Effect of temperature on lyoluminescence of divalent impurity doped potassium chloride

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The effect of temperature on the lyoluminescence (LL) of divalent impurity doped potassium chloride has been reported. When gamma irradiated doped potassium chloride are dissolved in heated water, the LL intensity initially increases with time, attains a maximum value, then it decreases and finally disappears. The peak I_m of LL intensity versus time curve initially increases with temperature attains an optimum value at a particular temperature and then it decreases with further increase in temperature. However, the total intensity I_T and time t_m corresponding to the peak of LL intensity versus time curves decrease with increasing temperature of the solution. The peak intensity I_m is optimum at a particular temperature because of the competition between increase in rate of dissolution of KCl with temperature and decrease in efficiency η and density of F-centres with temperature. The value of time t_m decreases with increasing temperature of the solution because of the increasing rate constant for the recombination of hydrated electrons with holes. The efficiency η and n_F decrease with temperature and therefore, the total intensity I_T decreases with increasing temperature of the solvent. The decay time τ depends inversely on the rate of dissolution α of solute in the solvent. Since α increase with increasing temperature of the solution, τ decreases with increasing temperature of the solution. A plausible explanation for the experimental results is given.

1. Introduction

In alkali halide crystals, the irradiation energy is mainly stored as the electron and hole centers called F-centers and V_2-center, respectively [1, 2]. This stored energy can be released by dissolution of irradiated alkali halide crystals in a solvent: e.g., in pure water stored energy is mostly converted to light by the recombination of irradiation separated electrons and holes at the solid/solution interface of dissolving alkali halide powder. In general, this kind of dissolution induced light emitting process is called lyoluminescence (LL). It was first reported by Wiedmann and Schmidt in 1895 [3, 4]. Lyoluminescence was rediscovered in 1959 by Ahnstrom and Ehrenstein[5], in which they described in a brief note the experiments that were remarkable in breadth coverage of the phenomenon; simultaneously it was reported by westermark and Grapengiesser [6].

The investigation of temperature dependence of luminescence provides some interesting and important information regarding the nature of the luminescence. Extensive studies have been made on the temperature dependence of luminescence of several organic and inorganic compounds. It is a well-known fact that chemical reactions are either kinetically controlled or thermodynamically controlled. Hence the dependence of LL on temperature is an important parameter. Most of the substances, which were show luminescence at room temperature, have their luminescence efficiency quenched at some higher temperature, while in case of many other substances which are not luminescent at room temperature become luminescent at higher temperature [7, 8].

Atari et al.[9] have found that the temperature of the solvent is an important factor in the LL emission from NaCl, but do not state a quantitative dependence or optimum temperature. All work was done at 20ºC. Ettinger and Puite [10] have reported that there is a profound effect on the LL yield, which increases with temperature. In the case of NaCl in water the yield increases three times, as the temperature rises from 20ºC to 60 ºC. Arnikar et al.[11] studied the LL intensity of irradiated alkali halides crystals under isothermal annealing conditions. They have assumed that if the irradiated crystal is held at high temperature T for time t, a certain fraction n/n_0 of the trapped electrons will be de-excited thermally. This fraction depends on (i) the ratio of trapping potential E and the equilibrium thermal energy KT and (ii) the time t. The fraction of the trapped electrons remaining I - n/n_0 would be a measure of the relative intensity I/I_0 of LL obtainable on dissolution, I_0 being the intensity from annealed sample measured under same conditions. These quantities are related by the following equations:

$$I/I_0 = I - n/n_0 = \exp(K_1 t)$$

and

$$K_1 = A \exp(-E/KT)$$

where, K_1 is the first order rate constant for thermal annealing at temperature T (K), K is the Boltzmann constant and A is a frequency factor. It is known that the

number of newly created dislocations increases with temperature of samples. It seems that initial increase in LL intensity with temperature should be due to the increase in the number of newly created dislocations. Since the effect of temperature on it has been the subject matter of great interest, it has helped in understanding the basic mechanism of LL excitation in samples [12].

Thus, the dependence of luminescence on temperature is extremely interesting from the experimental and theoretical points of view. To date the dependence of LL of alkali halides on temperature has not been studied in a satisfactory way. The present paper reports the effect of temperature on the lyoluminescence (LL) of Ba, Sr, Ca doped KCl sample. An attempts has been made to correlate the newly investigation data with prior investigation and theories.

2. Experimental

The divalent impurity doped potassium chloride crystals were grown from the slow cooling of their melt. For the measurement of LL, the crystals were crushed into powder form and then separated by using sieves of

particular dimensions. Then the powders were coloured by exposing them to ^{60}Co source. For the LL measurements, 2 ml of distilled water filled in a glass tube was heated at a particular temperature i.e. 20, 40, 60 and 80°C and then a small quantity of the coloured powder was dropped in the test tube placed closed to photomultiplier tube kept in a box. The intensity of LL produced is detected by RCA-931 photomultiplier tube whose output was connected to a programmable 4 ½ digital multimeter,SM 5015. All experiments have been conducted in a dark room.

