*Indian J. Phys.* **68A** (1), 105 – 112 (1994)

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**I J P A**
- an international journal

# Variation of order of kinetics with dose of X-irradiation in LiF single crystals

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*Received 17 August 1993, accepted 31 August 1993*

**Abstract** : Evaluation of trapping parameters of thermally stimulated glow peaks in LiF single crystals is accomplished by a technique named isothermal monochromatic luminescence decay method. This method has the advantage of ascertaining intermediate order of kinetics from the luminescence decay curves. It is observed that 535 K and 568 K glow peaks are found to obey intermediate order of kinetics (*b*) and the values of *b* are found to be 1.2 and 1.3 respectively when the LiF crystals are X-irradiated for 15 mins. However, as the X-irradiation dose is increased, both the glow peaks exhibit a decrease in the order of kinetics. The results are explained in a way that as long as the saturation defect concentration is not attained, the glow curves exhibit intermediate order of kinetics, because of availability of vacant traps for retrapping to take place and as the X-ray dose increases, the availability of vacant traps decreases with the result that the order of kinetics decreases with the dose of X-irradiation.

**Keywords** : Thermally stimulated luminescence, order of kinetics, LiF single crystals.

**PACS No** : 78.60.K

In the thermally stimulated luminescence measurements, knowledge of order of kinetics is a pre-requisite condition for analysis of TL glow peaks. Various methods of evaluating the trapping parameters from the experimental glow curves are known [1,2]. However, the problem of evaluation of trap parameter is yet unsolved because any of the analytical methods demands a completely or fairly isolated glow peaks for ascertaining the order of kinetics and in turn for determining the activation energy and frequency factor. In this paper, the evaluation of trap parameters in LiF single crystals is accomplished by the technique named isothermal monochromatic luminescence decay method. This method has an advantage of ascertaining even the intermediate order of kinetics from the luminescence decay curves.

The Randall and Wilkins theory [3] for first order kinetics and the Garlick and Gibson's theory [4] for second order kinetics have been extended by the workers for the intermediate order of kinetics [5,6,7] and the general equation for the phosphorescence decay can be written as :

$$I = -\frac{dn}{dt} = s'n^b \exp\left(-\frac{E}{KT}\right) \tag{1}$$

where, $I$ is the TL intensity, $E$ activation energy, $K$ Boltzmann constant, $s'$ the pre-exponential factor, $b$ the order of kinetics, $n$ the concentration of electrons.

The solution of this equation can be written as

$$\left(\frac{I_0}{I}\right)^{\frac{b-1}{b}} - 1 = n_0^{b-1}s'\left[\exp\left(-\frac{E}{KT}\right)\right](b-1)t. \tag{2}$$

At a constant temperature, plot of $\left[\frac{I_0}{I}\right]^{\frac{b-1}{b}} - 1$ *vs* $t$ yields a straight line and the slope of which is given by

$$p = n_0^{b-1}s'(b-1)\exp\left(-\frac{E}{KT}\right),$$

$$\ln p = \ln\left[n_0^{b-1}s'(b-1)\right] - \frac{E}{KT} \tag{3}$$

Again using the slopes $p$ for different temperature from the straight line nature of

$\left[\frac{I_0}{I}\right]^{\frac{b-1}{b}} - 1$ *vs* time plots, $\ln p$ *vs* $\frac{1}{T}$ plots are obtained, which are straignt line in nature. The slope of the straight line nature of $\ln p$ *vs* $\frac{1}{T}$ yields the activation energy.

Laboratory grown single crystals of LiF of approximate size 6 × 4 × 1 $\text{mm}^3$ cleaved from the same bulk were used for the study. All the samples were heated to 400°C for 10 minutes under vacuum at $10^{-3}$ Torr and then quenched to RT before X-irradiating them. The crystals were irradiated under vacuum by $X$-rays obtained from $M_0$ target of Machlett tube operated at 30 kV and 10 mA. The glow curves were recorded at uniform heating rate of (30 ± 0.5) k/min and the luminescence emission was detected by RCA IP28B and the photo current amplified by the electrometer amplifier was fed to an mV potentiometric recorder. Jarel-Ash 1/4 m grating monochromator was used for recording monochromatic thermoluminescence golw curves.

