

Temperature effect on lyoluminescence of potassium halide microcrystals in luminol solution

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When γ -irradiated microcrystals of potassium halides are dissolved in the luminol solution, the lyoluminescence (LL) intensity initially increases linearly with time, attains an optimum value and then decreases and finally disappears. The LL intensity was detected by PMT whose output was connected to X-Y recorder. Temperature dependence of LL intensity shows that initially the peak of LL intensity (I_m) increases with temperature, attains a peak value, and then decreases with further increase in temperature. Also, the total intensity I_T initially increases, attains an optimum value and then it decreases with further increase in temperature. The decay time decreases with increasing temperature of the solvent, from where the value of activation energy E_a can be calculated. A plausible explanation for the experimental results is given.

Keywords: Activation energy, Luminol (3 amino-phthalahydrazide), Lyoluminescence

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1 Introduction

Lyoluminescence is the phenomenon of light emission when certain substances irradiated with ionizing radiation, are dissolved in a suitable solvent. It was first reported by Wiedeman and Schmidt¹ in 1895. Lyoluminescence was rediscovered in 1959 by Ahnstrom and Ehrenstein², in which they described in a brief note the experiments that were remarkable in breadth coverage of the phenomenon, simultaneously it was reported by Westermarck and Grapengiesser³. Ahnstrom^{4,5} was the first to discuss the use of LL in the study of free radical reactions and the role of F-centres in the LL of irradiated NaCl dissolved in the fluorescence solution. Atari *et al.*⁶ have found that the temperature of the solvent was an important factor in LL emission from NaCl but do not state a quantitative dependence or optimum temperature, and the experiments were performed at 20°C. The investigation of the temperature dependence of LL provides some interesting and important information regarding the nature of luminescence centres^{7,8}. It is generally found that in the substances showing luminescence at room temperature, the luminescence is quenched at some higher temperature, and on the other hand, many substances which are not luminescent at room temperature show this phenomenon at low temperature.

Atari and Ettinger⁹ have studied the effect of solvent temperature on the LL yield of mannose, xylose and glucose. They have found that these three saccharides exhibited similar behaviour showing clear decrease in LL yield with the rise in solvent (water) temperature up to 60°C. Ettinger and Puite¹⁰ have reported that when the solvent is an aqueous solution of luminol, this decreasing trend is not found, rather the trend is a slow decrease up to 40°C followed by a rapid increase beyond that temperature. Temperton *et al.*¹¹ have reported in the case of glutamine that the LL yield from samples irradiated to dose of 1 KGy, decreases as solvent (water) temperature is increased from 9.5 to 18°C. Puite¹² has shown that a post-irradiation heat treatment of 114°C for 5 h increased the LL yield from glutamine. Kundu and Mitra¹³ melted γ -irradiated saccharides and kept them liquid for several minutes and then measured LL. The effect of temperature of solvent on the lyoluminescence yield in saccharides has been studied by Mahapatra *et al.*¹⁴ employing photon counting technique for the solvent temperature in the range 10-90°C.

In the present paper, the effect of temperature of luminol solution on the LL of KCl, KBr and KI microcrystals has been reported.

2 Experimental Details

The pure KCl, KBr and KI, microcrystals were grown from their melt using slow cooling method, i.e. Czochralski method. For the measurement of lyoluminescence, the crystals were crushed into microcrystals form, and the microcrystals having different grain sizes were separated by using sieves of particular dimensions, then these were coloured by exposing them to ^{60}Co gamma source. To study the effect of temperature on the lyoluminescence, 2 ml luminol solution of particular temperature was injected with the help of a syringe into 10 mg sample taken in a transparent glass tube placed close to the photomultiplier tube kept in a LL cell. The intensity of LL produced was detected by RCA-931 PMT whose output was connected to an X-Y recorder. The process was repeated by taking luminol solution of different temperatures.

