International Journal of Physics and Mathematical Sciences ISSN: 2277-2111 (Online)
An Open Access, Online International Journal Available at http://www.cibtech.org/jpms.htm
2016 Vol. 6 (1) January-March, pp. 63-67/Prasad.

Research Article

RECONSIDERATION OF TL STUDIES OF SILICATE MINERALS AT VARIOUS HEAT TREATMENTS AND IRRADIATIONS

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ABSTRACT

The present paper reinvestigates the order of kinetics involved in Thermoluminescence study of silicate materials, already reported in literature, in a new kinetic formalism. Here we study the variation of order of kinetics with experimental conditions. Thermoluminescence peaks are shifted on changing experimental conditions. Already reported values of order of kinetics of Thermoluminescence glow curves are changed, when analyzed according to new model for the appearance of thermoluminescence glow curve and its kinetic formalism. The new kinetic formalism of Thermoluminescence glow curve, related with the extent of retrapping and simultaneous recombination processes in thermoluminescence, gives more exact value of order of kinetics.

Keywords: *Order of Kinetics, Thermoluminescence, Retrapping, Recombination, Heat Treatment*

INTRODUCTION

Thermoluminescence (TL) is a radiation induced defectrelated process in crystalline materials. It is a very powerful technique used for dosimetry of ionizing radiations as the energy absorbed by the phosphor on being exposed to ionizing radiation can be easily detected as light on stimulating it with heat. TL provides very useful information about the charges trapped and energy transfer processes in a crystalline lattice resulting in light emission (Sangeeta *et al.*, 1992, Sabharwal *et al.*, 1999, Suresh *et al.*, 1994, Daniel *et al.*, 2014).

So, many works on Thermoluminescence of natural quartzes have been reported in literature. The glow curves of quartz are of quite complicated in nature and show variability in passing from one genetic type of the sample to another.

Generally, quartz exhibits TL glow peaks (Rao *et al.*, 2011) at about 85, 110, 180, 220, 325, 370, and 480^0C (for a heating rate of 5^0C/s).

In prospects of dating the preferred peaks are at 110, 325, and 375^0C.

The problem of exact mechanism involved in appearance of glow curves of material used for any practical applications like dosimetry and dating are still remains unsolved. This limitation in no way has limited the use of the technique because of the well-developed phenomenological explanation of the process with the introduction of the order of kinetics (Randall *et al.*, 1945, Garlick *et al.*, 1948, Chen, 1969).

The order of kinetics is of supreme importance not only from theoretical point of view but also for its practical applications (McKeever, 1994).

MATERIALS AND METHODS

Here we mainly reconsider the method of determination of order of kinetics in Thermoluminescence glow curves of Silicate Minerals which are already reported in literature (Rao *et al.*, 2011). Here, we follow the method as suggested by Prakash (2013) and Prasad *et al.*, (2012). This method reconsiders basic idea of Adirovitch regarding the appearance of TL glow curve, by introducing the concept of extent of retrapping $\boldsymbol{x}$ and recombination.

$\boldsymbol{x}$ represents the fraction or part of excited electrons which are retrapped such that $0 \leq \boldsymbol{x} \leq 1$. Obviously, retrapping depends on $\boldsymbol{x}$. For $\boldsymbol{x} = 0$, retrapping is zero corresponding to first order kinetics and for $\boldsymbol{x} = 0.5$, retrapping is 50% corresponding to second order kinetics and so on. They derive a general equation for intensity of TL glow curve involving any extent of retrapping.

$$I = (1-\boldsymbol{x})n_o s \exp[-\frac{E_a}{k\,T} - \frac{s\,(1-\boldsymbol{x})}{b}\int_{T_o}^{T}\exp(-\frac{E_a}{k\,T'})dT']$$

and condition for peak temperature is

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

where I is intensity of glow curve at temperature T, n_0 is the initial concentration of trapped electrons per unit volume at T_o corresponding to t = 0, E_a is activation energy or trap depth, *s* the pre exponential or escape frequency factor, *k* is Boltazmann's constant, T_o the initial temperature wherefrom TL glow curve starts to appear, b the constant linear heating rate and T′ an arbitrary temperature in the range T_o to T. In new suggested mechanism order of kinetics ℓ involved in TL process is given by the relation

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

Here we are reconsidering the TL glow curves of variety of quartzes, in different experimental conditions, chosen from different origin as already reported (Rao *et al.*, 2011).

