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Research Article

TL SPECTROSCOPY OF ERBIUM DOPED $CaZrO_3$ PHOSPHOR

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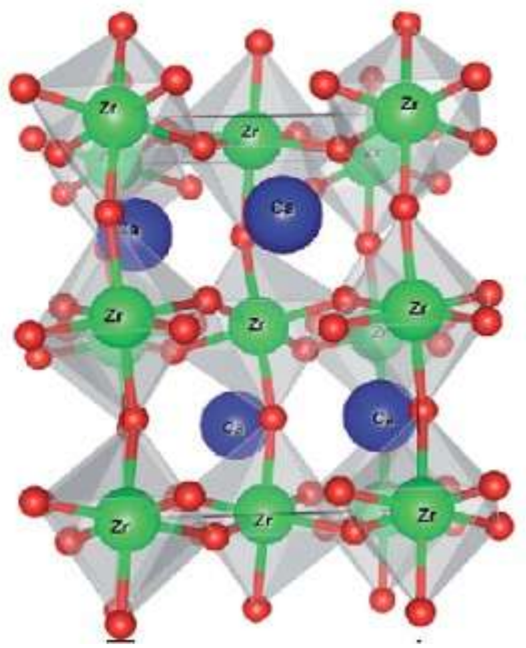
ABSTRACT
The manuscript reports the kinetic analysis of experimentally reported thermoluminescence study of $CaZrO_3$ phosphor doped by fixed concentration of Er^{3+} (1 mol%). In this analysis order of kinetics of the glow curve is re-evaluated as per the new method. It has been found that this parameter depends on the experimental conditions, where as decay parameters, activation energy and frequency factor, are the characteristic features of the glow curve and does not depend on experimental conditions. The new kinetic formalism is related with the extent of retrapping and simultaneous recombination processes in thermoluminescence process and gives more exact value of order of kinetics.

Keywords: Thermoluminescence, order of kinetics, phosphor, activation energy, frequency factor.

INTODUCTION
A large number of perovskite type oxides have been studied because of their interesting properties including superconductivity (Maeno *et. al.,* 1994), insulator-metal transition (Torrance *et. al*.,1992), ionic conduction characteristics (Bohnke *et. al*.,1996), dielectric properties, ferroelectricity (Samara 1971) and luminescence properties (Shimokawa *et. al.*,2015). Perovskite is one of the most frequently encountered structures in solid-state physics, and it accommodates most of the metal ions in the periodic table with a significant number of different anions. During the last few years, many experimental and theoretical investigations were devoted to the study of perovskite solids typically ABO_3. Generally, perovskites have the general formula ABX_3 where, A and B are two cations of very different sizes and X is an anion that

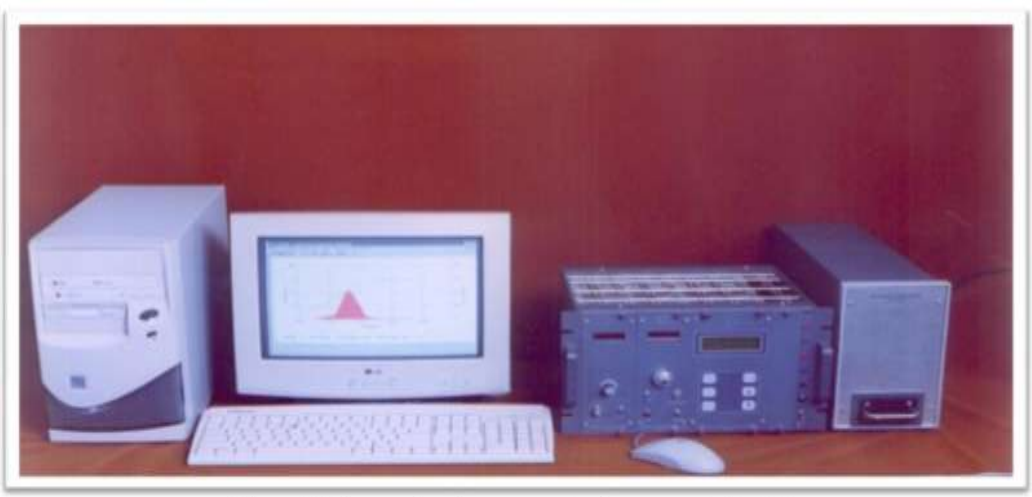


bonds to both (Warner, 2012).
Rare earth doped perovskite-type compounds, due to their potential advantages i.e. chemically stable and environment-friendly material system and also free from hazardous elements such as sulfur and cadmium (Shimokawa *et. al.,* 2015), nowadays have received considerable attention of researchers. As a host,