3. Results and discussion

Fig. 2 (a), (b) and (c) shows the time dependence of LL intensity of γ-irradiated KCl:Sr,Ca,Ba (1500ppm) sample for different temperatures. It is seen that the LL intensity initially increases with increasing temperature of the solution, attain an optimum value at 60^0C, then decreases with further increase in temperature of the solvent. It is also observed that the t_m i.e. time corresponding to peak LL intensity decreases with increase in temperature of the solution.

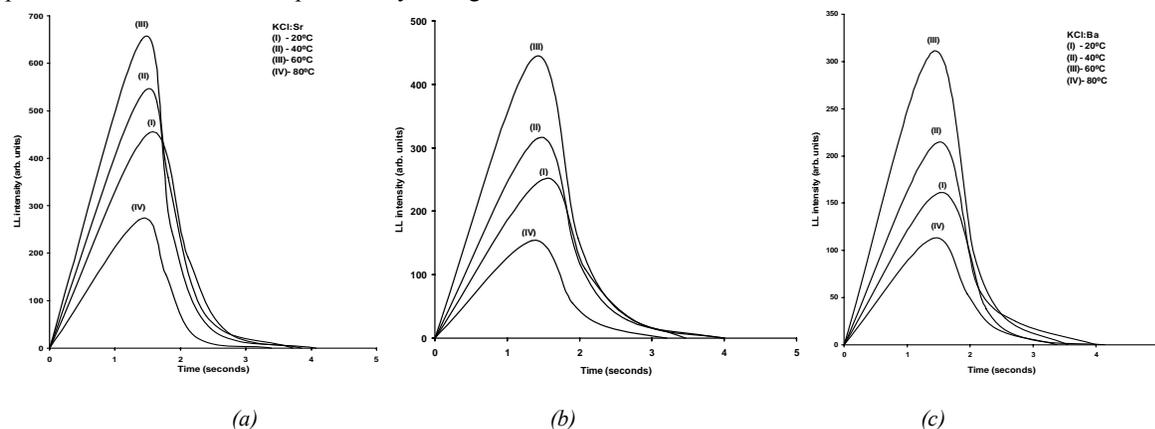(a)   (b)   (c)

Fig. 2. Time dependence of LL intensity of γ-irradiated sample (a) KCl:Sr (b) KCl:Ca (c) KCl:Ba for different temperature.

Fig. 3 shows the dependence on LL intensity I_m of divalent impurity doped KCl sample for different temperatures. It is seen from the figure that initially I increases with increasing temperature of the solution and it attains an optimum value at 60^0C, then it decreases with further increase in the temperature of the solution.

Fig. 4 shows the dependence of the time t_m of the LL of divalent impurity doped KCl sample for different temperatures. It is seen from the figure that the t_m decreases with increasing temperature of the solution.
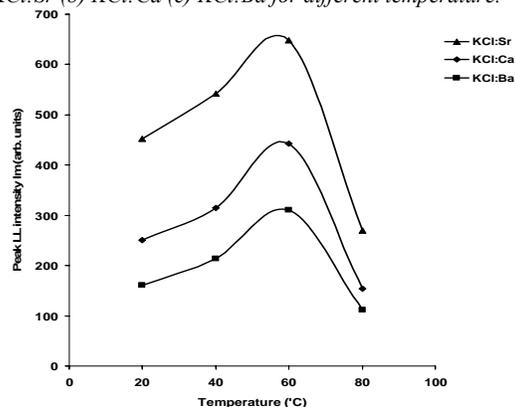

Fig . 3. Dependence of I_m on different temperature of the solution.
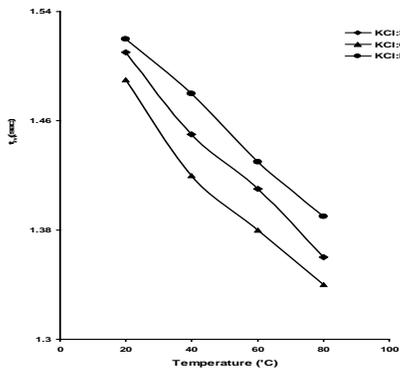
Fig. 4. Dependence of t_m on the different temperature of the solution.