3 Results

Figures 1-3 show time-dependence of the glow curve of γ -irradiated microcrystals of pure KCl, KBr and KI for different temperatures of the luminol solution, respectively. When γ -irradiated microcrystals are dissolved in a 30-70°C heated luminol solution, then the LL intensity increases with time, attains a maximum value, then it decreases and finally disappears.

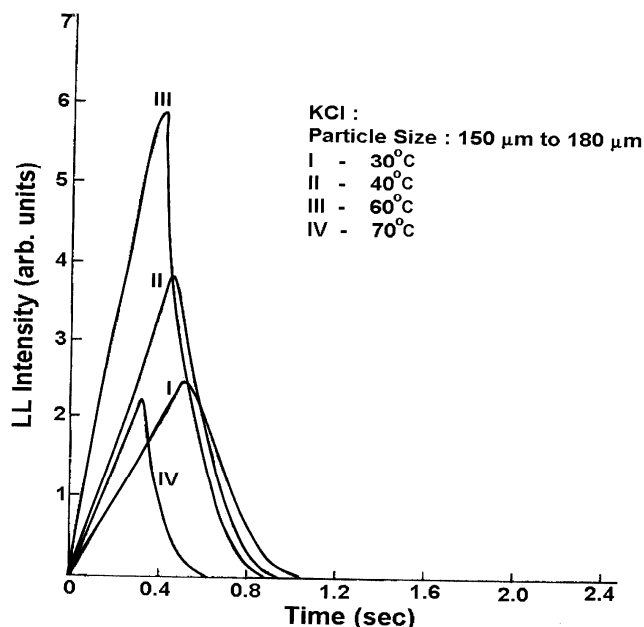


Fig. 1—Time dependence of LL intensity of the γ -irradiated KCl microcrystals for different temperatures of luminol solution

Figure 4 shows the dependence of peak LL intensity I_m versus temperature. The peak LL intensity initially increases with increase in the temperature, attains the maximum value and starts decreasing with further increase in temperature. Fig. 5 shows the total intensity I_T versus temperature. The total intensity

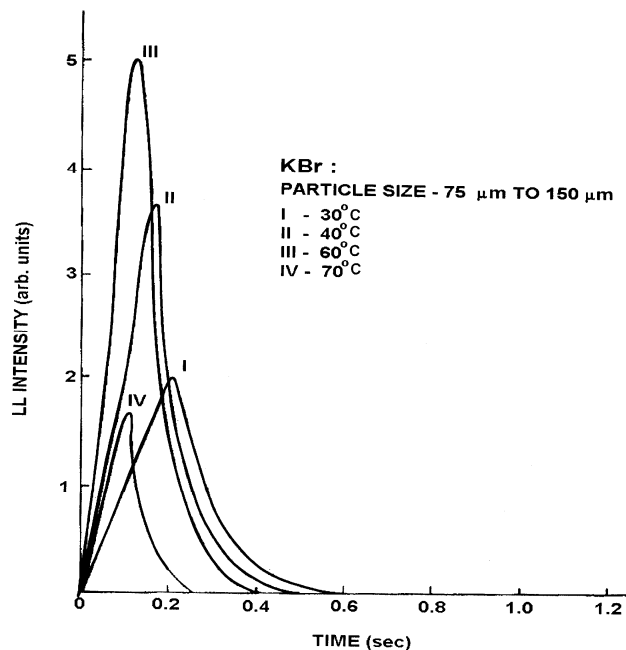


Fig. 2—Time dependence of LL intensity of the γ -irradiated KBr microcrystals for different temperatures of luminol solution