The first procedural step in Isothermal Monochromatic Luminescence Decay method (IMDL) is the recording of monochromatic glow curves (*i.e*. recording glow curves by setting the monochromator at different emission wave lengths which are obtained from the thermoluminescence spectra). Then exposing the crystal to suitable dose of $X$-rays, the crystal is quickly raised to a chosen temperature on the rising side of the MTL glow peaks and then maintaining the temperature constant, the decay of luminescence with time is recorded. This procedure is repeated for two more temperatures. In the case of first order and second order kinetics, the plots of ln $I$ *vs* time and $\left(\frac{I_0}{I}\right)^{1/2} - 1$ *vs* time respectively should yield straight lines. If the straight line nature is not obtained in either case, then the experimental data is fitted to the straight line nature of $\left(\frac{I_0}{I}\right)^{\frac{b-1}{b}} - 1$ *vs* time plots (where $1 < b \leq 2$) by choosing different test values of '$b$', among which the value of $b$ which gives the best fit straight line, gives the order of kinetics. The slopes ($p$) of these straight line plots at different temperatures are noted and again ln $p$ *vs* $\frac{1}{T}$ plots are obtained, the slope ($m = -\frac{E}{k}$) of which gives the thermal activation energy.

The MTL (monochromatic thermoluminescence) glow curves of LiF crystals, X-irradiated at RT were recorded by setting the monochromator at the emission wavelengths

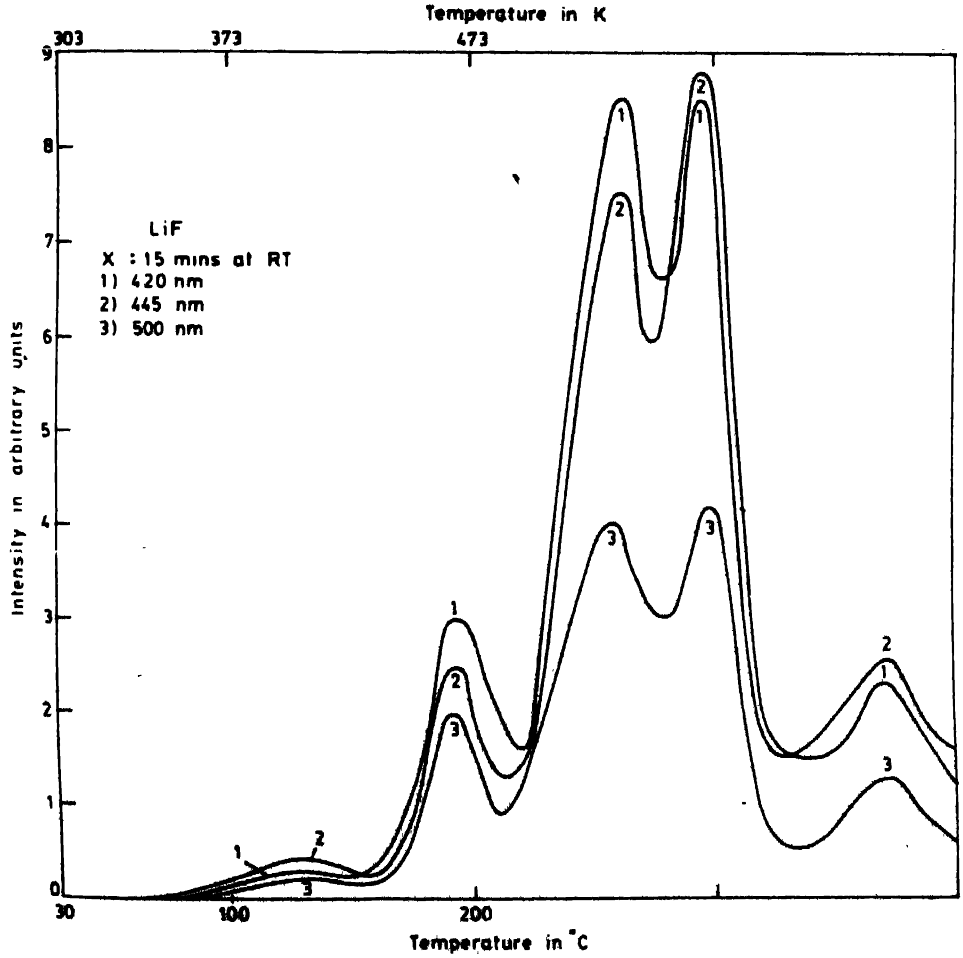

Figure 1. MTL Glow curves of RT, X-irradiated LiF crystals.