Perovskite-type alkaline earth zirconates ($MZrO_3$, M = Ca, Sr and Ba) are also important (Koopmans *et. al*., 1983). Eu^{3+}-doped $CaZrO_3$ exhibits intense red luminescence under UV excitation (Zhang *et. al*.,2008, Li *et.al*., 2011, Huang *et. al*.,2010), Calcium zirconate, $CaZrO_3$, also known as lakargiite is a refractory compound, which congruently melts at 2340°C (Galuskin *et. al*.,2008). $CaZrO_3$ is an orthorhombic (crystalline structure) perovskite consisting of slightly deformed [ZrO_6] octahedral and [CaO_8] (Rog *et. al*., 2002, Ross *et.al*.,2003). At 1750°C $CaZrO_3$ undergoes polymorph transformation where orthorhombic $CaZrO_3$ to cubic $CaZrO_3$ (Ianos *et. al*., 2010).
Thermoluminescence (TL) technique is one of the most efficient and convenient tool for luminescent characterization of the material. Here in this paper we reevaluate order of kinetics parameter of Erbium doped $CaZrO_3$ Phosphor from its TL spectrum, which is already in literature (Tiwari *et. al*., 2015).

MATERIALS AND METHODS

Following solid state reaction method Phosphor of CaZrO3 doped with Er^{3+} ions with fixed molar concentration of Er^{3+} (1 mol%) was prepared by Tiwari et.al. (Tiwari *et al*., 2015). $CaCO_3$, ZrO_2, Eu_2O_3 and H_3BO_3 precursors (as flux) used for synthesis of $CaZrO_3:Er^{3+}$ doped phosphor. The composition of each chemical weighed in proper stoichiometric ratio then mixed thoroughly for 45 minutes using mortar and pestle. The grinded sample was placed in an alumina crucible and subsequently fired at 1000^0C for 1 hour for calcinations and then at 1250^0C for 3 hours for sintering in a muffle furnace.
Every heating was followed by intermediate grinding. Finally the samples were cooled slowly to room temperature in the furnace and ground again into powder for subsequent characterization (Tiwari *et. al*., 2015, Dubey *et. al*., 2013, Dubey *et. al*., 2010, Dubey *et. al*., 2014, Dubey *et. al*., 2015, Cooke *et. al*. 2006, Yan *et. al*., 2005). The obtained phosphor under the TL examination is given UV radiation using 254 nm UV source Thermoluminescence glow curves were recorded at room temperature by Tiwari et.al. using TLD reader I1009 supplied by Nucleonix Sys. Pvt. Ltd. Hyderabad.



TL glow curve of $CaZrO_3$ doped with 1 mol% Er^{3+} with different UV exposure time at constant heating rate i.e. 6.7^0Cs^{-1} as reported by Tiwari et.al. (Tiwari *et. al*., 2015) is shown in Fig.1. Figure also shows the effect of different UV exposure on peak temperature of TL glow curve of the phosphor.
Tiwari et. al. (2015) estimated TL decay parameters for $CaZrO_3:Er^{3+}$phosphor by curve fitting techniques CGCD curve of experimental data and the peak shape method proposed by Chen and others. The trap levels lying at different depths in the band gap between the conduction and the valence bands of a solid show different TL spectrum. These trap levels are characterized by trapping parameters namely trap depth and frequency factor. The loss of dosimetry information stored in the materials after irradiation is strongly dependent on the position of trapping levels within the forbidden gap which is known as trap depth or

activation energy (Ea). The frequency factor (s) represents the product of the number of times an electron hits the wall and the wall reflection coefficient, treating the trap as a potential well.

