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Thermoluminescence studies of trapping centres in KCl*

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Six thermoluminescence (TL) peaks in the range 30–400°C have been isolated by experimental as well as numerical computational techniques in X-irradiated KCl crystals Thermal activation energy (E), frequency factors (s or $s'n_0$)) and the order of recombination kinetics of these peaks have been established by total curve fitting of TL curves obtained in samples which have undergone different treatments

The nature of charge carriers producing the observed TL has been studied by means of photostimulated TL By X-irradiation at temperatures above 30°C and F-stimulation at 30°C two TL peaks around 135° and 175°C have been generated, from which we conclude that these two peaks are due to thermal release of F-centre electrons The TL peak around 90°C which is always present in crystals irradiated at 30°C is found not to be F-stimulable, which may possibly be due to thermal release of trapped holes

The present investigation shows a set of four TL peaks around 175, 205, 235 and 266°C having almost the same activation energy (E) but different frequency factors (s or $s'n_0$) We propose that these TL peaks are due to thermal release of F centre electrons trapped in different local environments.

1. Introduction

Thermoluminescence (TL) of alkali halides has been widely investigated to determine the thermal activation energy (E), the frequency factor (s or $s'n_0$) and the order of kinetics of recombination. Among the alkali halides KCl (pure as well as doped with suitable impurities) is probable the most extensively studied material (Halperin *et al* 1957, Braner & Halperin 1957, Jain & Mehendru 1965, 1970, Mehendru 1970, Mattern *et al* 1970, Ausin & Alvarez Rivas 1972*a*, 1972*b*. Gartia & Ratnam 1975*a*, 1975*b*, Ratnam & Gartia 1975). In spite of the considerable effort there is disagreement in the data reported by the different investigators. In our earlier papers (Gartia & Ratnam 1975*b*, Ratnam & Gartia 1975) on the TL studies in alkali halides the importance of isolation of pure TL peaks in the determination of thermal activation energy (E) as well as the order of kinetics of recombination was high-lighted. However, it was not possible to isolate all the TL peaks by experimental techniques alone

In the present work the TL peaks which could not be isolated by experimental techniques like high temperature (upto 200°C) X-irradiation alone, F-bleaching

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at 30°C alone and irradiation at high temperatures (105, 155 and 200°C) followed by F-stimulation at 30°C; are isolated by numerical computation. It is shown that there is a unique set of six TL peaks in the range 30–400°C in X-irradiated KCl, their relative intensities being dependent on the treatment given to the sample before recording the TL curve The role of F-centre electron in the TL process of X-irradiated KCl which is still controversial is discussed.

2. Experimental

Several pieces of laboratory grown KCl crystals of approximate size $1 \times 1 \times 0{\cdot}1$ cm^3 cut from the same bulk were used for study. They were all heat treated—kept at 400°C for 30 min. in vacuum and quenched to RT (30°C) before performing the experiments. Irradiation dose was 30 min. of 30 kV, 10 mA X-rays in all the cases The rate of heating was $28 \pm 0{\cdot}5$ degree/min The method of recording the glow curve and other details are described in our previous papers (Gartia & Ratnam 1975*a*, 1975*b*). F-stimulation/bleaching was done for times varying between 5 to 240 min in the sample holder compartment of Spectromom 202 spectrophotometer at RT.

3 Results

3.1. *Analysis of the 266°C peak*

In our earlier paper it has been shown that KCl crystal irradiated at 200°C gives rise to an isolated TL peak at 266°C (Ratnam & Gartia 1975). In this case since the peak does not show any satellite peaks all the three experimental parameters, T_m (glow peak temperature), T_1 (lower half-width temperature) and T_2 (higher half-width temperature) can be determined accurately The geometrical factor $\mu_g = \delta/w$, where $\delta = T_2 - T_m$ and $w = T_2 - T_1$ of this peak is found to be 0·40. According to Chen (1969) $\mu_g = 0{\cdot}42$ for first order and 0·52 for second order TL peak This indicates that the 266°C peak follows first order kinetics. To determine the order of kinetics, E and s of this peak accurately the theoretical TL peak is numerically computed, the TL intensity being calculated at intervals of 4°C Since the geometrical factor (μ_g) shows the peak to follow first order kinetics the following equations of Randall & Wilkins (1945) is used for numerical computation

$$I = sn_0 \exp\left(-\frac{E}{kT}\right) \exp\left[-\left(\frac{s}{\beta}\right) \int_{T_0}^{T} \exp\left(\frac{-E}{kT'}\right) dT'\right] \quad \ldots (1)$$

and the condition for maximum is

$$\frac{\beta E}{(kT_m^2)} = s \exp\left(-\frac{E}{kT_m}\right) \quad \ldots (2)$$

where the parameters have their usual meanings (see Chen 1969) Since all the parameters in eq (2) are known one can calculate the frequency factor s (Sec^{-1}) for different values of E. The value of s is calculated by computer simulation of I using the method of least squares. The numerical computations are carried out on an I B.M 1620 computer. The theoretical TL curve with $E = 1{\cdot}32$ eV and $s = 5{\cdot}5 \times 10^{10}$ (Sec^{-1}) is found to give the best fit with the experimental curve (figure 1).

