EFFECT OF LYOLUMINESCENCE DECAY IN IMPURITY DOPED KCl MICROCRYSTALLINE POWDER IN LYOLUMINESCENCE DOSIMETRY OF IONIZATION RADIATIONS

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The lyoluminescence (LL) intensity of gamma irradiated KCl:Sr microcrystalline powder of different particle sizes have been investigated. In the mesh range 150-355 μm, the peak LL intensity initially increases with increasing particle size attains an optimum value for particular size and then it decreases for further increase in particle size of the sample. The LL glow curves show that LL decay times consist of two components for all particle sizes. The dependence of decay time, especially the longer component on the particle size has been investigated. Particle size has no significant effect on the shorter decay component in LL emission. Experiments on gamma irradiated crystals have proved that the light emission originates from the recombination of released F-centres with trapped holes (V_2-centres) at the water-solid interface. The incorporation of bivalent alkali in solid potassium chloride leads to an enhancement of lyoluminescence. A possible explanation for the experimental results has been attempted. The results presented here may be considered as of only academic interest in solid state materials.

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1. Introduction

When strongly energized alkali halides crystals produce a glow when exposure to high energy radiation like x-rays, γ-rays, etc. are followed by immersion in a liquid solvent. This phenomenon is called lyoluminescence. A variety of solid substances can store X-ray or γ-ray energy in the form of trapped electrons and holes [1-2]. In alkali halide crystals, the irradiation energy is mainly stored as the electron and hole centre called F-centre and V_2–centre, respectively [1-3]. This stored energy can be released by dissolution of irradiated alkali halides crystals in a solvent. A phenomenon of emission of light during the dissolution of alkali chlorides treated with cathode rays was first observed in 1895 by Weidmann and Schmidt [4] who named it as lyoluminescence (LL). After nearly 60 years, interest in the study was reviewed by the work of Ahnstrom and Ehrenstein [5], Westermark and Grapengiesser [6]. These workers observed the emission of light during dissolution of a number of substances such as glucose, succhrose, glycin and NaCl, LiF, KI which were previously irradiated by X-ray or γ-radiation or by high energy electrons or fast neutrons. Lyoluminescence has found its application in various fields like radiation damage studies in solids, radiotherapy, radiation processing of food etc. Thus, both organic and inorganic solids were found showing LL.

According to the mechanism of Atari, when an energized halide crystal is dissolved in solution, the entire process of LL takes place in two stages: one in the solid phase of the sample when it is irradiated with an x-ray or a γ-ray and the other in the liquid phase when it undergoes dissolution. When an alkali halide crystal dissolved in water, two effects occur simultaneously; an electron is released from an F-centre and a hydrated electron (e^{-}_{aq}) is formed. The large quenching effect of the hydrated electron acceptors indicates that the released F centre undergoes hydration before its recombination with a V_2 centre at the water-solid interface gives rise to the luminescence. Schematically the process reads as follows:

$$\text{F-center} \xrightarrow{\text{Hydration}} e^{-}_{aq}$$

$$e^{-}_{aq} + V_2\text{-center} \xrightarrow{\text{Recombination}} h\nu \text{ (Water-solid interface)}$$

The increase in luminosity of colored halde crystals is due to the presence of trace impurities in these crystals. The released F centres on hydration recombine with the acceptor impurities (I) at the water-solid interface:

$$\text{F-center} \xrightarrow{\text{Hydration}} e^{-}_{aq}$$

$$e^{-}_{aq} + \text{I} \xrightarrow{\text{Recombination}} (\text{I}^{-})^{*} + h\nu \text{ (Water-solid interface).}$$

The LL signal obtained during the dissolution of previously irradiated materialsis expressed in the form of a glow curve. These curves begin with a high peak followed by an exponentially decreasing intensity. Quite a number of studies have been undertaken to understand the LL emission. However the survey of literature shows that the particle size studies have been mainly restricted to organic compounds. Ettinger and Puite (1982) have been noted the effect of grain size on LL from organic phosphors.