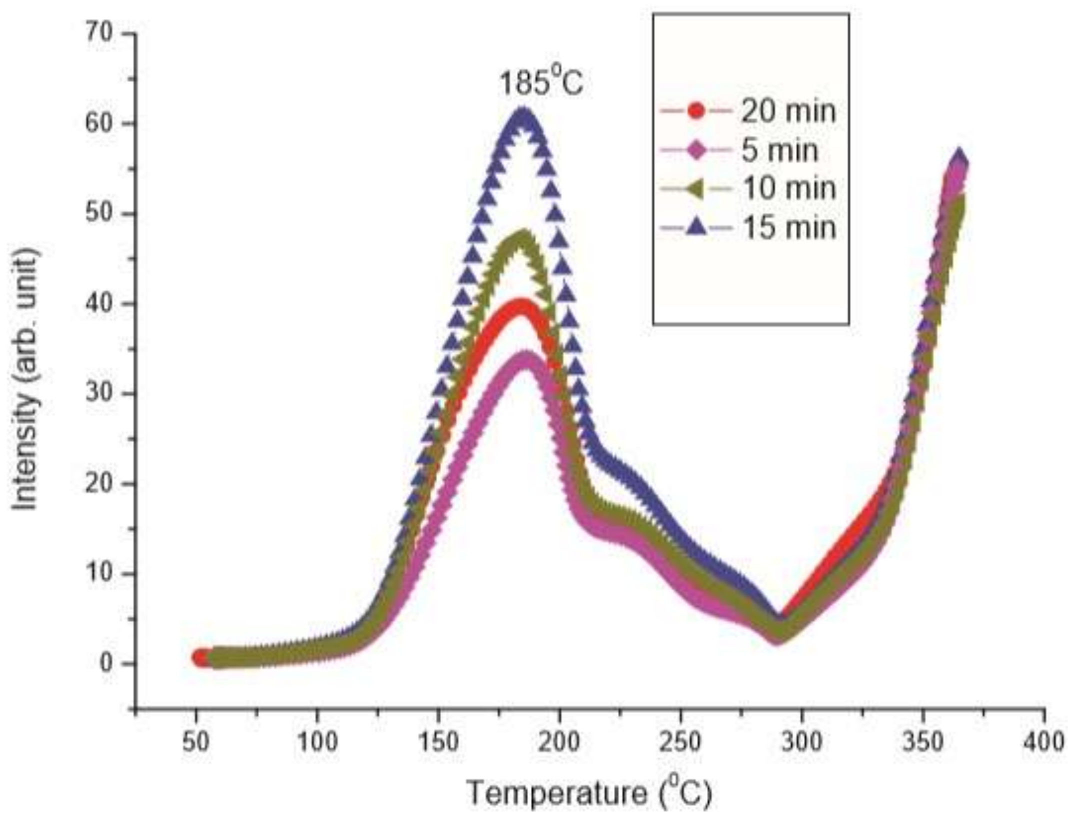


Figure 1: TL spectrum for Er^{3+}(1%) doped CaZrO3 for different UV exposure time (Tiwari *et. al*., 2015)

RESULTS AND DISCUSSION

The evaluated TL decay parameters as reported by Tiwari et. al. (2015) along with peak temperature values are given in Table.1. Different researchers follow slightly dissimilar mechanism responsible for thermoluminescence but peak temperature in all is given by the equation

$$T_m^2 = \frac{b\, E_a \tau_m}{k}$$

where b is heating rate, τ_m is relaxation time at peak temperature and k is Boltzmann's constant. τ_m is given by

$$\tau_m = \tau_0 \exp[\frac{E_a}{kT_m}]$$

where τ_0 is fundamental relaxation time and is inverse of frequency factor s.

