



Thermoluminescence (TL) Glow curves of doped and undoped KCl in $SrCl_2$ system

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Abstract- Thermoluminescence (TL) also called as thermally stimulated luminescence refers to a process in which a solid, usually a crystalline form, emit light while being heated following excitation. This paper begins giving the theory of thermoluminescence (TL). The basic mechanism of TL has been explained and the role of crystal imperfections in observing such an emission has been put forth. The one trapping - one recombination centre model has been discussed along with accompanied first order and second order kinetics. Finally the results of TL studies in doped and undoped KCl in $SrCl_2$ system.

I. INTRODUCTION:

Thermoluminescence (TL) is the process in which mineral emit light while it is being heated. It is a stimulated emission process occurring when the thermally excited emission of light follows the previous absorption of energy from radiation. Energy absorbs from the ionizing radiation free electrons to move through the crystal lattice and some are trapped at imperfection in the lattice. Subsequent heating of the crystal can release some of these trapped electrons with an associated emission of light. The phenomenon of thermoluminescence (TL) of minerals was know empirically as early as 1663. Not only diamonds but a large number of minerals like quartz, feldspar, calcite and flint were found to emit light energy on warming. Three centuries later in 1989, Roth and Poly reported the first law of thermoluminescence which states that the thermoluminescence of minerals is roughly proportional to the irradiation dose to which they had been exposed. An important observation for making TL a useful tool for dating was that, if the same mineral is reheated, no more light is emitted, and it is only after the application of a new radiation dose that the light may again be emitted. Thermo luminescent is the thermally stimulated emission of light from an insulator or a semiconductor, following the previous absorption of energy from ionizing radiation. The thermoluminescence process can be understood in terms of and structure model of insulators. When a suitable substance is irradiated, electrons are raised from valence band to the conduction band. On return to valence band, some electrons are trapped at some defect locations or trap centres (T), where they can stay for a long time, holes are also simultaneously trapped at recombination centres (R). The trapped electrons are released from their respective trap centres, when the system is heated. Such released electrons may quickly recombine with an oppositely charged recombination (R) centre, resulting in appearance of a TL glow curve.

Let m and n represent the density of holes and electrons in the recombination and trap centres at R and T respectively. The recombination is the process by which ' m ' decreases. Thus the TL intensity, is given by

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$$I = - dm / dt = m n_c A_m \tag{1}$$

where n_c is the density of electrons in the conduction band and A_m the recombination probability. The rate of decrease of 'n' i.e. $(- dn / dt)$ will, of course, depend upon the excitation of electron into the conduction band and also on their retrapping. Thus

$$(- dn / dt) = n s \exp(- E / kT) - (N - n) n_c A_n \tag{2}$$

where s , E , N and A_n represent pre- exponential factor, activation energy for trap, density of total number of trap centres and retrapping probability respectively. The first term on the right hand side of Eqn.(2) represents the rate of release of electrons from their respective trap centres and the second term represents the rate of retrapping.

The charge neutrality, however, requires

$$m = n + n_c \tag{3}$$

Now combining Eqns (1), (2) and (3) we get

$$(dn_c / dt) = n s \exp(- E / kT) - (N - n) n_c A_n - m n_c A_m \tag{4}$$

Chen and Mc Keever assumed a quasi – equilibrium situation for the problem, assuming n_c to be almost constant.

Therefore,

$$(dn_c / dt) = 0$$

and

$$n \approx m$$

The Eqn.(4) accordingly yields

$$n s \exp(- E / kT) = (N - n) n_c A_n + m n_c A_m$$

or

$$n_c = [n s \exp(- E / kT)] / [(N - n) A_n + m A_m]$$

Therefore TL intensity

$$\begin{aligned} I(t) &= (- dm / dt) \\ (- dn / dt) &= m n_c A_m \\ &= [A_m m n s \exp(- E / kT)] / [(N - n) A_n + m A_m] \end{aligned}$$

As the temperature of the sample is raised, electrons and holes escape from their traps at an increasing rate. The free charges can recombine with each other or with other defects and often give out luminescence by their recombination. The resulting thermoluminescence or glow reaches maximum and then decreases to zero as the supply of trapped electrons and holes gets exhausted. The plot of luminescence intensity versus the sample temperature, obtained at constant heating rate is called the glow curve.

The glow curve may however contain one or more glow peaks depending upon, how many types of traps are present in the material. The simulated first and second order glow curves are shown in Fig.1. The basic difference between the first – and second order kinetics is reflected in the symmetry of the TL peak. The characteristic feature of the first-order peak is that it is asymmetric. Above the temperature of the maximum TL, the TL intensity decreases very rapidly with increasing T, because in first order kinetics re-trapping does not play a role. The characteristic feature of the second order peak is that it is almost symmetric, because re-trapping slows down the process of annihilation.

