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Trapping Parameters in $KMgSO_4F$:X (X = Cu, Dy and Eu)

Anuradha Poddar[a], and V.M. Pendsey[b]*
[a] Department of Physics, DRB Sindhu Mahavidyalaya, Nagpur, - 440017, India
[b] Department of Electronics, DRB Sindhu Mahavidyalaya, Nagpur, - 440017, India

***Abstract*:- $KMgSO_4F$: Cu, $KMgSO_4F$: Dy and $KMgSO_4F$: Eu material are synthesized by wet chemical method and studied for its trapping parameters such as geometrical factor (μ), Order of Kinetics (b), Trap depth (E) and frequency factor (s) associated with the isolated TL glow curve by Chen's half width method to get the information mechanism of trapping and recombination of charge carrier with the traps. Thermoluminescence (TL) glow curve of $KMgSO_4F$: Cu/Dy/Eu has been investigated in detail at various concentrations; between the temperatures range of 50 to 300 ºC. All TL glow curves showed single peak at 197.76 ºC, 172.91 ºC and 180.26 ºC respectively. The release of hole or electron from defect centers at the characteristic trap site indicates the luminescence process in this material.**

1. INTRODUCTION

Most research of TL concentrates on the development of new phosphors exhibiting improved performance and on measuring set-ups [1]. CaF2 doped with rare earth impurity ions was extensively studied because of its high sensitivity and its ability to store the incident energy [2-3] which is suitable for radiation dosimetry. The material has been marketed as a commercial thermoluminescence (TL) dosimeter, CaF2:Dy, under the commercial name TLD-200. TL technique has a wide range of applications such as radiation detectors, solid-state dosimeters for industrial and medical radiation dosimetry applications, dating techniques in archaeology, geology and to study the variety of defect centers created by ionizing radiation [4-9] .Till date no material has been found to possess all features and thus a search in this area is in constant progress. The present work is also a small step taken forward in the same direction for a search of an ideal TL phosphor.

Sulfate based TL materials are synthesized and studied because of their well desired characteristics like a high temperature low peak, linear response with ionizing radiation exposure, negligible fading and an easy methods of preparation [10]. There are several thermoluminescent materials such as CaSO4: Eu,Ag, K2Ca2(SO4)3:Eu, KMgSO4Cl doped with Dy, Ce and Mn etc. of which almost all has been studied for improvement in the thermoluminescence characteristics and the trapping parameters [11–13]. Many researchers have investigated luminescence properties of mixed sulfate phosphors for their use as dosimeters of ionizing radiations [14–20]. In three-parameter model, TL is described by the three parameters namely activation energy (E) , order of kinetics (b) and frequency factor (s) . This work reports for the first time the TL response of the phosphors to gamma radiation in mixed halo-sulfate phosphor $KMgSO_4F$ doped with different concentration of the Copper, Dysprosium and Europium prepared by wet chemical method. The focus in this paper is mainly on studying the Trapping parameters such as geometrical factor (μ) hence order of kinetics (b), Trap depth (E) and frequency factor (s) all have been calculated by Chen's method for 5 Gy dose of ^{60}Co for heating rate of 5 ºC .

According to a theoretical analysis of Thermoluminescence (TL) phenomenon done by Randall and Wilkins [21], electrons are trapped during thermal excitation at some lattice sites. When the crystal is heated, electrons are released into the conduction band and recombine with holes at the recombination sites, resulting in TL emission. In practice, phosphors have more than a single trap and a single recombination center, which results in a curve of TL. TL investigations have also shown that defect centres play a crucial role in TL analysis. The formation and the stability of the defect centres depend on the method of preparation of phosphors and the activators. TL strongly depends on the host material, the type of activator, radiation induced defect centre, dose and type of ionizing radiation. Dosimetric characteristics of TL materials are mainly depends on kinetic parameters. Kinetic parameters quantitatively describe the trapping-emitting centers responsible for the TL emission. Therefore, determination of the kinetic parameters is an active area of research for better understanding of TL process. There are various methods for evaluating the trapping parameters such as glow peak shape, various heating rates and initial rise method.