I. Chert (a form a–quartz) from near the limestone deposit is heated up to 400ºC. The heatingrate in most of the cases is from 300ºC/min, and recorded using a commercial recording system model TL-1404. The sample size is ~100µ (after grounded). It was irradiated with γ–rays from a^{60}Co source with dose rate of 0.5Gy/Sec (Prokein *et al.*, 1994).

II. Synthetic single crystals of α-quartz (Premium Q) with or without firing / air swept were irradiated with γ-radiation from a ^{60}Co source with dose rate of 0.041Gy/sec at roomtemperature. TL was recorded at a heating rate of 2^{0}C/sec in nitrogen atmosphere (Yang *et al.*, 1988).

III. Isolated 380^{0}C peaks of quartz (flint) at various doses of irradiation (60, 120, 240, 480, 960 and 1920 Gy) at a heating rate of 10^{0}C/sec (Valladas, 1992).

IV. Two natural TL curves with and without standard preheat (for 5 min. at 200^{0}C) at a heating rate of 5^{0}C/s (Roberts *et al.*, 1994).

RESULTS AND DISCUSSION

The TL glow curves recorded for natural silicate mineral is subjected to various heat treatments and irradiations are shown in Figure 1and Figure 2. The important parameters (some are already reported and some are calculated as per new concept of extent of retrapping and corresponding order of kinetics) of the glow peaks are presented in Table 1.

The trapping parameters E_a and *s* are also presented in Table 1. The values of the trapping parameters (E_a, *s*) are same as evaluated by different well established methods.

Thus, results of the 100^{0}Cpeak of chert / quartz shows that the order of kinetics is not consistent following non-first-order kinetics.

Isolated 375^{0}C glow peak of flint presented by Valladas (1992) under various doses (60, 120, 240, 480, 960 and 1920 Gy) of irradiation with a uniform heating rate b= 10^{0}C/s is shown elsewhere while the peak parameters are presented in Table 2.

The results show that with the increase of dose the peak temperature (Tm) shifts to lower temperature. In agreement with the conclusion of Prokein and Wagner, the present rigorous curve fitting (Rao *et al.*, 2011, Chen *et al.*, 1997) demonstrates nonfirst order kinetics for all the natural TL peaks of quartz relevant to dating.

The values of E and s, obtained by Prokein and Wagner, for the 280^{0}C peak by initial rise (IR) and peak shift with heating rate (PS), are in very good agreement with the present data, which confirms the theoretical prediction of Gartia *et al.*, (1992) and Singh *et al.*, (1990). The values of the trap-depth (E_a) and frequency factor (*s*) obtained by Rao *et al.*, (2011) for110, 325 and 375^{0}C peaks are similar to the results of earlier workers.

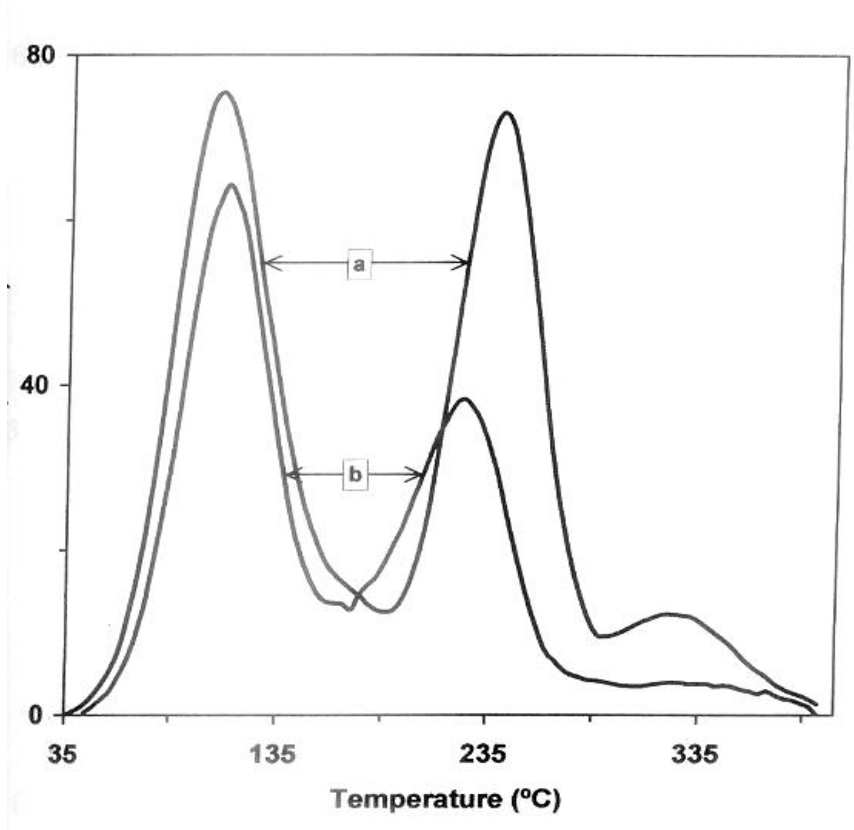

Figure 1: Glow Curve of Chert (a) NTL + 15 min γ-Radiation (b) 6- min Laser Bleached and 2-hrs γ-Radiation (Ankamma Rao *et al.*, 2011)

