International Journal of Engineering, Science and Mathematics
Vol. 7Issue 3, March 2018,
ISSN: 2320-0294 Impact Factor: 6.765
Journal Homepage: http://www.ijesm.co.in, Email: ijesmj@gmail.com Double-Blind Peer Reviewed Refereed Open Access International Journal - Included in the International Serial Directories Indexed & Listed at: Ulrich's Periodicals Directory ©, U.S.A., Open J-Gage as well as in Cabell's Directories of Publishing Opportunities, U.S.A

Kinetic Study of TL Glow Curve of Natural Fluorite

Dr.Devendra Prasad

Abstract

Phosphor materials are very useful for display devices as well as for dosimetric uses. Characterization of material is must for selection of suitable one. Thermoluminescence is one of the most efficient and convenient tool for characterization of material. In the present paper we reconsider the Thermoluminescence studies of Natural Fluorite and ϒ- irradiated Natural Fluorite material, already reported in literature, to evaluate order of kinetics involved. Here a new method of analysis is adopted for the analysis of Thermoluminescence glow curves in order to evaluate order of kinetics. Order of kinetics involved in process depends on extent of retrapping. It is found that order of kinetics increases with irradiation dose.

Keywords:

Thermoluminescence, Orders of kinetics, Phosphors, Irradiation Dose, Retrapping.

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1. Introduction

Phosphor is luminescent material that emits light when exposed to radiation such as ϒ-ray,ultraviolet light, visible, infrared radiation or an electron beam. Thousands of phosphors have been synthesized, each one having its own characteristic colour of emission and period of time during which light is emitted after excitation ceases. Phosphors excited by ultraviolet, visible, and infrared radiation are used principally in the fluorescent lamps commonly employed for general illumination. The dosimetricuse of these materials are of great importance. Thermoluminescence (TL), is extensively used as a technique in dosimetry. The energy absorbed by a phosphor on being exposed to some ionizing radiation is released as light on subsequently heating it. The intensity of light emitted by the phosphor on being heated gives an idea of the concentration of defect centres caused by the interaction of ionizing radiation with matter. Further, TL is a convenient technique to understand the charge trapping and detrapping mechanisms that result from the interaction of the radiation with the existing defects in material. However, there is no simple model or explanation for TL mechanism because of the wide variety of processes involved. In the structure of the inorganic phosphors there exist point defects, naturally occurring or artificially created, which induce electronic states in the forbidden band; these defects have great importance on understanding the TL phenomenon [1-5]. It is a simple, efficient, convenient and relatively inexpensive experimental technique to study various aspects of the role of defects and impurities in solids with considerably reliability [6-8]. The polycrystalline materials exhibit a glow curve with one or more peaks when the trapped electrons are released and then captured by luminescence centers by thermal stimulation. This glow curve, also known as TL spectrum or Thermogram, is a graphical representation of the luminescence intensity as a function of temperature, providing information about decay parameters , such as activation energy (E_a), frequency factor (s) and the order of the kinetics (ℓ) [9-12]. TL response depends strongly on the material, the type of impurity, radiation induced defect centers, dose and type of ionizing radiation [13-22]. As the TL intensity is related to the radiation dose, TL is widely used in radiation dosimetry and in geological dating [23]. Because of high demand of sensitive TL dosimetry phosphors numerous research work carrying regularly on different phosphor materials. Among the various natural minerals, who demonstrate the thermoluminescence phenomenon, only a small fraction satisfy the requirements for use as thermoluminescence dosimeters (TLDs) (McKeever, 1985)[23]. Natural calcium fluoride (CaF_2; fluorite, commercially fluoraspar) with a large variety of colors such as white, pink, green, violet, etc., is a common mineral in nature and one of the most sensitive thermoluminescent materials for radiation dose monitoring. Since the mineral fluorite is abundantly available in the Earth's crust and thus can be obtained easily, many studies have been done exploring the possibility of using it for personal and/or environmental dosimetry as well as identifying its TL mechanisms [24-27]. A significant amount of these studies are closely connected with the main TL characteristics of natural fluorite as-sourced and when doped with rare-earth minerals [28-32]. Natural fluorite contains many activators, which are predominantly rare earth ions. Annealing is used with TL materials to establish the background (i.e., the thermoluminescence signal at zero radiation dose) and the sensitivity (i.e. the TL signal per unit radiation dose) of the material, and to maintain the stability of these parameters [33-35]. Yegingilet. al.[36], have developed and optimized the conditions necessary to erase the effects of the natural dose with a natural CaF2 sample to establish the background and sensitivity with an initial high temperature thermal treatment followed by low temperature annealing. The glow curve obtained with the sample irradiated with a 90Sr/90Y beta source at a dose of 2 Gy is presented and the kinetic parameters of the peaks appearing in the glow curve are calculated. The effects of high temperature annealing and very high beta dose are clarified, and the reusability of the dosimetric peak is examined. The fading characteristics of some of the peaks in the glow curve of the phosphor are analyzed.