2. EXPERIMENTAL

$KMgSO_4F$ (pure) and $KMgSO_4F$:Cu phosphors were prepared by a wet chemical method. $MgSO_4$ and KF of AR grade were taken in a stoichimetric ratio and dissolved separately in double distilled de-ionized water, resulting in a solution of $KMgSO_4F$. Confirming that no undissolved constituents were left behind and all the salts had completely dissolved in water and thus reacted.

$$MgSO_4 + KF \rightarrow KMgSO_4F$$

Then water-soluble sulfate salt of Copper was added to the solution to obtain $KMgSO_4F$:Cu The compounds $KMgSO_4F$ (pure) and $KMgSO_4F$: Cu in its powder form was obtained by evaporating on 80 ºC for 8 hours. The powder was used in further study. The same procedure was adopted for $KMgSO_4F$: Dy and $KMgSO_4F$: Eu (in this case instead of copper the sulfate salt of dysprosium or europium was used). Formation of the compounds was confirmed by taking the x-ray diffraction (XRD) [22]. X-

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Ray diffraction pattern (XRD) of $KMgSO_4F$ prepared material did not indicate presence of the constituents $MgSO_4$ or KF and other likely phases; these results indicate that the final product was formed in homogeneous form. Taking the same amount of samples (5 mg), thermoluminescence (TL) emission spectra were recorded using Nucleonix Thermoluminecence Reader (Integrated PC Based), TL 10091.

3 RESULTS AND DISCUSSION

3.1 Analysis of trapping parameters

Fig. 1 discusses multi-level TL model for competing trapping and luminescent centers. The shallow traps get emptied earlier and the deep traps (acting as a reservoir) may replace them subsequently or they also can go directly to the conduction band and recombine with the luminescence centers during their back journey [23]. Here on the basis of the TL results the trapping parameters were calculated by Chen's half width method. **Fig. 2** shows a glow curve for the sample $KMgSO_4F$:Cu quenched at 250 ºC then exposed to γ-radiation from ^{60}Co source at room temperature for 5Gy at the heating rate of 5 ºC/s and a dose rate of 0.36 kGy/hr. TL glow curve of $KMgSO_4F$:Dy and $KMgSO_4F$:Eu are shown in figure 3 and 4. Single prominent TL glow peak has been observed at about 172.91 ºC and180.26 ºC respectively, when exposed to γ –rays for 5 Gy at the rate of 0.36 $kGyh^{-1}$. The TL glow curves of all γ -irradiated $KMgSO_4F$: X (X = Cu or Dy or Eu) samples show single glow peak indicating one set of trap is being activated within the particular temperature range due to γ –irradiated effect.

In this study Chen's peak shape method has been used to analyse the glow curves of $KMgSO_4F$:Cu, $KMgSO_4F$:Dy and $KMgSO_4F$:Eu halo-phosphors. For kinetic and trap depth analysis TL glow curves were recorded at a heating rate of $5Ks^{-1}$. All the samples were exposed to a low dose of 5Gy. The measured glow curves were analysed to resolve the individual peaks, assuming first order, second order and general order kinetics. The order of kinetics and activation energy of the isolated peak was found using Chen's set of empirical formulae. To determine the order of kinetics (b) and the symmetry factor (μ) given by Chen was made [24-25].

3.1.1 Order of kinetics (b):

Order of kinetics was determined by calculating symmetry factor μ of the glow peak by measuring the values of T_1,T_2 and T_M

$\mu = \delta/\omega = T_2 - T_M/T_2 - T_1$ …….. (1)

Table 2 gives the values of T_1, T_2, and T_M of glow curve of $KMgSO_4F$:Cu, $KMgSO_4F$:Dy and $KMgSO_4F$:Eu halo-phosphors, putting these values in Eq.1 symmetry factor μ is calculated and shown in table 2, It suggests that all the peaks obeys second order kinetics. The calculated values of kinetic parameters are listed in Table-2.

Moreover, Balarine and Furetta have proposed the following factor [26]

$\gamma = \delta/\tau = T_2 - T_M/T_M - T_1$ …….. (2)

This parameter ranges from 0.7 to 0.9 for the first order kinetics. and from 1.05 to 1.20 for second order kinetics , Balarine parameter γ and the geometrical factor (μ) calculated by Chen's method shown in Table 2. The geometrical factor is 0.52 and Balarine parameter (γ) is laying in between 1.05 to 1.20 , indicating that it obeys second-order kinetics. This means, in principle that a re-trapping effect should be present.

3.1.2 Activation energy (E):

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

$E_\gamma = c_\gamma (kT^2_M/\gamma) - b_\gamma (2kTm)$ ……(3)

Where, γ is τ, δ, or ω are the constants cγ and bγ for the three equations (τ, δ, or ω). They are calculated total half intensity width ($\omega = T_2-T_1$), the high temp half width ($\delta = T_2-T_M$), and low temp half width ($\tau = T_M-T_1$) where T_M is peak temperature corresponding to maximum intensity, T_1 & T_2 are temperature on either side of T_M corresponding to half of maximum intensity. The trap depth was calculated by the Chen's equation.