An important factor is the fraction of radiation energy deposited in surrounding air in the sample compound with the energy deposited in the phosphor. Result showed lower yield for finer particle size as found in earlier result reported by Ettinger. Another factor explaining particle size dependence might be insensitive surface layers. Balogun and Adesanmi (1989) offer the interesting speculation that increased packing ratio explains reduced sensitivity due to the increase in non-radiative radical reactions (i.e. reactions prior to the dissolution) and also explain the observed increase in dissolution time. According to interphase model of, Ahnstrom (1965), interphase reaction will take place only in a limited space, called a “cage”. The size of the cage is defined as the space occupied by the partially hydrated electrons and Cl atoms in the crystal surface and the fully hydrated species in the solution, sufficiently close to the crystal surface. Thus as in LL from organic phosphors, surface effects and therefore particle size will be an important parameter in LL from inorganic phosphors. For the development of LL dosimetric material investigation of different parameters are required such as density of colour centres, rate of dissolution of the sample, temperature of solution and the mass of the dissolved sample. Out of, this dissolution rate of the sample is dependent on the particle size of the powder.

Therefore in the present work, we have investigated the dependence of LL intensity on the particle size of divalent impurity doped KCl samples with water as solvent. Since decay time is an important parameter for LL dosimetry, it would be instructive to see whether LL decay time experiments with KCl:Sr powder of different particle sizes would indicates the dependence of decay time on the particle size of microcrystals.

2. Materials and methods

All experimental inorganic materials were purchased from various suppliers in a purity grade higher than 99.9% and used without further purification. 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, and then the powders were irradiated using the ^{60}Co source irradiation facility available at Kamla Nehru College, Nagpur. Samples were irradiated for several hours at a dose rate of 2.806×10^3 Gy/hr. For LL measurements, ~50 mg of irradiated powder sample was placed in cuvate, and 2ml of solvent was injected into it using syringe in each case, thus the intensity of LL produced is detected by RCA-931 photomultiplier tube whose output was recorded on programmable 4 ½ digital multimeter, SM 5015. All experiments have been conducted in a dark room at room temperature. Doubly distilled water (pH~7.0) has been used as the solvent. The experiments have been carried for four different particle sizes. All these measurements have been repeated several times in identical experimental conditions to ensure reproducibility.

3. Results and discussion

Figure 1 shows the typical LL glow curves for KCl:Sr powder exposed to γ-rays of 5.6 × 10^3 Gy dose for different particle sizes. The figure 1 shows that when γ-irradiated microcrystals are dissolved in a fixed volume (2 c.c.) of distilled water, initially the LL intensity increases with time, attains a optimum value I_m at a particular time t_m, then it decreases and finally disappears. Width of the LL glow peaks increases with increasing particle size of microcrystalline powder, the LL peak intensity increase due to the formation of radiolysis products during γ-ray irradiation, but above 250μm size of the KCl:Sr powder, the LL intensity decreases and then becomes constant. The variation of LL peak intensity in figure 2 (curve a), shows that above 250 μm size of microcrystalline powder of KCl:Sr, the LL intensity may vary with radiolysis products as well as by the dissolution rate.

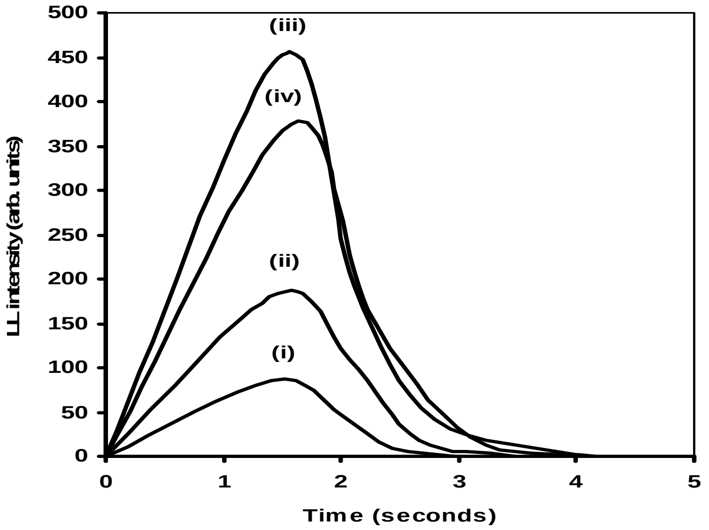

Fig. 1. LL glow curves of KCl:Sr microcrystalline powder of different particle size with water used as solvent, exposed to γ-dose = 5.6 × 10^3 Gy Particle sizes: (i) 0-150 μm, (ii) 150-212 μm, (iii) 212-250 μm, (iv) 250-355 μm.