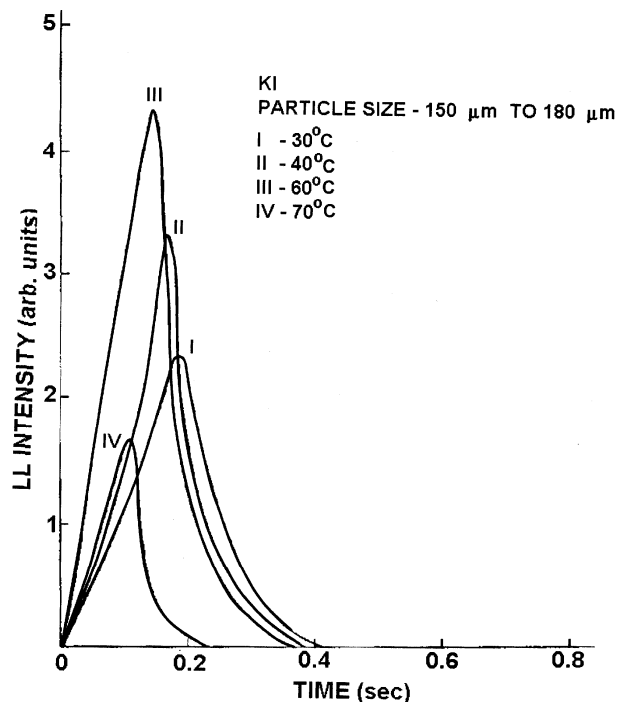


Fig. 3—Time dependence of LL intensity of the γ -irradiated KI microcrystals for different temperatures of luminol solution

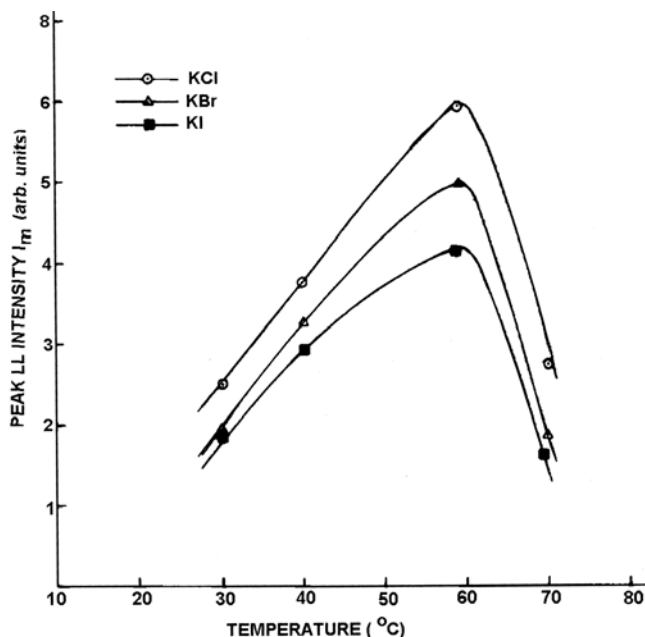


Fig. 4—Dependence of I_m of pure potassium halides microcrystals on the different temperatures of luminol solution

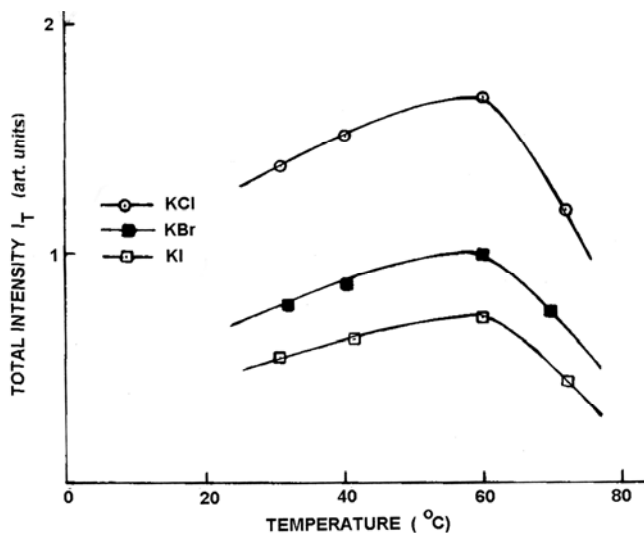


Fig. 5—Dependence of I_T of pure potassium halides microcrystals on the different temperatures of luminol solution

initially increases with increase in temperature, attains a maximum value and then starts decreasing with further increasing the temperature. Fig. 6 shows the dependence of time t_m on temperature. It is seen that the time t_m decreases with increasing temperature of the solvent. Figures 7-9 show the plot of $\log I$ versus $(t - t_m)$ for KCl, KBr and KI microcrystals for