Where E_γ is trap depth and c_γ and b_γ are constants of Chen's equation. γ was replaced by τ, δ, or ω as per the case. Chen's method does not require knowledge of the kinetic order, which is found by using the symmetry factor μ from the peak shape. The values of cγ and bγ are summarized as below-

$c_\tau = 1.510 + 3.0(\mu - 0.42)$, $b_\tau = 1.58 + 4.2(\mu - 0.42)$

$c_\delta = 0.976 + 7.3(\mu - 0.42)$, $b_\delta = 0$

$c_\omega = 2.52 + 10.2(\mu - 0.42)$, $b_\omega = 1$,

With μ = 0.42 for the case of first-order TL glow peaks, and μ = 0.52 for the case of second-order peaks.

For second order kinetics the values of τ, δ, and ω are tabulated in Table 1. The activation energy E (eV) has been calculated with the equations for second order kinetics. The values of E are given in Table 3.Grosweiner analysed the TL curve for the second order kinetics and derived the formula for the trap depth (E) as

$E = (GkT_MT_1)/\tau$ ……. (4)

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Where G = 1.51, $\tau = T_M - T_1$ where T_M is the temperature of the TL peak maximum intensity (I_M) and $T_1 < T_M$ is the temperature at the TL intensity $I = 0.5\ I_M$. It has been observed that the values of T_M has been shifted to higher tempreture side after doping the compound.

3.1.3 Frequency factor (s):

Frequency factor was calculated by the equation given by Chen and Winer

$$\beta E/kT^2_M = s[1+ \{(b-1)\ 2kT_M\}/E]\exp(-E/kT_M) \quad \ldots\ldots\ldots\ldots\ldots(5)$$

Where β is heating rate, k is Boltzman's constant, taken as 8.617×10^{-5}. The frequency factor was calculated by the equation (5).