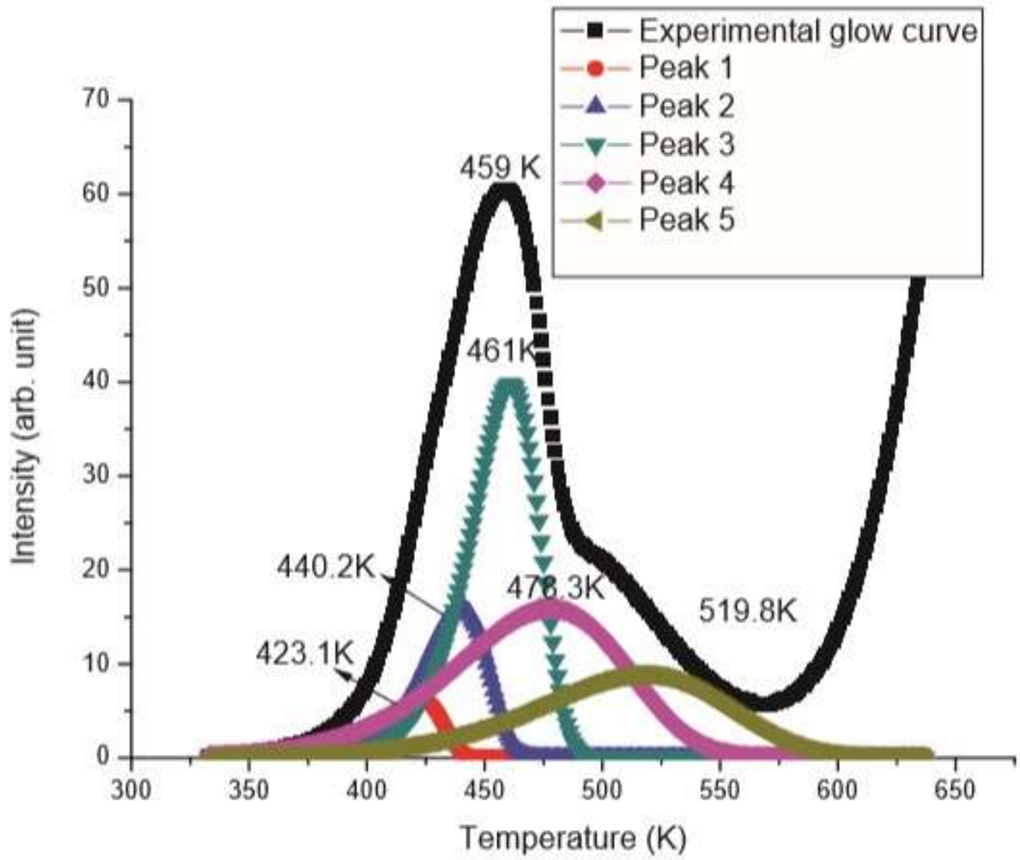


Figure 2: Deconvoluted glow curve of CaZrO3:Er^{3+}(1%) for 15 minute UV exposure time (Tiwari *et. al.*, 2015)

Table.1 Reported TL decay parameters and evaluated order of kinetics for TL response of Erbium Doped $CaZrO_3$ Phosphor

Peak Temperature T_m (K)	Activation Energy E_a (eV)	Frequency Factor s (s^{-1})	τ_m (s)	T_m^2 (K^2)	$\frac{bE_a\tau_m}{k}$ (K^2)	Order of Kinetics ℓ
407.6	1.34	3.00E+15	1.23E+01	166137.76	1.29E+06	1.29E-01
421.2	1.24	5.00E+13	1.37E+01	177409.44	1.32E+06	1.34E-01
440.2	1.22	7.00E+12	1.33E+01	193776.04	1.26E+06	1.54E-01
433	0.58	1.00E+05	5.63E+01	187489	2.54E+06	7.38E-02
463	0.52	1.00E+05	4.57E+00	214369	1.85E+05	1.16E+00

Thus, accountable dosimetry study of thermoluminescent material is based on its trapping parameters. The trap parameters are analyzed by peak shape method proposed by Chen and others with the help of glow curve deconvolution technique and shown in Fig.2 as reported in literature (Tiwari *et. al*., 2015). Trapping parameters as already reported for five distinct fitted curve of UV induced sample are given in Table.1. From fifth and sixth columns of table 1 it is clear that the reported values of activation energy and relaxation time do not satisfy the well established peak temperature relation. In order to remove this shortcoming a new model has been suggested by Prakash (2013), for the appearance TL glow curve which is based on extent of retrapping and simultaneous recombination. According to this model equation for TL intensity is given by

$$I = (1-x)n_0 s \exp[(-\frac{E_a}{kT}) - \frac{s\,(1-x)}{b}\int_{T_0}^{T}\exp(-\frac{E_a}{kT'})dT'\,]$$

And accordingly peak temperature is given by

$$T_m^2 = \frac{\ell\, b\, E_a \tau_m}{k}$$

Where I is TL intensity at temperature T, n_0 is the initial concentration of trapped carriers per unit volume, T_o the temperature at which TL glow curve starts to appear, T′ any arbitrary temperature in the range T_o to T. Extent of retrapping ***x*** is related with order of kinetics ℓ as

$$\ell = \frac{1}{(1-x)}$$

Following this proposed model a new method of analysis has been proposed by Prasad et.al.[24]. As per the new method of analysis order of kinetics is evaluated for different peaks of Fig.2 glow curve and are given in seventh column of Table.1.

Conclusion

In this study, the experimental TL study of Erbium Doped $CaZrO_3$ Phosphor, as reported by Tiwari et. al., are re-examined to find out more correct values of order of kinetics corresponding to different CGCD resolved glow peaks of TL glow curves. It is found that the evaluated values of order of kinetics are different from reported one. It gives more information about trap centers in broad TL glow curve. Activation energy, frequency factor along with order of kinetics gives the information of dosimetry loss in prepared phosphor and its usability in environmental monitoring and for personal monitoring. CGCD is the advance tool for analysis of complicated TL glow curves.

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