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# Decay parameters and extent of retrapping involved in thermoluminescence spectrum of $CdSiO_3$ with various dopants

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**Abstract**

Thermoluminescence (TL) spectroscopy is an efficient and convenient tool to analyze the persistent luminescence inside the materials. In the present work a new method has been used to analyze the experimentally reported TL spectra of undoped and doped $CdSiO_3$ to evaluate the decay parameters and extent of retrapping along with order of kinetics involved. Used method is free from approximations of recombination and retrapping probabilities. The thermoluminescence analysis discovered a best trap structure considering both the facile release of electrons at room temperature and the efficient storage of the excitation energy.

***Keywords:*** *Persistent luminescence Thermoluminescence, Decay parameters, Extent of retrapping, Order of kinetics.*

## 1. Introduction

The emission of radiation from material after the removal of an excitation radiation source is defined as persistent luminescence. If the persistent energy is trapped at trap levels inside material and released after inducing thermally, thermoluminescence (TL) occurs. The plot of TL intensity vs temperature is known as TL spectrum or glow curve. T L technique is quite helpful in characterizing materials having persistent luminescence. Every peak of T L spectrum is related with distinct trap depth and their characteristic properties are described by analyzing corresponding spectrum. The area of the corresponding resolved glow peak provides the idea of trap densities. Some of the important potential fields where the T L characterization of material is required are dosimetry[1], dating[2], in development of scintillators[3] and persistent luminescence[4]. Long-lasting afterglow persistent luminescent material is used for light in the darkness after irradiation with sunlight or some other artificial light source. Safety indication, lighting in crisis, instrument in automobile, luminous paint and optical data storage, etc.are the fields where these materials are widely used. Aluminate based luminescent materials have been investigated by many researchers and the efficient luminescent materials based on alkaline-earth aluminates are $SrAl_2O_4$:Dy,Eu (green)[5], $CaAl_2O_4$:Nd,Eu (violet)[6] and $Sr_4Al_{14}O_{25}$:Dy,Eu (blue)[7]. All these materials require very high temperature (above 1200–1350$^0$C) for preparation by high-temperature solid-state reaction method.There is a new technique of the synthesis—the sol–gel synthesis method, in which temperature can be decreased[8]. Due to their stability,visible light transparency, and relatively easy preparation Silicate compounds have also been extensively studied among the host matrix used for long-lasting luminescent materials. $R^{3+}$-doped CdSiO3 phosphors show great potential for practical applications, a systematic study of their properties is advisable. For the development of any novel luminescent materials, the underlying mechanism(s) based on a coherent set of several optical and other properties of the material has to be considered. In the case of the persistent luminescence materials, such properties include the host band gap energy, the trap structure, as well as the energy level positions of the emitting centers and defects capable of storing the excitation energy [9,10].

In the present work analysis has been done on experimentally reported different TL spectrums of undoped and $R^{3+}$-doped $CdSiO_3$ material to evaluate decay parameters, namely activation energy, escape frequency factor along with extent of retrapping and order of kinetics. Although most of the workers report the resolved or deconvoluted TL spectrum along with decay parameters, here a new method of analysis is adopted for the analysis of spectrum. The adopted method is originally Bucci et. al.[11] method in which concept of extent of retrapping or order of kinetics is reasonably incorporated.

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## 2. Method of Analysis

The T L spectrum or glow curve is characteristic of the different trap levels that lie in the band gap of the material. A reliable study regarding characteristic properties of a thermoluminescent material should be based on a good knowledge of its decay parameters that include activation energy or trap depth ($E_a$), escape frequency factor (s) and extent of retrapping (***x***) along with order of kinetics (ℓ). In the considered method of analysis as suggested by Prakash [12], T L intensity involving any extent of retrapping is given by

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

where ***x*** is the extent of retrapping in T L process, $n_o$ the initial concentration of trapped carriers per unit volume, s the escape frequency factor or pre-exponential factor, $E_a$ the trap depth or activation energy, k the Boltzmann's constant, b the linear heating rate, $T_o$ the temperature at which TL glow curve starts to appear and T' an arbitrary temperature in the range $T_o$ to T. Temperature $T_m$ at which peak of the T L spectrum appears is given by the relation

$$T_m^2 = \frac{b\,E_a\tau_m}{(1-x)\,k} \quad \ldots (2)$$

where $\tau_m$ is the relaxation time at the peak temperature $T_m$. Relaxation time τ at any temperature T is given by Arrhenius relation [13]

$$\tau = \tau_0 \exp\left(\frac{E_a}{k\,T}\right) \quad \ldots (3)$$

where $\tau_0$ is the fundamental relaxation time (inverse of escape frequency factor *s* ).