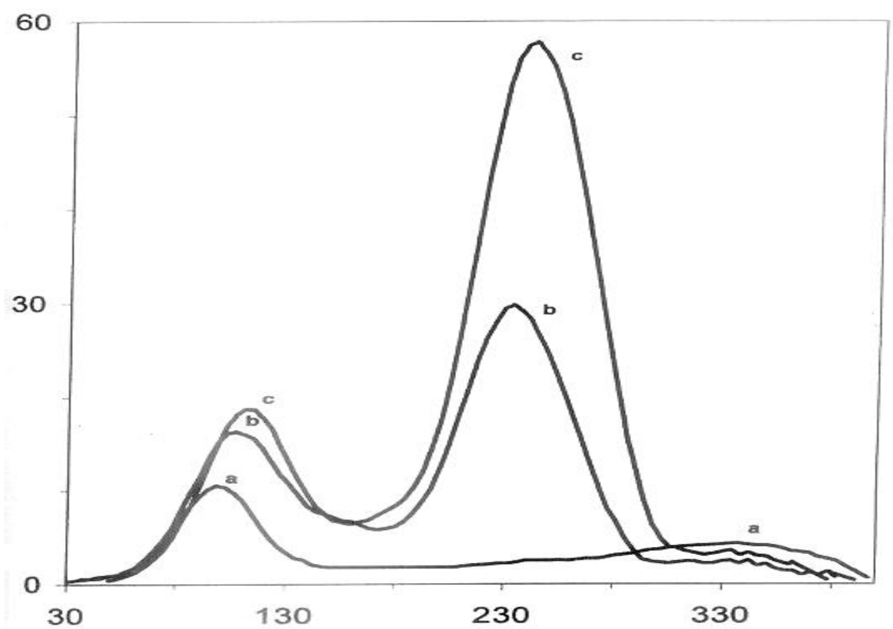

Figure 2: TL Glow Curve of γ-Irradiated (15min) Chart with Pre Heat Treated at Different Temperatures. Curves a, b and c are for Preheating at 300, 500 and 700oC (β= 3.38º C /Sec) (Rao *et al.*, 2011)

Table 1: Peak Temperature Tm, Heating Rate (b), Trapping Parameters and Order of Kinetics of Chert and Quartz

Material	**Specification**	**Expt. Parameters Rao *et al.*, 2011**		**Trapping Parameters Rao *et al.*, 2011**		**Order of Kinetics ℓ**
		T_m(⁰K)	**b (⁰K/s)**	**E_a (eV)**	**s (sec^{-1})**	
Chert	NTL +15 min γ-irradiated	378.0	3.37	0.814	$1.5x10^{10}$	0.943846225
	6min. Laser +2 hr γ – irradiated	382.7	3.37	0.817	$1.2x10^{10}$	0.95699391
	Preheat at 300ºC +15 min. γ - irradiated	371.6	3.38	0.821	$2.9x10^{10}$	0.910973913
	Preheat at 500oC +15min. g–irradiated	379.6	3.38	0.827	$2.0x10^{10}$	0.930004866
	Preheat at 700oC +15min.g–irradiated	385.4	3.38	0.841	$2.1x10^{10}$	0.949985097
Quartz	Unfired	393.0	2.00	0.796	$2.1x10^{9}$	10.86995228
	Fired	369.0	2.00	0.846	$3.0x10^{11}$	5.795213583
	Unswept	370.0	2.00	0.822	$2.3x10^{10}$	1.048750922
	Swept	362.0	2.00	0.743	$2.5x10^{9}$	0.859447319

Table 2: Dependence of Peak Parameters on Irradiation Dose for the 370⁰C Glow Peak of Flint (Rao *et al.*, 2011)

Irradiation dose	**Peak Intensity I_m (au)**	**Peak Temperature T_m (⁰K)**
60	5	640.69
120	12	637.31
240	28	634.54
480	51	629.92
960	82	625.31
1920	110	620.69

Conclusion

The natural TL peaks of quartz confirms the values of trapping parameters obtained by earlier workers using conventional simple methods like initial-rise (IR), isothermal decay (ID) and peak shifting with heating rates (PS). The information provided in this paper in terms of the values of E_a, s as reported by Rao *et al.*, (2011) and ℓ , as calculated according to new concept of order of kinetics based on extent of retrapping ***x*** involved in concerned thermoluminescence process, are expected to help in deconvolution complex natural TL curves which will enable one to evaluate the areas ofthe individual glow peaks, a vital information for practical application of quartz in dating. The value of trapping parameters as established does not question to the utility of these peaks in TL dating. The results as shown in Table 2 shows that with the increase of irradiation dose the peak temperature (*Tm*) shifts to lower temperature.