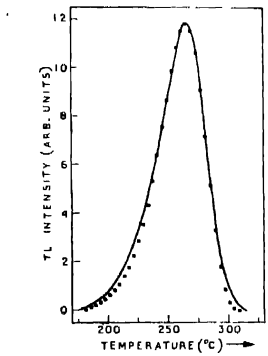

Fig. 1. Thermoluminescence curve of KCl crystal irradiated by 30 kV, 10 mA X-rays for 30 min at 200°C The continuous curve is the experimentally recorded one and dots represent intensities of the numerically computed curve using Randall-Wilkins' equation.

For crystals irradiated at 155 and 105°C two overlapping peaks are observed in the region 240–270°C (Curve A of figures 2 and 3). However crystals irradiated at those above mentioned temperatures followed by 15 min. of F-stimulation at 30°C show a well resolved peak around 260°C (Curve B of figures 2 and 3) Since $\delta\,(T_2 - T_m)$ of this peak in both the cases is close to that of 266°C peak of 200°C irradiated sample, least square fitting of the falling side of this peak is attempted using first order kinetics equation of Randall & Wilkins (1945). The numerically computed TL curve with $E = 1{\cdot}45$ eV and $s = 2 \times 10^{12}$ (Sec^{-1}) gives the best fit for both the cases (curve B of figures 2 and 3).

3.2. *Analysis of the 135°C peak*

In our earlier paper (Ratnam & Gartia 1975) we have shown that by a proper selection of the temperature of X-irradiation and the time of F-stimulation a pure TL peak around 135°C can be generated in KCl. Since geometrical factor (μ_g)

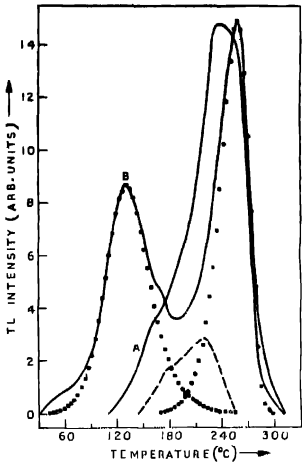

Fig. 2 Thermoluminescence curve of KCl irradiated by 30 kV, 10 mA X-rays at 155°C, (A) for as-irradiated crystal, (B) for crystal having undergone 15 min. *F*-stimulation at 30°C. Dots represent the intensities of the numerically computed TL peaks. The difference curve is shown by discontinuous curve

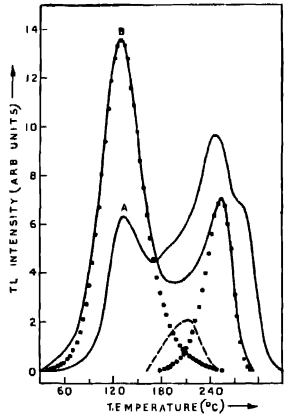

Fig. 3. Thermoluminescence curve of KCl irradiated by 30 kV, 10 mA, X-rays at 105°C: (A) for as-irradiated crystal, (B) for crystal having undergone 15 min *F*-stimulation at 30°C. Dots represent the intensities of the numerically computed TL peaks. The difference curve is shown by discontinuous curve.

of this peak shows that it follows second order kinetics the following equation of Garlick & Gibson (1948) is used for numerical computation.

$$I = s'n_0^2 \exp\left(-\frac{E}{kT}\right)\left[1+\left(\frac{s'n_0}{\beta}\right)\int_{T_0}^{T}\exp\left(-\frac{E}{kT'}\right)dT'\right]^{-2}. \quad \ldots (3)$$

The condition for maximum in this case is—

$$1+\left(\frac{s'n_0}{\beta}\right)\int_{T_0}^{T_m}\exp\left(-\frac{E}{kT'}\right)dT' = \frac{2kT_m^2 s'n_0}{\beta E}\exp\left(-\frac{E}{kT_m}\right) \quad \ldots (4)$$

The numerically computed curve with $E = 0{\cdot}78$ eV and $s'n_0 = 1{\cdot}3\times10^8$ (sec^{-1}) is found to give the best fit with the experimental curve (curve B of figures 2 and 3).