420, 445 and 500 nm, as shown in Figure 1. These MTL glow curves exhibit glow peaks at 397, 467, 538, 568 and 643 K of which 535 and 568 K glow peaks are very strong.

In order to evaluate the trap parameters of 568 K glow peak of RT, $X$-irradiated LiF crystals, the three temperatures chosen are 567, 561 and 553 K. The crystals were X-irradiated for 15 mins at RT and IMLD curves were recorded for the 420 and 445 nm emissions. The best fit of straight line nature of $\left(I_0/I\right)^{\frac{b-1}{b}} - 1$ *vs* time plots were obtained

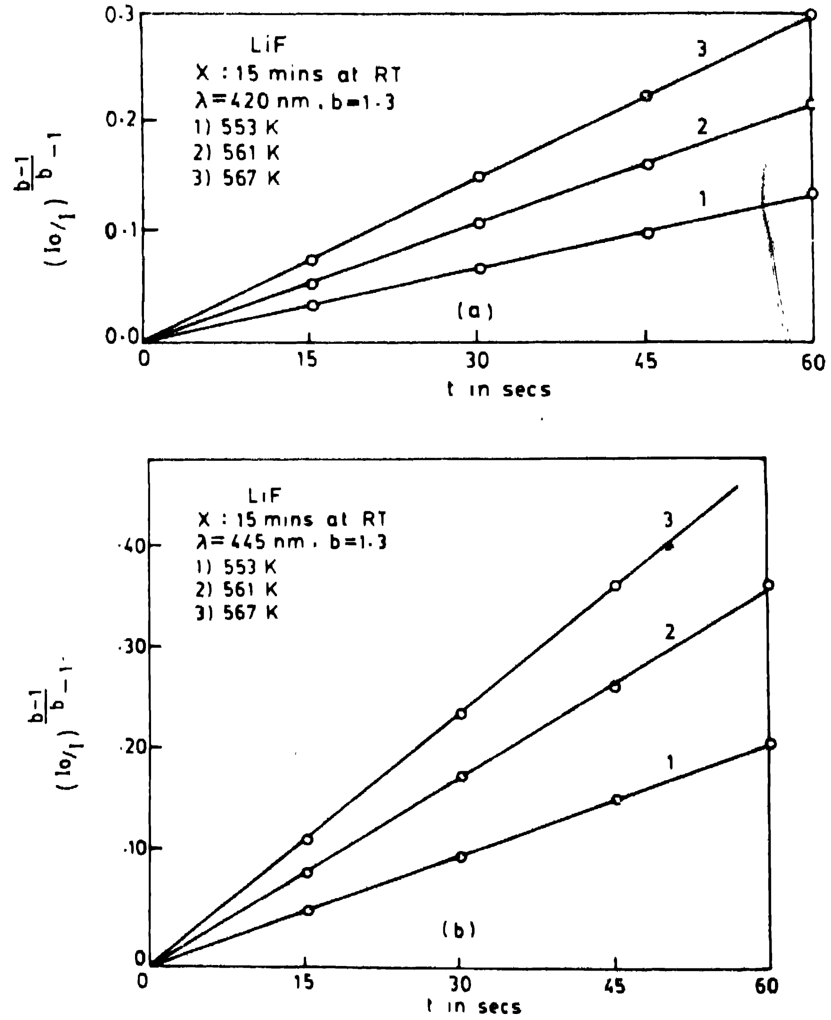

**Figure 2.** (a) and (b) IMLD curves for the 567K glow peak of RT, X-irradiated LiF Crystals

for $b$ = 1.3 as shown in Figures 2(a) and 2(b). The straight line nature of the plots reveal that the 568 K glow peak obeys intermediate order of kinetics and is equal to 1.3. The activation energy corresponding to 568 glow peak is calculated from slopes of ln $p$ *vs* $\frac{1}{T}$ Figure 2(c) and is found to be 1.63±0.03 eV.