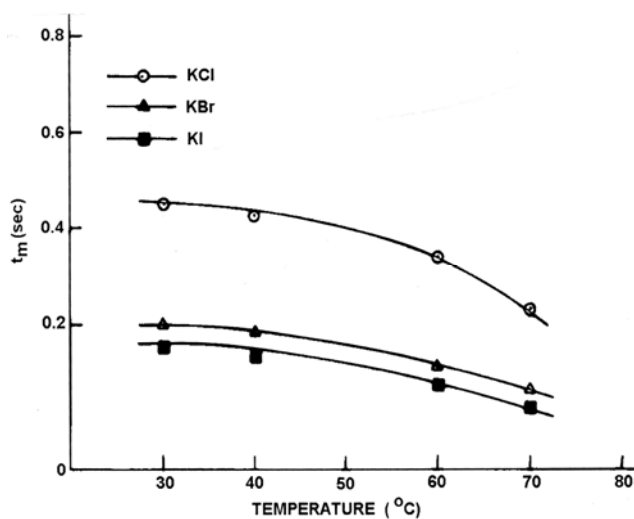


Fig. 6—Dependence of t_m of pure potassium halides microcrystals on the different temperatures of luminol solution

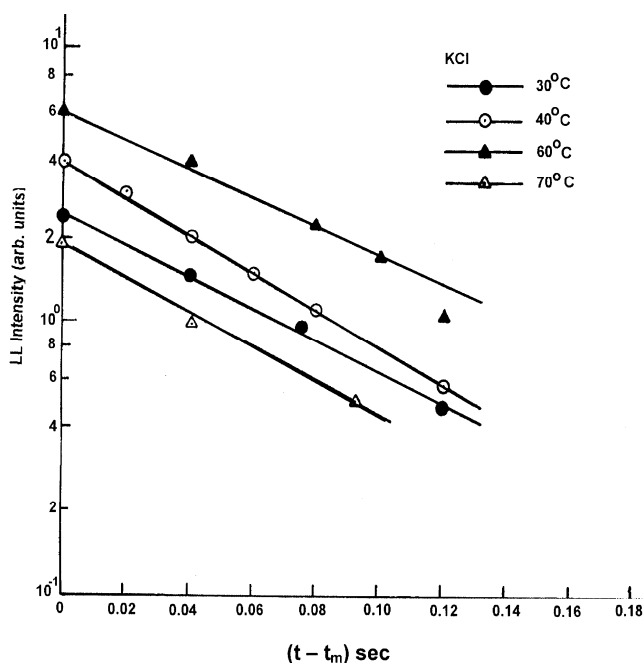


Fig. 7—Plot of $\log I$ versus $(t - t_m)$ of KCl

different temperatures of the luminol solution. It is seen that the plot between $\log I$ versus $(t - t_m)$ is a straight line with a negative slope. This plot indicates the exponential decay of LL intensity and can be expressed by the relation:

$$I = I_0 \exp [-(t - t_m)/\tau]$$

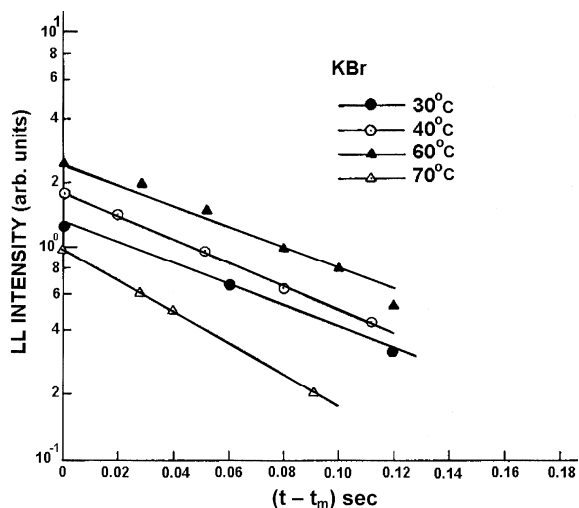
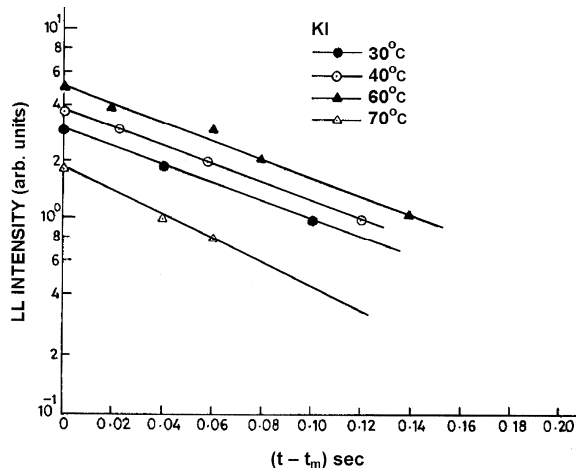
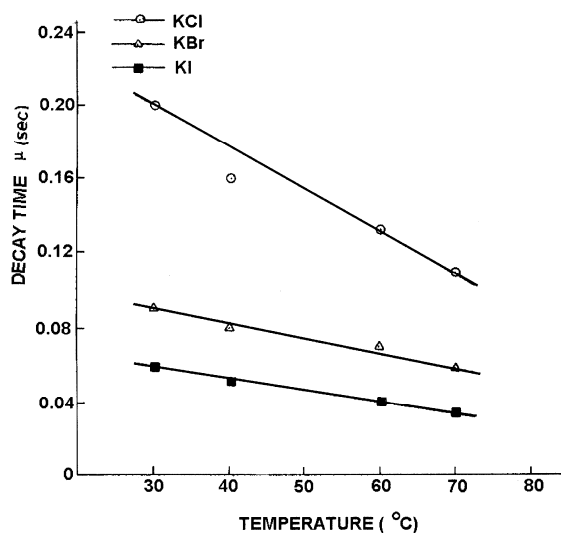
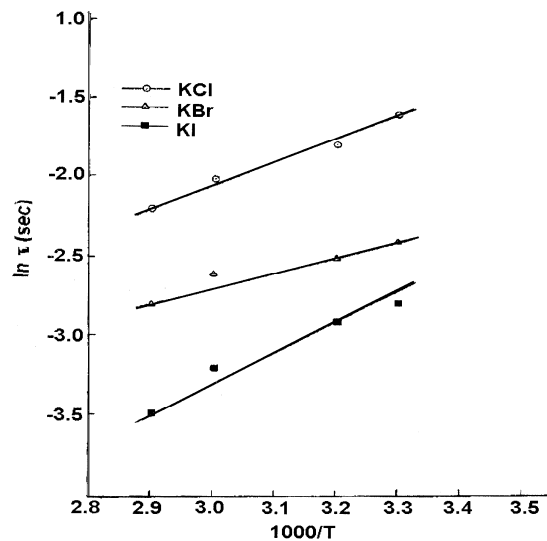
Fig. 8 — Plot of $\log I$ versus $(t-t_m)$ of KBrFig. 9 — Plot of $\log I$ versus $(t-t_m)$ of KI

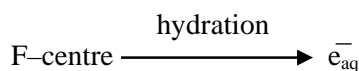
Figure 10 shows the dependence of decay time (τ) of LL intensity on the temperature of the solvent for KCl, KBr and KI microcrystals. It is evident that τ decreases with increasing temperature of luminol solution. Figure 11 shows that the plot of $\ln \tau$ versus $1000/T$ is a straight line with negative slope. From this curve, the value of activation energy E_a is determined and it is found to be 0.43, 0.95 and 1.43 eV for KCl, KBr and KI microcrystals, respectively.