ACKNOWLEDGEMENT
The author is indebted to Prof. Jai Prakash, Ex Pro Vice Chancellor, Pt. D D U Gorakhpur University, Gorakhpur for inculcating research temper, and also thankful to Director of his institute for providing necessary facilities for this research work.

REFERENCES
Rao KA, Niyaz SkP, Rao NVP and Murthy KVR (2011). Thermally Stimulated Luminescence Studies of Silicate Minerals, *Archives of Physics Research* **2**(4) 89.
Chen R (1969). Glow Curves with General Order Kinetics**,** *Journal of the Electrochemical Society* **116** 1254.
Chen R and McKeever SWS (1997). *Theory of Thermoluminescence and Related Phenomena*, (World Scientific, Singapore) 275.
Garlick GFJ and Gibson AF (1948). The Electron Trap Mechanism of Luminescence in Sulphide and Silicate Phosphors, *Proceedings of the Physical Society* **60** 574.
Gartia RK, Singh SD and Mazumdar PS (1992). Determination of the activation energy of a thermally stimulated luminescence peak for the case of a temperature-dependent frequency factor, *Journal of Physics D* **25** 530.
Daniel DJ, Annalakshmi O, Madhusoodanan U and Ramasamy P (2014). Thermoluminescence characteristics and dosimetric aspects of fluoroperovskites ($NaMgF_3:Eu^{2+}$, Ce^{3+}), *Journal of Rare Earths* **32**(6) 496.
McKeever SWS (1994). Editorial, Rad. Measurements, 23: 85.
Prakash J (2013) Thermoluminescence Glow Curve Involving any Extent of Retrapping or any Order of Kinetic, *Pramana— Journal of Physics* **81**(3) 521.
Prasad D, Thakur AN and Prakash J (2012). TL glow curve analysis technique for evaluation of decay parameters and order of kinetics, *Ultra Scientist* **24**(3)B 489.
Prokein J and Wagner GA (1994). Analysis of thermoluminescent glow peaks in quartz derived from the KTB-drill hole**,** *Radiation Measurements* **23** 85.
Randall JT and Wilkins MHF (1945). Phosphorescence and Electron Traps. I. The Study of Trap Distributions**,** *Proceedings of the Royal Society of London* **184** 365.
Randall JT and Wilkins MHF (1945). Phosphorescence and Electron Traps. II. The Interpretation of Long-Period Phosphorescence, *Proceedings of the Royal Society of London* **184**(3) 90.
Roberts RG, Jones R, Spoone NA, Head MJ, Muny AS and Smith MA (1994). The human colonisation of Australia: optical dates of 53,000 and 60,000 years bracket human arrival at Deaf Adder Gorge, Northern Territory, *Quaternary Science Reviews* **13** 575.
Sabharwal SC and Sangeeta HP (1999). Study of growth imperfections, optical absorption, thermoluminescence and radiation hardness of $CdWO_4$ crystals. *Journal of Crystal Growth* **200** 191.
Sangeeta HP and Sabharwal SC (1992). Crystal stoichiometry and thermoluminescence of $Bi4Ge_3O_{12}$ and $Y_3Al_5O_{12}$. *Journal of Crystal Growth* **118** 396.
Singh TSC, Mazumdar PS and Gartia RK (1990). A critical appraisal of methods of various heating rates for the determination of the activation energy of a thermoluminescence peak, *Journal of Physics D*, **23** 562.
Suresh N, Jyoti G, Gupta SC, Sikka SK, Sangeeta SK and Sabharwal SC (1994). Shock-induced amorphization of *q*-GeO_2. *Journal of Applied Physics* **76** 1530.
Valladas H (1992). Thermoluminescence dating of flint, *Quaternary Science Reviews* **11** 1.
Yang XH and McKeever SWS (1988). Characterization of the pre-dose effect using ESR and TL *Nuclear Tracks Radiation Measurements* **14** 75.