Similarly the trap parameters of 535 K glow peak of RT, X-irradiated LiF single crystals were evaluated by choosing three temperatures at 520, 528 and 535 K. The crystals were X-irradiated for 15 minutes and the IMLD curves were recorded for 420 and 445 nm emissions. The best fit of the straight line nature of $(I_0/I)^{\frac{b-1}{b}} - 1$ *vs* time plots were obtained for $b = 1.2$ as shown in Figures 3(a) and 3(b). The results reveal that 535 K glow peak obeys intermediate order of kinetics whose value is 1.2. The activation energy of 535 K glow peak is calculated from the slopes of ln $p$ *vs* $\frac{1}{T}$ plots (Figure 3(c)) and is found to be 1.40 ± 0.03 eV.

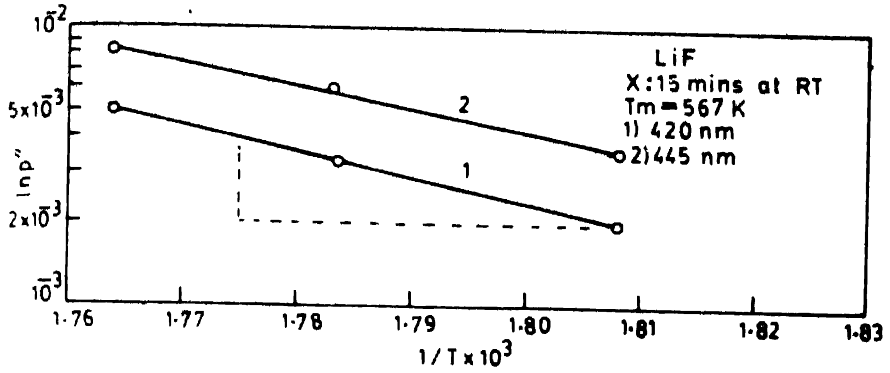

**Figure 2.** (c) Plot of ln p *vs* 1/T for the 567K glow peak of RT, X irradiated LiF crystals

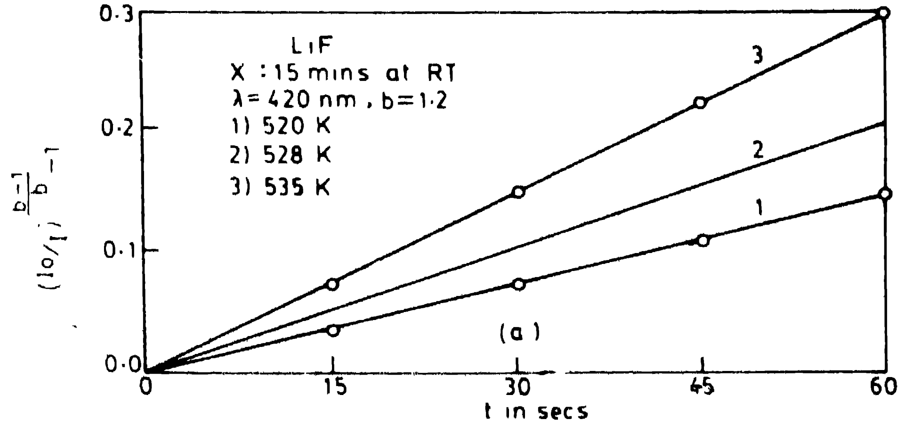

**Figure 3.** (a) IMLD curves for the 535K glow peak of RT, X-irradiated LiF crystals.

In order to study the change in the order of kinetics for different doses, LiF crystals were irradiated at RT for different doses, *i.e.* for 1 hr and 2 hr irradiation and IMLD curves for the two glow peaks 568 and 535 K were recorded at 420 nm emission wave length. The different values '$b$' were computed to obtain the straight line nature of $(I_0/I)^{\frac{b-1}{b}} - 1$ *versus* time plots. (Figures 4(a)) and 4(b). The best fit values of '$b$' for 568 K glow peak are