Prakash [12] established above equations (1) and (2) by considering the BFG method and shortcoming of then established peak temperature relation as given by relation

$$T_m^2 = \frac{b\,E_a\tau_m}{k} \quad \ldots (4)$$

In considered method of analysis plot of *ln (n/I )* against *(1/T )* results in a straight line where n is is the density of electrons in the trap centers at temperature T and is given by the relation

$$n = \frac{1}{b}\int_T^{\infty} I(T')\,dT' \quad \ldots (5)$$

and

$$n_0 = \frac{1}{b}\int_{T_0}^{\infty} I(T')dT' \quad \ldots (6)$$

The slope of the *ln (n/I )* vs *(1/T )* line gives the value of activation energy $E_a$ and from the intercept one gets the value of escape frequency factor *s*. By putting the values of $E_a$ and s in equation (2), one gets the value of extent of retrapping ***x*** in corresponding TL process. Extent of retrapping ***x*** is related with the order of kinetics ℓ through the relation

$$\ell = \frac{1}{1-x} \quad \ldots (7)$$

It is obvious that for ***x*** = 0, one gets the value of ℓ as 1. In such a case of ***x*** = 0, all the above equations become identical to corresponding equations of Bucci et.al. method [11].

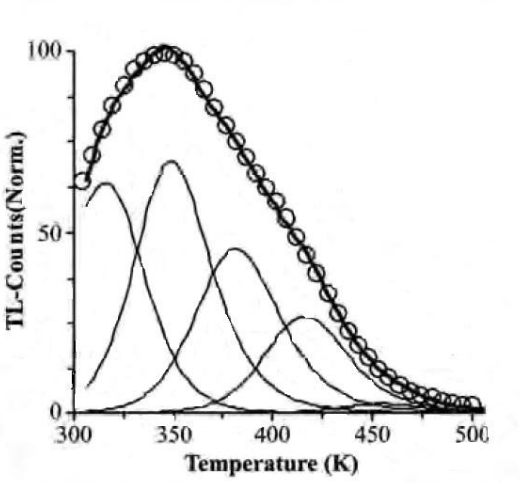


**Fig.1 Deconvoluted T L spectra of $Eu^{3+}$ doped $CdSiO_3$[14].**

## 3. Results and Discussion

Considering the above discussed method of analysis, an attempt has been made to reanalyze the experimentally reported T L glow curves or spectrums of doped and undoped $CdSiO_3$ as reported by different researchers [14,15] engaged in same work. Such two representative TL spectra are shown in Figs.1 and 2. The first TL spectra are as deconvoluted and reported by Mashangva et. al.[14]. They reported the deconvoluted TL spectra of undoped and $R^{3+}$-doped $CdSiO_3$ where R

**Table.1 Evaluated values of $E_a$, s, *x* and ℓ along with reported experimental parameter $T_m$[14].**

| Sample [14] | $T_m$ ($^0$K) | $E_a$ (eV) | s (s) | *x* (%) | ℓ |
|---|---|---|---|---|---|
| Undoped CdSi $O_3$ | 344.0 | 0.78 | 1.20E+11 | 65.9 | 2.9 |
| | 413.7 | 0.53 | 4.20E+05 | 51.0 | 2.0 |
| | 450.0 | 0.67 | 5.40E+06 | 54.6 | 2.2 |
| $CdSiO_3$: $Eu^{3+}$ | 348.6 | 0.34 | 8.40E+03 | 36.3 | 1.6 |
| | 381.4 | 0.62 | 2.50E+07 | 38.3 | 1.6 |
| | 416.3 | 0.73 | 1.10E+08 | 38.8 | 1.6 |
| $CdSiO_3$: $Sm^{3+}$ | 348.9 | 0.52 | 4.60E+06 | 30.0 | 1.4 |
| | 385.7 | 0.68 | 1.00E+08 | 18.4 | 1.2 |
| | 412.0 | 0.86 | 7.00E+09 | 44.3 | 1.8 |
| $CdSiO_3$: $Nd^{3+}$ | 343.6 | 0.43 | 2.80E+05 | 38.7 | 1.6 |
| | 380.0 | 0.38 | 1.10E+04 | 39.1 | 1.6 |
| | 413.2 | 0.65 | 1.40E+07 | 46.5 | 1.9 |
| $CdSiO_3$: $Y^{3+}$ | 352.9 | 0.45 | 3.50E+05 | 36.0 | 1.6 |
| | 381.9 | 0.60 | 1.20E+07 | 34.1 | 1.5 |