In present paper we reconsider the TL study of natural fluorite in a new kinetic formalism and analyze the reported data to evaluate involved order of kinetics.

2. Material used and method of analysis

The present study has been made on experimental study reported by Yegingilet. al.[36] and the material used by them is natural calcium fluoride sample and was obtained from the Akcakent region of Turkey, supplied by the Department of Geology Engineering, University of Cukurova in Adana. The selected natural crystal was light green in color and fluorite samples were analyzed in both powder and crystal forms. The crystals were pulverized using an agatemortar and sieved to obtain a powder with grain size between 90 and 140 m. To ensure good thermal contact, approximately 3 mg of a sample was fixed by silicone spray on an aluminum disc of 10 mm, within a diameter of 3 mm. The sample is properly go through annealing process.

All irradiations were done at room temperature using beta rays from a $^{90}Sr/^{90}Y$ source with an activity of 1.48 GBq (40 mCi) which emits beta particles with a maximum energy of 2.27 MeV. The dose rate from the source was 6.689 Gy min^{-1} at the time of irradiation. Each sample is of approximately 3 mg and all the experiments were carried out in the dark to prevent possible decrease in luminescence that can occur from exposure to light.

The glow curve thus obtained is characterize by different trap levels that lie in the band gap of the material. The use of thermoluminescent material as a dosimetric material and as a phosphor is based on a good knowledge of its kinetic parameters that include trap depth (E_a), order of kinetics (ℓ) and frequency factor (s). Among the various methods to obtain the number of glow peaks in the complex glow curves and their kinetic parameters that best describe the peaks [38], computerized glow curve deconvolution (CGCD) method has become very popular.

3. Result and discussion:

In order to understand the characteristic glow curves of the virgin natural CaF_2 samples, the TL glow curves were obtained by heating samples from room temperature (RT) up to 450^0C at a heating rate of 2 ^{0}C s^{-1}. The glow curves of natural fluorite, as reported by Yegingilet. al.[36], without any irradiation and at above 250^0C were highly complex, consisting of a group of high temperature overlapping TL peaks are shown in Fig.1. There are two prominent peaks having considerably large full widths at half peak intensity are observed which indicated that the peaks have more than one peak. In order to evaluate TL decay parameters and order of kinetics, these complex glow curve may be resolved by CGCD method. But the decay parameters are highly

affected by small changes in shape of the glowcurves as well as the position of the individual peaks in the glow curve and the kinetic parameters obtained for the natural glow curves using the CGCD method are unlikely to produce reliable results. Yegingilet. al.[36] use the additive dose (AD) method to evaluate different parameters. In this method samples were irradiated at different levels of dose (1, 2, 4 and 10 Gy) to check for dose dependence of the peak temperature (T_m); Fig. 2 shows the glow intensity vs. temperature obtained with irradiated calcium fluoride at a heating rate of 2^0C s^{-1}. TL decay parameters are calculated for resolved glow peaks of Fig.2 are calculated by Yegingilet. al.[36] as presented in Table.1. They estimated that all the peaks of Fig.2 correspond to first order kinetics. There are so many different theories are proposed for the appearance of TL glow curve. In all the theories equation for peak temperature is same and is