Though curve B of figures 2 and 3 show two well-defined peaks the difference curve (obtained by subtracting the numerically computed TL peaks from the experimental curve) shows in both the cases two overlapping peaks in the region of 180 and 220°C. The analysis of these peaks is done in the following sections No attempt is made to analyse these in figures 2 and 3 as they are not well-defined

3.3 *Analysis of other TL peaks*

TL curve of 240 mm *F*-bleached crystal shows a prominent TL peak at 135°C with shoulders around 90, 200 and 235°C (figure 4) Since we have

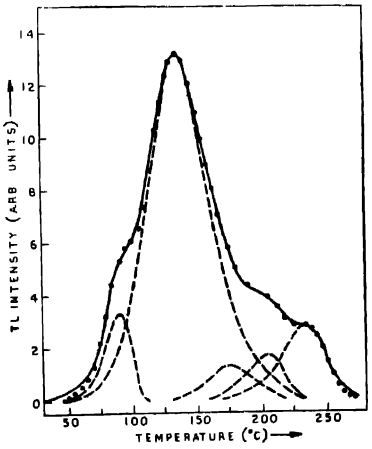

Fig. 4. Thermoluminescence curve of KCl irradiated by 30 kV, 10 mA X-rays for 30 min at 30°C and *F*-bleached for 240 min. at the same temperature. The continuous curve is the experimentally recorded one and the discontinuous curves are the numerically computed TL curves Dots represent the total theoretical TL curve (the computed TL peaks added together).

already successfully analysed the 135°C peak, this curve is selected for analysis by numerical computation The entire TL curve can be fitted by five TL peaks occurring at 90, 135, 175, 205 and 235°C (figure 4) In the experimental curve itself the presence of all the above mentioned TL peaks, except the one at 175°C, are clearly seen though it is difficult to locate their temperature maxima (T_m) exactly However TL curve of KCl crystal irradiated at 155°C followed by 60 min of F-stimulation at 30°C shows two prominent TL peaks at 138 and 263°C with an additional prominent shoulder around 175°C (figure 5) In this case the TL curve can be fitted by five peaks at 135, 175, 205, 230 and 263°C

The values of E, s or $s'n_0$ and also the order of kinetics of all the TL peaks reported above are shown in table 1

Table 1 Thermal activation energy (E), frequency factor (s or $s'n_0$) and the order of kinetics of recombination of the six TL peaks in the range 30–400°C observed in X-irradiated KCl

Treatment	T (°C)	E (eV)	s or $s'n_0$	Order of kinetics
200°C irradiation	266	1·32	$5{\cdot}5\times10^{10}$	First
155°C irradiation + 15 min. F-stimulation	258	1·45	$2{\cdot}0\times10^{12}$	First
	131	0·78	$1{\cdot}3\times10^{8}$	Second
105°C irradiation + 15 min F-stimulation	255	1·45	$2{\cdot}0\times10^{12}$	First
	131	0·78	$1{\cdot}3\times10^{8}$	Second
155°C irradiation + 60 min F-stimulation	263	1·44	$9{\cdot}5\times10^{11}$	First
	230	1·32	$5{\cdot}0\times10^{11}$	First
	205	1·44	$5{\cdot}2\times10^{13}$	First
	175	1·44	$5{\cdot}8\times10^{14}$	Second
	135	0·84	$6{\cdot}0\times10^{8}$	Second
30°C irradiation + 240 min. F-bleaching	235	1·32	$3{\cdot}5\times10^{11}$	First
	205	1·44	$5{\cdot}2\times10^{13}$	First
	175	1·44	$5{\cdot}8\times10^{14}$	Second
	135	0·84	$6{\cdot}0\times10^{8}$	Second
	90	1·12	$1{\cdot}6\times10^{14}$	First

4 Discussion

Jain & Mehendru (1965, 1970) have shown that only two TL peaks are observed in RT X-irradiated spectroscopically pure KCl crystal However, they have reported additional TL peaks in doped or strained samples. They have attributed the 135 and 190°C peaks to the first and second stage F centres, whereas 95 and 270°C peaks have been attributed to the presence of impurities and plastic deformation respectively They have also shown that there is an intimate relation between the TL output and the F centre concentration of the sample. This result has been further supported by Ausin & Alvarez-Rivas (1972a, 1972b)

Braner & Halperin (1957) have shown that F centres bleach at stages corresponding to the different TL peak temperatures. Ausin & Alvarez-Rivas (1972*a*) have also shown that there is an annealing step of F centres corresponding to each TL peak when the temperature of the samples is raised at a constant rate. These results confirm that F centres definitely play a key role in the TL process. Now the question that arises is : what is the exact role F centres play in the TL process ?