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|---|---|---|---|---|---|
| $CdSiO_3$: $Tb^{3+}$ | 339.0 | 0.68 | 2.90E+09 | 39.0 | 1.6 |
| | 360.0 | 0.74 | 7.40E+09 | 59.0 | 2.4 |
| | 387.0 | 0.56 | 1.90E+06 | 10.3 | 1.1 |

is $Eu^{3+}$,$Y^{3+}$,$Tb^{3+}$, $Sm^{3+}$ and $Nd^{3+}$. Different deconvoluted peaks of the spectra are analyzed as per the considered method and the evaluated decay parameters namely, activation energy, escape frequency factor and extent of retrapping along with order of kinetics are presented in table 1. The second TL spectra are as deconvoluted and reported by Lucas et.al.[15].

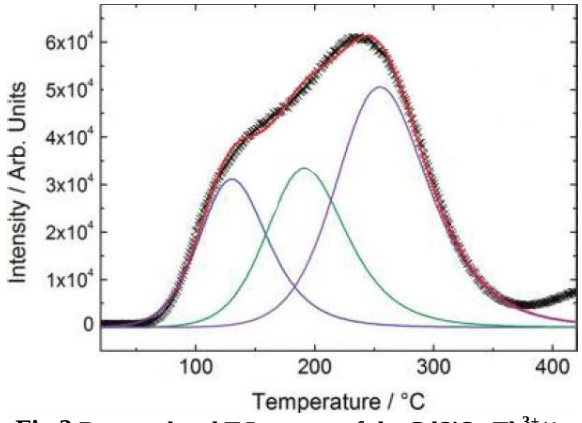


**Fig.2 Deconvoluted T Lspectra of the $CdSiO_3$:$Tb^{3+}$(1 mol % Tb) material[15].**

For this Lucas et. al. prepared the polycrystalline $CdSiO_3$:$Tb^{3+}$prepared with a conventional solid state reaction. Stoichiometric amounts of cadmium acetate ($Cd(CH_3COO)_2 \cdot 2H_2O$, 99%, Vetec), fumed silica ($SiO_2$, 99%, Rhodia), and rare earth nitrates ($Tb(NO_3)_3 \cdot 6H_2O$) were ground intimately and then heated in air at 950 °C for seven hours in aluminosilicate crucibles. The materials were doped with the 0.1, 1.0, and 10% nominal concentrations of $Tb^{3+}$ (in mol % of the $Cd^{2+}$ amount). The terbium nitrates used for doping were obtained from the terbium oxides (99.99%, CSTARM) with a reaction with concentrated nitric acid.

**Table.1 Evaluated values of $E_a$, s, *x* and ℓ along with reported experimental parameter $T_m$[15].**

| Sample [15] | $T_m$ ($^0$K) | $E_a$ (eV) | s (s) | *x* (%) | ℓ |
|---|---|---|---|---|---|
| $CdSiO_3$:$Tb^{3+}$ | 403.56 | 0.52 | 7.4E+5 | 29.2 | 1.4 |
| | 464.67 | 0.56 | 3.1E+5 | 39.4 | 1.7 |
| | 528.56 | 0.72 | 2.1E+6 | 45.3 | 1.8 |

The TL spectra of the CdSiO3:Tb3+ phosphors were recorded by Lucas et.al.[15] with an upgraded Risø TL/OSL-DA-12 instrument with a linear heating rate of 5 °C/s as shown in Fig.2. In this spectra the different deconvoluted peaks are analyzed as per the considered method of analysis and evaluated values are tabulated in table.2. It is obvious from the both tables 1& 2 that the values of TL decay parameters are different for different peaks of TL spectra. Evaluated values of $E_a$ and s are different from the already reported [14,15] particularly because of the use of different methods of analysis. The evaluated values are obtained following Prakash [12] method whereas the reported values are obtained following Pagonis [16] and Chung method [17,18].

## 4. Conclusions

Experimentally reported different TL spectra of UV irradiated undoped and doped with different rare-earth elements $CdSiO_3$ have been analyzed following the method suggested by Prakash and TL decay parameters extent of retrapping alongwith order of kinetics are evaluated. Considered method of analysis is in fact modified Bucci et. al. method. Simplifying assumptions have been removed by Prakash in developing TL intensity equation. It is obvious that the Prakash method is simpler and convenient for the evaluation of TL decay parameters and extent of retrapping along with order of kinetics. The evaluated parameters will help in selecting the proper doping element as well as host material for different applications of luminescent material.

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