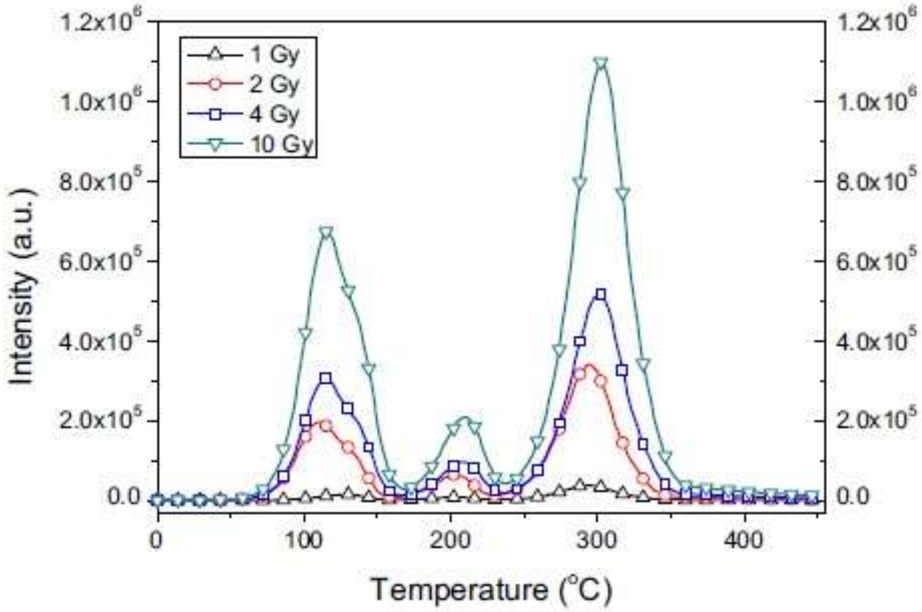

Fig.1 TL Glow curves of CaF_2:natural after beta exposures of 1 Gy, 2 Gy, 4 Gy and 10 Gy as indicated [36].

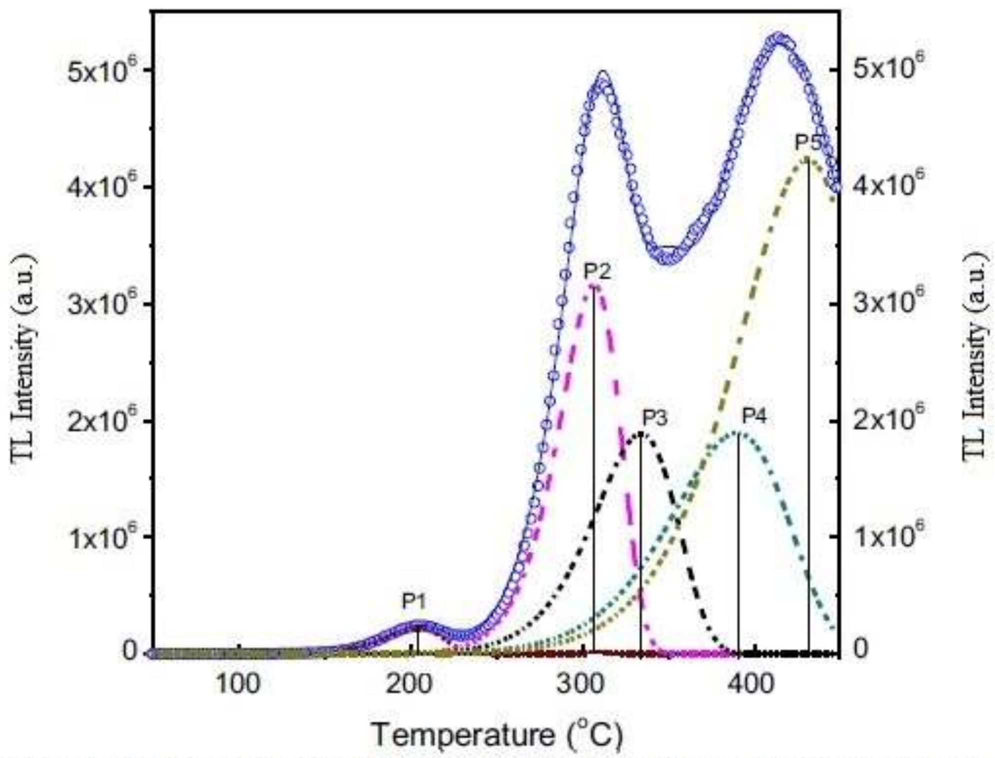

Fig.2 Analyzed glow curve of natural fluorite as received from the ground without irradiation. The circles are the experimental data points and the dashed curves are the components peaks and solid line is the sum of all the individual peaks [36].

given by

$$T_m^2 = \frac{bE_a\tau_m}{k}$$

where b is linear heating rate, E_a is activation energy, τ_m is relaxation time at peak temperature and k is Boltzman's constant. Relaxation time at peak temperature is given by Arrhenius relation

$$\tau_m = \tau_0 \exp(\frac{E_a}{kT_m})$$

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

Table.1
Reported TL decay parameters and evaluated order of kinetics for TL response of Natural Fluorite without irradiation.

Peak	E_a (eV)	s (s^{-1})	τ_0 (s)	T_m (^0K)	T_m^2 ($^0K^2$)	$(bE_a\tau_m)/k$ ($^0K^2$)	ℓ
P1	1.13	9.72E+10	1.03E-11	477.5	228006.3	228109.2	0.999549
P2	1.58	6.48E+12	1.54E-13	578	334084	338723.3	0.986304
P3	1.26	2.17E+09	4.61E-10	604.9	365904	424417.1	0.862133
P4	1.06	6.58E+06	1.52E-07	664	440896	415426.4	1.06131
P5	1.1	3.99E+06	2.51E-07	704.9	496884	468810.2	1.059883

From sixth and seventh columns 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 [38] 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

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

and accordingly peak temperature condition is now 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 $\boldsymbol{x}$ 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.[39].
As per the new method of analysis order of kinetics is evaluated for different peaks of Fig.2 glow curve and are given in eighth column of Table.1.
Yegingilet. al.[36] also evaluated the activation energy and frequency factor for the observed thermoluminescenceglowcurves of CaF2:natural irradiated with 2 Gy by using CGCD. Reported glow curves and CGCD resolved peaks are shown in Fig.3.