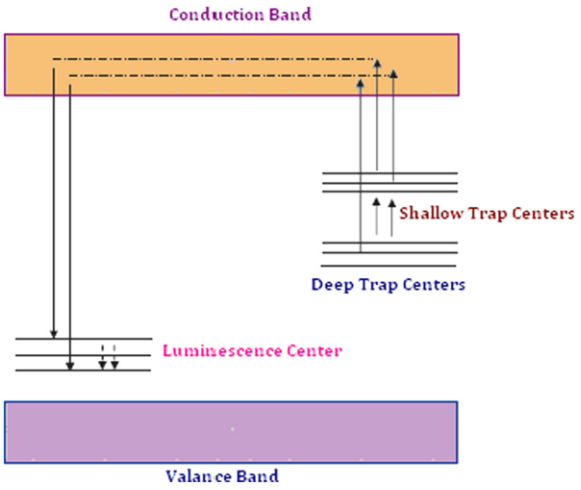

Fig.1

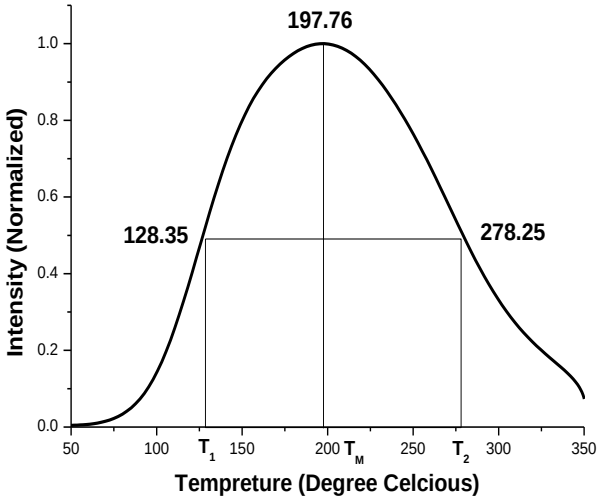

Fig. 2

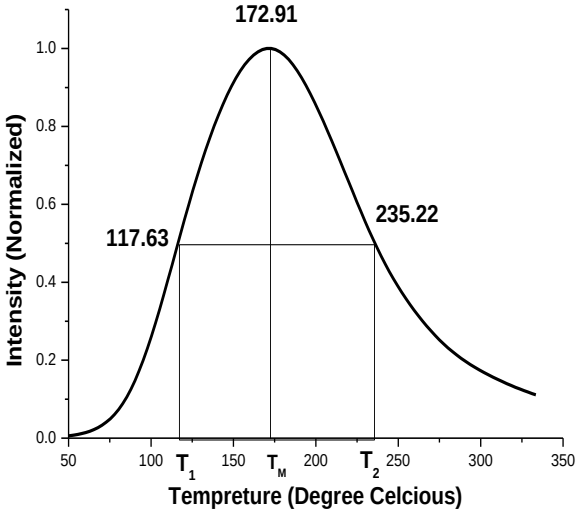

Fig. 3

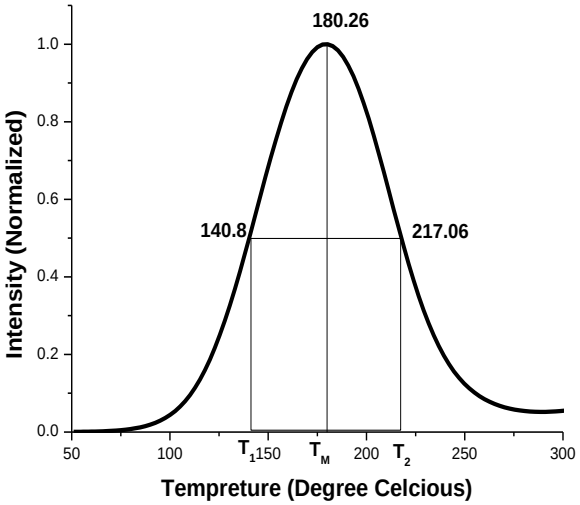

Fig.4

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Table 1: Values of c_γ and b_γ depends on τ, δ, and ω

Values	τ	δ	ω
c_γ	1.81	1.71	3.54
b_γ	1.0	2.0	0

Table 2: The geometrical factor (μ) calculated by Chen's method

Phosphor	T_1 (K)	T_2 (K)	T_M (K)	$\mu = T_2 - T_M/T_2 - T_1$	$\gamma = \delta/\tau$
$KMgSO_4F$	385.05	477.4	427.3	0.54	1.18
$KMgSO_4F$:Cu	401.35	551.25	470.76	0.53	1.15
$KMgSO_4F$:Eu	419.80	490.06	453.26	0.49	1.09
$KMgSO_4F$:Dy	390.63	508.22	445.91	0.52	1.12

Table 3: Trapping parameters, Trap depth calculated by Chen's method

Phosphor	E_τ (eV)	E_δ (eV)	E_ω (eV)	Mean E (eV)	E (eV) by Grosweiner formula
KMgSO4F:Cu	0.3356	0.4057	0.3698	0.3704	0.3541
KMgSO4F :Eu	0.8014	0.8226	0.8138	0.8126	0.7399
KMgSO4F:Dy	0.4073	0.4702	0.4389	0.4388	0.4099

Table 4: Trapping parameters, frequency factor (s) calculated by Chen's method

Phosphor	S_τ (s^{-1})	S_δ (s^{-1})	S_ω (s^{-1})	Mean S (s^{-1})
KMgSO4F:Cu	2.77×10^2	1.951×10^3	7.92×10^2	1.006×10^3
KMgSO4F :Eu	1.6802×10^8	2.9748×10^8	2.2726×10^8	2.3092×10^8
KMgSO4F:Dy	4.011×10^3	2.4329×10^4	9.898×10^3	1.2746×10^4

CONCLUSION

Wet chemical synthesis is easy process to prepare phosphors $KMgSO_4F$:Cu, $KMgSO_4F$:Dy and $KMgSO_4F$:Eu as a TL material. The TL glow curve of γ-irradiated $KMgSO_4F$:Cu, compound has the simple structure with the prominent single TL glow peak at 197.76 °C whereas, $KMgSO_4F$:Dy and $KMgSO_4F$:Eu have at 172.91°C and 180.26 °C respectively. Single glow peak in this compound indicates only one set of traps is being activated within the particular temperature range.

The glow curves of $KMgSO_4F$:Cu, $KMgSO_4F$:Dy and $KMgSO_4F$:Eu obey the second-order kinetics. The activation energy E and frequency factor s have been calculated with the equations for second order kinetics. The kinetic parameters calculated by Chen's half width method These studies indicate that the $KMgSO_4F$:(Cu, Dy, and Eu) phosphor have potential for its use in radiation dosimetric applications.

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