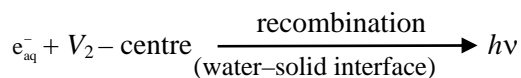
4 Conclusion

When γ -irradiated microcrystals of pure potassium halides are dissolved in luminol solution in the temperature range 30-70°C, the LL emission is found to increase nearly three times. The increase in intensity is because of the enhanced solubility of the microcrystals with rise in temperature of luminol solution. When potassium halide microcrystals are

Fig. 10 — Dependence of the decay time τ of the LL intensity on the temperature of the luminol solution for pure potassium halide microcrystalsFig. 11 — Plot of $\ln \tau$ versus $1000/T$ for pure potassium halide microcrystals

irradiated lattice defects are developed, some electrons from valence band jump to the conduction band, subsequently these electrons drift and get trapped in an anion vacancy and the formation of F-centre takes place. When luminol solution of higher temperature is injected, the electrons are released from F-centres and the formation of hydrated electrons take place. The hydrated electron radiatively combines with the holes on the surface of the crystallites and gives rise to LL emission. The mechanism of LL may be described as:





The expression for peak intensity of LL (I_m), particular time (t_m), and total intensity (I_T) and I which are as given¹⁵ below:

$$I_m = \eta \gamma \alpha n_F N_o \quad \dots (1)$$

$$t_m = \frac{1}{(\beta - \alpha)} \ln(\beta/\alpha) \quad \dots (2)$$

$$I_T = \eta \gamma n_F N_o \quad \dots (3)$$

$$I = \eta \gamma \alpha n_F N_o \exp[-(t - t_m)/\tau] \quad \dots (4)$$

where β is the rate constant for the recombination of hydrated electrons with holes; $\alpha = 1/\tau$ the rate of dissolution of solute in the solvent; η the probability of radiative recombination; γ the factor correlating the number of hydrated electrons, the number of dissolved F-centres and n_F is the density of F-centres, and N_o the initial number of the molecules of solute.

Eq. (1) shows that peak intensity I_m should be optimum for a particular temperature of the solvent. Eq. (2) shows that time (t_m) should decrease with temperature of the solvent because rate of dissolution of solute in the solution increases with increasing temperature of the solvent. Eq. (3) shows that total the LL intensity I_T should increase with temperature of the solution because γ , the factor correlating the number of hydrated electrons, and the number of dissolved F-centres increases with temperature of the solvent. However, at higher temperature of the solution, the density of F-centres decreases due to thermal bleaching, hence, I_T should have an optimum value for a particular temperature of the solution. Eq. (4) shows that the LL intensity should decrease exponentially with time.

The decay time τ may be expressed as:

$$\tau = \tau_o \exp [E_a/kT] \quad \dots(5)$$

where k and τ_o are constants, E_a the activation energy, and T is the absolute temperature of the solution.

To find the value of activation energy E_a , the Eq. (5) may be written as:

$$\ln \tau = \ln \tau_o + E_a/kT$$

$$\text{or, } \ln \tau = \ln \tau_o + M \times 1000/T \quad \dots(6)$$

where, $M = E_a/1000k$, or $E_a = M \times 1000k$

The values of E_a are found to be 0.43, 0.95 and 1.43 eV for KCl, KBr and KI microcrystals, respectively. As the uncertainty found in measurements of the LL intensity is nearly 5%, the uncertainty in the estimated value of E_a may lie in the range of 5%. Thus, there is a good agreement between the experimental and theoretical results.

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