μ_g) for the 135°C glow peak of CaB$_4$O$_7$: Mn is found to be 0.52 which suggest that this peak obey second order kinetics.

Activation energy :

Activation energy (E) is calculated by using the Chen's equations which gives the trap depth in terms of τ, δ, ω. A general formula for E was given by :

$$E = \frac{c_\gamma k T_m^2}{\gamma} - b_\gamma 2 k T_m , \tag{8}$$

where γ is τ, δ or ω. The constants c_γ and b_γ for the three equations (τ, δ and ω) and for second order kinetics are $C_\tau = 1.81$, $b_\tau = 2.0$, $C_\delta = 1.71$, $b_\delta = 0$, $C_\omega = 3.54$, $b_\omega = 1.0$.

The activation energy for the 135°C glow peak of CaB$_4$O$_7$: Mn when calculated by equation (8) using low temp. half width, high temp. half width and full width of the peak at its half height are found to be 0.81 eV, 0.83 eV and 0.82 eV giving mean value of activation energy 0.82 eV.

Frequency factor :

Once order of kinetics and activation energy are determined, the frequency factor (s) can be calculated by the equation given by Chen & Winer :

$$\frac{qE}{kT_m^2} = s\left[1 + (b-1)\frac{2kT_m}{E}\right]\exp\left(-\frac{E}{kT_m}\right) \tag{9}$$

where q is the heating rate.

The frequency factor for the 135°C glow peak of CaB$_4$O$_7$: Mn when calculated by using equation (9) is found to be 2.96×10^9 sec^{-1}.

Table 2 gives the values of trapping parameters of the 135°C glow peak of CaB$_4$O$_7$: Mn phosphor calculated by isothermal decay and Chen's methods. The results shows a very good agreement between the trapping parameters calculated by the two methods and indicates

Table 2. Trap parameters of 135°C glow peak of CaB_4O_7 : Mn phosphor.

Trap parameters	Method	
	Isothermal decay	Chen's
Order of kinetics	2	2
Activation energy (E) in eV	0.82	0.82
Frequency factor (s) in s^{-1}	4.68×10^9	2.96×10^9

the reliability of two methods and accuracy of the measurement of parameters.

4. Conclusions

(*i*) The compound CaB_4O_7 has orthorhombic structure at room temperature.

(*ii*) The addition of Mn impurity to undoped CaB_4O_7 enhances the TL intensity by about 40 times.

(*iii*) The 135°C glow peak of CaB_4O_7 : Mn phosphor is due to the second order kinetics with the activation energy 0.82 eV and frequency factor $4.68 \times 10^9 \, s^{-1}$.

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