Fig. 5 shows the dependence of the total intensity I_T of the LL of divalent impurity doped KCl sample for different temperatures. It is seen that the figure that initially I_T increases with increasing temperature of the solution and it attain an optimum value at 60^0C then it decreases with further increases in the temperature of the solution. Fig. 6 shows the dependence of decay time of LL intensity on the temperature of the solvent for KCl:Sr sample. The decay time decreases with increasing temperature of the solvent.
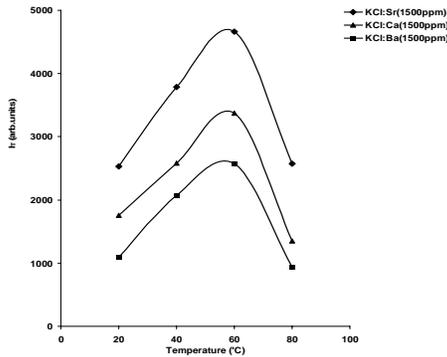

Fig. 5. Dependence of I_T on different temperature of the solution.
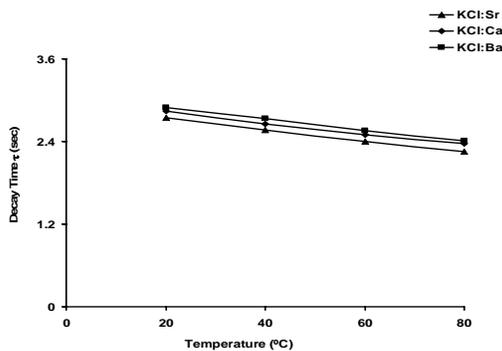

Fig. 6. Variation in decay time τ of KCl:Sr with temperature of the solvent(water) exposed to γ dose=5.6 $x10^3Gy$.
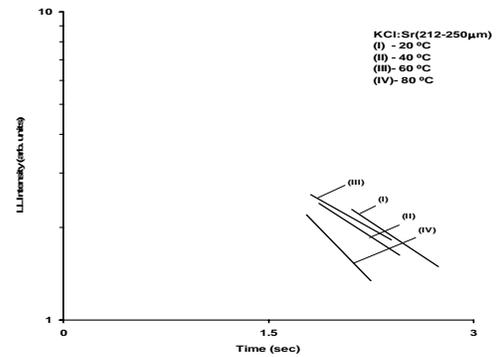

Fig. 7. Plot of log I versus (t-t_m) of KCl:Sr (1500ppm) samples on the different temperature.

Fig. 7 shows that the plot of log I versus (t - t_m) is strait line with a negative slop. This fact shows the exponential decay of LL intensity. The slop of log I versus (t - t_m) increases with increasing temperature of the solution. This plot indicates the relation

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

where, τ is the decay time of LL intensity. The slope of the log I versus t-t_m curves increases with increasing temperature of the solvent. Fig. 8 shows that the plot of ln τ verses 1000/T and which is straight line with negative slope. From this curves the value of the activation energy E_a has been calculated and it has found to be 0.0293 eV for KCl:Sr (1500ppm).
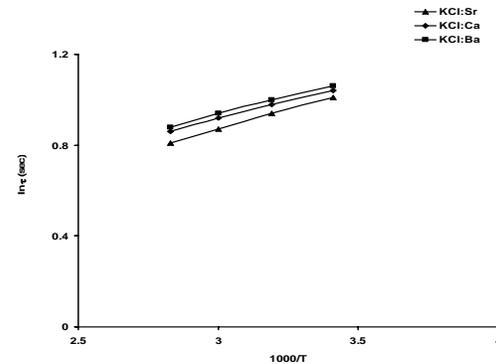

Fig. 8. Plot of (In τ) versus 1000/T for KCl: Sr(1500ppm) sample.

When coloured alkali halide samples are dissolved in water, then electrons are released from F-Centres and the formation of hydrated electrons (e^-_{aq}) takes place. Then the subsequent recombination of hydrated electrons with its counterpart (V_2-Centre) at the water-solid interface gives rise to luminescence. Schematically, the mechanism of LL may be described [13, 14, 15] by the following equation

Hydration

F-Centre --------------- (e^-_{aq})

Recombination

(e^-_{aq}) + V_2-Centre -------------------- hν

(Water-solid interface)
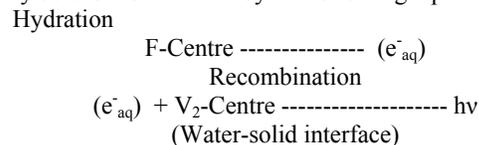
We derived the expression for I_m, I_T, t_m and I that are given below

$$I_m = \eta\Gamma\, n_F\, N_0\alpha \qquad (1)$$

$$I_T = \eta \Gamma\, n_F\, N_0 \qquad (2)$$

$$t_m \frac{1}{(\beta - \alpha)}\, ln(\beta/\alpha) \qquad (3)$$

$$I = \eta \Gamma \alpha\, n_F\, N_0 \exp[-(t-t_m)/\tau] \qquad (4)$$

where

η = probability of radiative recombination

n_F = density of F-centres

N_0 = initial mass of the sample.