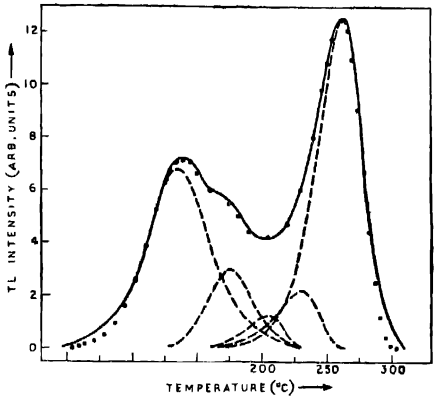

Fig. 5. Thermoluminescence curve of KCl irradiated by 30 kV, 10 mA, X-rays for 30 min at 155°C followed by 60 min of F-stimulation at 30°C. The continuous curve is the experimentally recorded one and the discontinuous curves are the numerically computed TL curves. Dot represents the total theoretical TL curve (the curves added together).

Ausin & Alvarez-Rivas (1972*a*) argue that F centres act as recombination centres for interstitials (hole type centres) which become thermally released from trapping sites. Their argument is based on the fact that the abnormal values of s or $s'n_0$ observed by them as compared to the expected range 10^8–10^{12} (sec^{-1}) rules out the possibility that TL process is due to untrapping of F centre electrons or pure electronic holes. However our results show that in all the cases the values of s or $s'n_0$ are always in the range 10^8–10^{14} (see table 1, column 4).

To specify the nature of the charge carriers giving rise to the observed TL peaks, though ordinary TL data is certainly not adequate, photostimulated TL can provide a way of detecting photoionization of centres allowing in some cases the separation of the processes due to electron carriers from those due to hole carriers. Braner & Israel (1963) have shown that using this technique one can specify the nature of charge carriers producing the observed TL peaks. We have shown in our earlier paper that by irradiating at high temperatures (105,

155 and 200°C) and stimulating with F-light at 30°C one can re-excite F-stimulable TL peaks around 135 and 175°C (Ratnam & Gartia 1975). Thermal activation energy (E) and frequency factor ($s'n_0$) of these two peaks occurring in RT irradiated, heavily bleached sample as well as in the F-stimulated sample are found to be practically the same (see table 1). It is interesting to note that even after 120 min F-stimulation of high temperature X-irradiated KCl crystals we never observed the 90°C peak which is always present in RT irradiated samples. The result indicates that the TL peaks occurring at 135 and 175°C are due to thermal release of F centre electrons whereas the peak around 90°C may be due to the release of trapped holes. Though Ausin & Alvarez-Rivas (1972*a*) report that the TL emission band has its maximum at 440 nm for all the TL peaks, the investigation of Katz *et al* (1972) shows that in addition to the main blue band (440 nm) there also exists a detectable green emission band (540 nm). They have detected this green band at the rise of the 87°C TL peak where the blue emission band was still weak. This supports our proposition in the sense that the recombination centre for 90°C peak is not the same as that of the 135 and 175°C peak.

The present investigation shows a set of four TL peaks around 175, 205, 235 and 266°C having almost the same activation energy, but different frequency factors (table 1). This immediately reminds one of the investigation of Hill & Schwed (1955) and Bonfigholi *et al* (1959) who have reported that all the TL peaks of NaCl occurring above RT have the same activation energy. In recent studies in copper activated KBr (Murti *et al* 1971) and NaCl (Murti & Murthy 1972) it has been shown that two or more TL peaks in the same material can have identical activation energy. The multiplicity of TL peaks in these studies has been attributed due to difference in the frequency factors, since a large value of frequency factor can lower the location of the peak temperature considerably. The variation of frequency factor in these studies has been attributed to the different local environments of the F centre electrons. That there are several types of F centres formed in different environments, which differ in both optical and thermal properties have been shown recently by Arsenovici & Townsend (1972). Therefore, we propose that the four TL peaks occurring around 175, 205, 235 and 266°C are due to thermal release of F centre electrons trapped in different local environments.

5. Conclusion

The present investigation has shown that TL can be profitably used to determine the thermal activation energy (E), frequency factor (s or $s'n_0$) and the order of kinetics as well provided the TL peaks are properly isolated. Depending upon the material, by suitable experimental techniques and numerical computation the individual TL peaks can be isolated from which the trapping parameters

can be determined with certainty as is shown in the present case The nature of the charge carriers whose thermal release give rise to the TL process can be identified by photostimulated TL

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