1.24 and 1.20 for the 1 hr and 2 hr X-irradiated crystals, and for 535 K glow peak, the best fit values of '*b*' are 1.15 and 1.10 for 1hr and 2 hr X-irradiated crystals. Thus, the effect of dose on the order of kinetics indicates that the order of kinetics decreases with the increase of X-ray dose. Similar behaviour was reported [8, 9] for the case of LiF crystals where one of

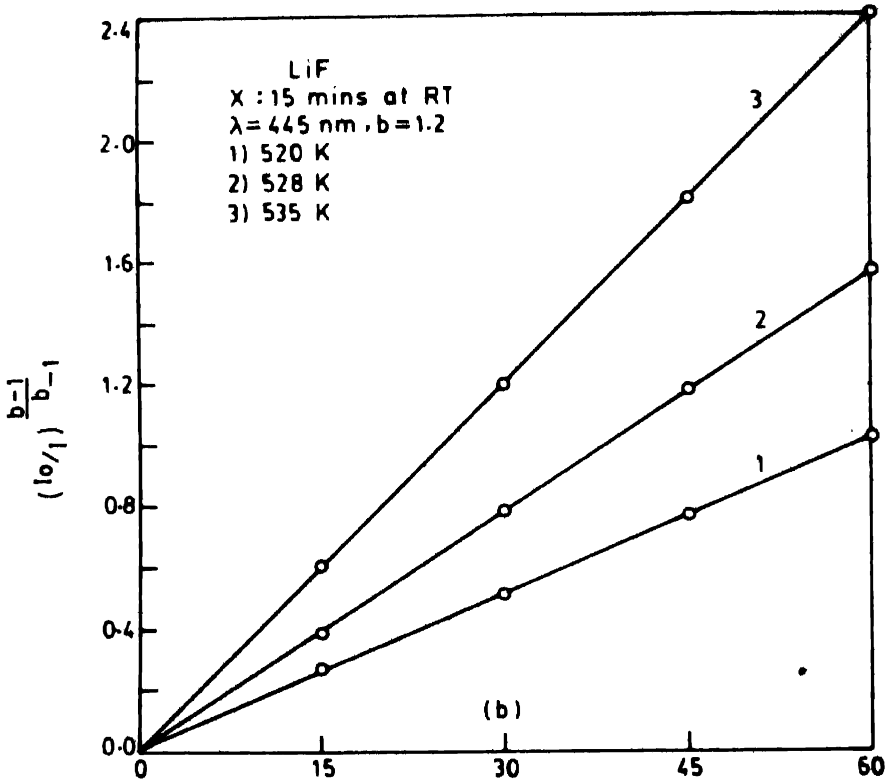

**Figure 3.** (b) IMLD curves for the 535K glow peak of RT, X-irradiated LiF crystals.

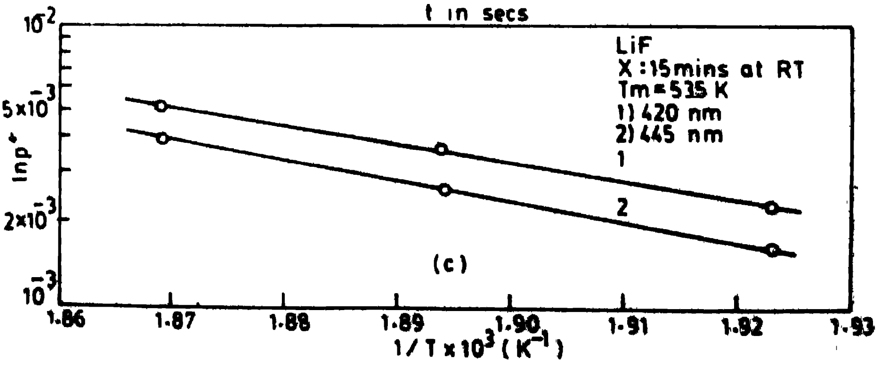

**Figure 3.** (c) Plot of ln *p* *vs* 1/*T* for the 535K glow peak of RT, X-irradiated LiF crystals.

the glow peaks [ V-th glow peak) of LiF obeys intermediate order of kinetics ($b$ = 1.6) and for saturation dose the glow peak obeys first order kinetics. Thus by the IMLD method, it is revealed that the glow peaks of LiF crystals obey the intermediate order of kinetics and the