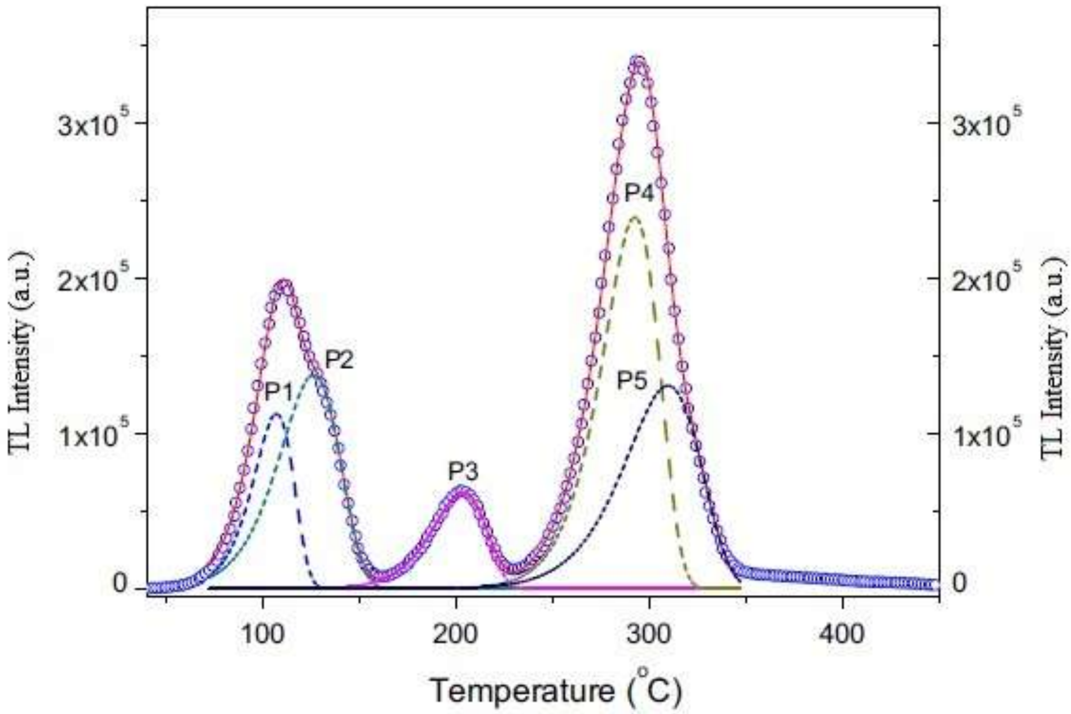

Fig.3 CGCD Resolved TL glow peaks of the glow curve from natural fluorite after 2 Gy irradiation. The circles are the experimental data points and the dashed curves are the component peaks and solid line is the sum of all the individual peaks [36].

Table.2
Reported TL decay parameters and evaluated order of kinetics for TL response of Natural Fluorite after 2Gy irradiation.

Peak	E_a (eV)	s (s^{-1})	τ_0 (s)	T_m (^0K)	T_m^2 ($^0K^2$)	$(bE_a\tau_m)/k$ ($^0K^2$)	ℓ
P1	1.16	4.10E+14	2.44E-15	383	146689	120786.5	1.214448
P2	0.85	6.70E+09	1.49E-10	403	162409	125670.8	1.292337
P3	1.38	6.46E+13	1.55E-14	478	228484	176145	1.297136
P4	1.83	2.90E+15	3.45E-16	568	322624	253319.4	1.273586
P5	1.44	2.90E+11	3.45E-12	583	339889	323806.5	1.049667

Reported values of decay parameters and evaluated values of order of kinetics are presented in Table.2

Conclusion:

In this study, the experimental TL study of natural fluorite material, as reported by Yegingil et. al., are reexamined to find out more correct values of order of kinetics corresponding to different CGCD resolved glow peaks of TL glow curves of before irradiation and after irradiation of above said material. It is found that the evaluated values of order of kinetics are different from reported one. Order of kinetics increases after irradiation means there is more retrapping and simultaneously less recombination process. These more correct values of order of kinetics may help in deciding the suitability of natural fluorite material for routine use in applied radiation protection dosimetry.

Acknowledgements:

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

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