α = $1/\tau$ = rate of dissolution of solute in the solvent.

Γ = factor defining the correlation of hydrated electrons with the number of dissolved F-centres.

β = rate constant for the recombination of hydrated electrons with holes.

Since α increases with increasing temperature and η and n_F may decrease with increasing temperature. Equation (i) indicates that I_m should be optimum for particular temperature of the solution.

Fig. 5 shows that initially the total intensity I_T increases with temperature of the solvent. This may be only because γ, the factor corrected the number of hydrated electrons and the number of dissolved F-Centres increases with temperature of the solvent. However at higher temperature of the solvent the density of F-Centres decreases due to thermal bleaching, hence I_T should have an optimum value for a particular temperature of the solvent.

Equation (iii) indicates that t_m depends on the value α and β. The value of rate constant for recombination of hydrated electron is generally higher than the value of the rate constant for the dissolution of solute in the solvent. As higher value of β will cause decrease in t_m, the value of t_m should decrease with increasing the temperature of the solution. Equation (iv) shows that the LL intensity I decrease exponentially with time whereby the decay time τ depends inversely on the rate of dissolution of solute in the solvent.

Since α increase with increasing temperature of the solution, τ should decrease with increasing temperature of the solution and it may be expressed as

$$\tau = \tau_0 \exp [E_a/kT] \qquad (5)$$

where, k and τ_0 are constants, E_a is the activation energy, and T is the absolute temperature of the solution. To find the value of activation energy E_a, the equation (v) may be written as:

$$\ln \tau = \ln \tau_0 + E_a/kT$$

or,

$$\ln \tau = \ln \tau_0 + M \times 1000/T \qquad (6)$$

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

The value of the activation energy E_a is calculated by using above equation and the results shown in (Fig. 8). The value of E_a is found to be 0.0293eV, 0.0272, and 0.0251eV for KCl:Sr, KCl:Ba and KCl:Ca microcrystalline powders respectively. There is a good correlation exists between the experimental and theoretical results [16].

4. Conclusions

(i) When γ-irradiated Sr, Ca and Ba doped KCl samples are dissolved into water, initially the LL intensity increases, attains on optimum value, then it decreases and finally disappears. The important features regarding the glow curve are (a) peak LL intensity I_m (b) time t_m (c) total intensity I_T given by the area below the LL intensity versus time curve and (d) decay time (τ) of LL intensity.

(ii) The LL intensity with respect to temperature is found to be increasing with temperature; it attains an optimum value at 60ºC, and then decreases with further increase in temperature. The slope of In l versus (t-t_m) decreases with increasing temperature of the solution.

(iii) The value of the activation energy E_a has been calculated and it has found to be .0293 eV, .0251eV, .0272 eV for KCl:Sr, KCl:Ca, KCl:Ba respectively.

References

[1] J. Schulman, W. Compton, Color centres in solids, Pergamon, Oxford, 1962.
[2] G. Reynolds, J. Lumin. **54,** 43 (1992).
[3] N. Atari., J. Lumin. **21,** 305 (1980).
[4] E. Wiedemann, G. C. Schmidt, Ann. Phys. Chem. **54**, 604 (1895).
[5] G. Ahnstrom, G. V. Ehrenstein , Acta. Chem. Scand. **13,** 855 (1959).
[6] T. Westermark, B. Grapengisser, Nature **188**, 395 (1960).
[7] A. Raman, I. K. Oommen, Appl. Rad. Isot. **54,** 387 (2001).
[8] B. P. Chandra, P. K. Khare, Bhavna Chourasia., Ind. J. Pure & Appl. Phys. **39**, 392 (2001).
[9] N. Atari, K. V. Ettinger, Radiat. Effects **20**, 135 (1973)
[10] K. V. Ettinger, K. J. Puite, Int. J. Appl. Radiat. Isot. **33**, 1115 (1982)
[11] H. J. Arnikar, V. K. Deo, A. S. Gijare J. Univ.,Poona., **42**, 65 (1972)
[12] R. S. Chandok, B. P. Chandra, Ind. J. Pure and appl. phys. **44**, 519 (2006).
[13] E. Galand, C. Pagnoulle, J. Niezette, J. Garsou, J. Lum. **75** (1), 27 (1997).
[14] S. J. Dhoble, P. M. Bhujbal, N. S. Dhoble, S. V. Moharil, Nuclear Instruments and Methods in Physics Research B **192**, 280 (2002).
[15] B. P. Chandra, R. K. Tiwari, R. Mor, D. P. Bisen, J. Lumin. **5**, 127 (1997).
[16] R. S. Kher, S. J. Dhoble, Ind. J. Pure & App. Phys. **44**, 227 (2006).

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