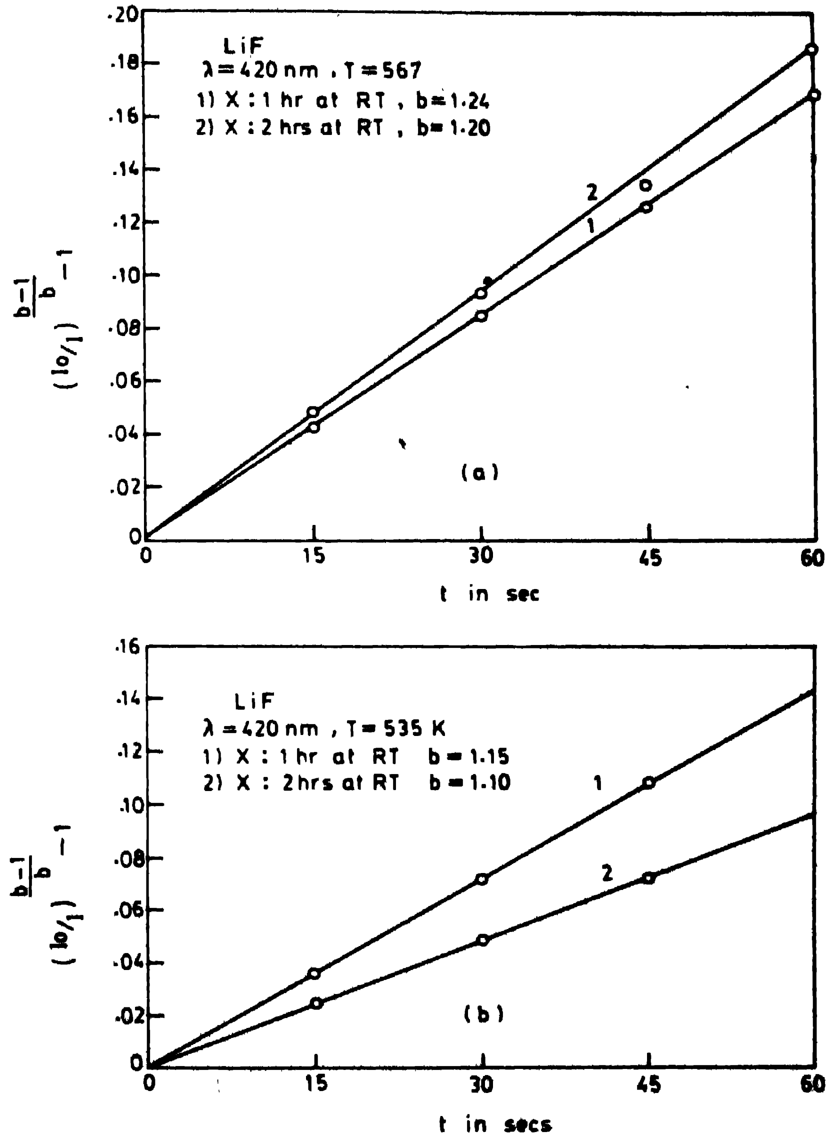

**Figure 4.** IMLD curves of LiF crystals X-irradiated at RT for (a) 567K and (b) 535K glow peaks.

order of kinetics decreasing with the increase of X-ray dose, tends to unity as the dose approaches the dose corresponding to the saturation defect centre concentration. It is worth mentioning that the first order of kinetics arise when the probability of retrapping is very much negligible compared to the probability of recombination whereas the second order of kinetics arise when the probability of retrapping is equal to the probability of recombination. If neither of the two cases are satisfied, then general order or intermediate order of kinetics results. Thus it is understood that as long as the saturation defect concentration is not attained, the glow peaks exhibit intermediate order of kinetics because of availability of vacant traps for retrapping to take place. As the X-ray dose increases, the availability of vacant traps decreases with the result that the probability of retrapping decreases and hence the order of kinetics decreases with the dose.

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