The discussion of the model of Randall and Wilkins is based on the relatively simple situation in which only one kind of trap and one kind of recombination centre are active. The two examples discussed so far, first and second order kinetics is only special cases. Even if the simplifying conditions are assumed to be true in general, the resulting equations consist of many intermediate cases that do not have a distinct order of kinetics. In practice and in particular in natural minerals, several trapping and recombination sites exist giving rise to a multitude of peaks, which may not overlap for a general description of the TL process, we need to take into account that the traps show a wide distribution of energy values. In addition we have to take into account several highly relevant processes, including trapping of charge carriers by recombination (luminescence) centres, trapping by non-radiative centers, mutual recombination, recombination's with defects of opposite charges at trapping centers, redistribution of electrons and holes over the available traps and luminescence (re-trapping) due to thermal excitation into the conduction and valence band.

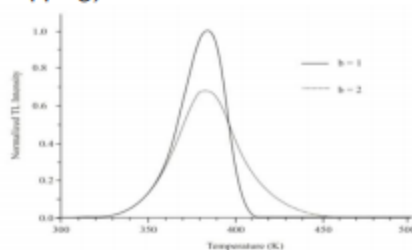


Fig.1. Comparison of first order ($b=1$) and second order ($b=2$) TL glow peaks.

II. EXPERIMENTAL DETAIL:

Preparation of Samples:

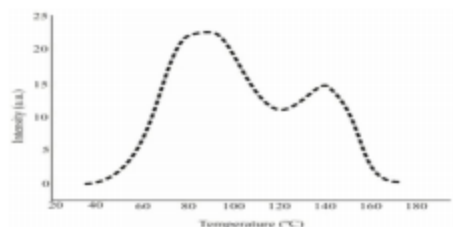
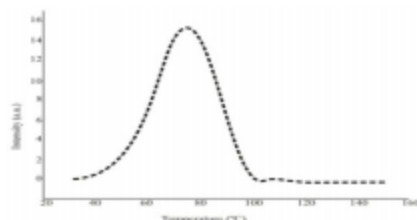
The polycrystalline undoped and doped samples of KCl systems, as mentioned were prepared by the saturated solution method. The saturated solution of KCl was prepared in distilled water and one percent by weight of dopant chloride (SrCl_2) was added to the mother solution. The resulting liquor was filtered and left for evaporation at $80^\circ\text{C} - 90^\circ\text{C}$ to yield crystallites of required compounds. These crystallites were reground and pressed in a die to yield appropriate pellets for experiment.

Irradiation of Samples:

The different undoped and doped samples of KCl were irradiated with X-rays of 20 m.A. & 30 k.V. at RT (27°C) for production of colour centres in them. The exposure time for each sample was kept about the same (900 s) for all samples. The irradiated samples were then kept in a blackened container to avoid photo-bleaching of the colour centres.

III. RESULTS & DISCUSSIONS:

The plot of intensity of glow light as a function of absolute temperature (T) then provides different glow peaks for further study. The glow peaks for the undoped sample of KCl are shown in Fig. 2 & 3, further shows the glow peak plot for KCl : SrCl₂ system. It is seen that two well resolved glow peaks are observed in undoped KCl system, whereas a single unresolved peak is seen for the doped KCl system. The temperatures corresponding to the maxima of glow peaks estimated from the analysis of the glow peak plots are shown in Table 1.

**Fig.2. Glow peaks for undoped KCl****Fig.3. Glow peaks for KCl : SrCl₂ System****IV.CONCLUSION:**

The electrons originated due to X-ray irradiation of KCl crystals could be trapped at anion vacancy sites created due to Schottky/Frenkel defects. Such electrons could thus form usual F-centres. However, if MCl₂ doping is appreciable, as is the case presently with M as Sr, quite a large number of I-V pairs would be created prominently inside a KCl crystal. There is thus a likelihood of electrons being trapped at K⁺ sites, close to the vacancy end of I-V pair. With heavy doping of M²⁺, the second mode of trapping of electrons will be quite probable, as the number of Schottky/Frenkel defects in the KCl crystal will be at a relatively low level.

Table.1: The positions of glow peaks in undoped and Sr²⁺ - doped KCl

Sample	Positions of glow peaks T _{g1} , T _{g2} (K)
Undoped KCl (Sample – 1)	362 ± 5K 420 ± 5K
Undoped KCl (Sample – 2)	356 ± 5K 427 ± 5K
KCl : SrCl ₂	340 ± 5K

When no external doping is done, a very small number of inherent M²⁺ impurities would always be present in a KCl crystal and allow electrons to be trapped effectively through both the mechanisms as above. The observation of two glow peaks in KCl crystals with no additional M²⁺ doping is thus understood. The above also explains observation of only one peak in appreciably doped KCl crystals.

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