Fig. 2 (curve b) shows the variation of t_m with particle size of KCl powder with water as solvent. Value of t_m increases with particle size of KCl:Sr powder. The increasing order of the curve with the particle size is due to recombination of radiolysis products which is much more in the surface of microcrystalline powder.

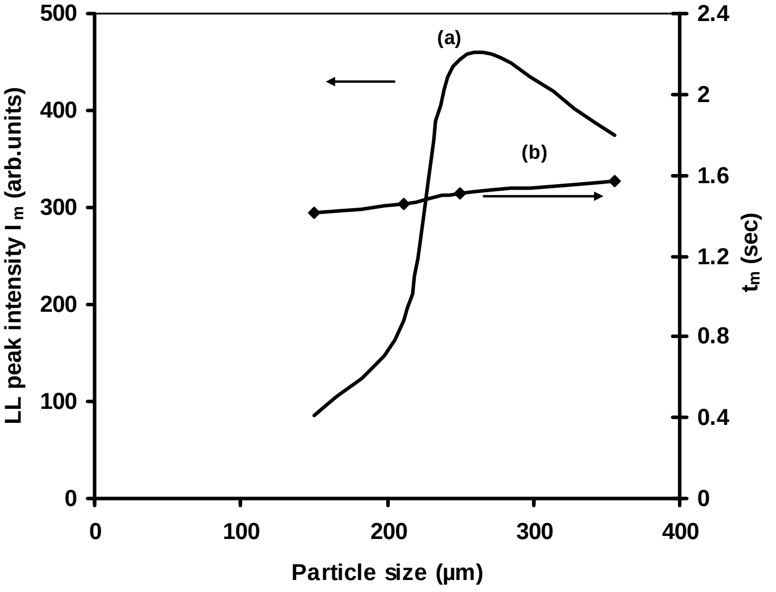

Fig. 2. Variation in LL glow peak heights (I_m) (curve a) and time t_m (curve b) with particle size of KCl:Sr with water used as solvent, exposed to γ-dose = 5.6 × 10^3 Gy.

Fig. 3 (curve a) shows that the the total LL intensity (I_T) increases with particle size upto 250 μm. It may be due to increasing size of microcrystalline powder being dissolved which increases the rate of recombination of radiolysis products upto 250 μm size. I_T decreases with further increases in particle size of microcrystals from 300 to 400 μm. Above 300 μm, the rate of radiolysis product increases, while rate of dissolution decreases. After attaining the LL peak at maximum intensity (I_m), the decay of LL intensity depends on the nature of particles (figure 3, curve b). It is seen from the curve that decay time τ increases up to certain particle size of the sample.

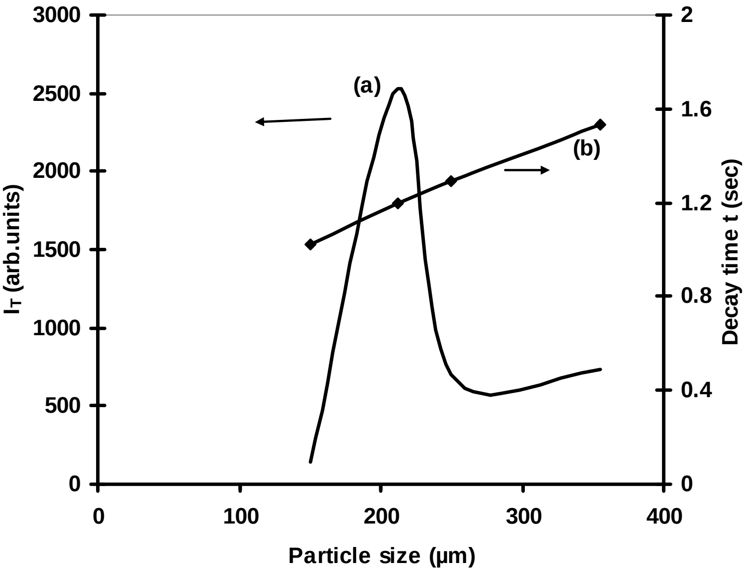

Fig. 3. Variation in total LL intensity I_T (curve a) and decay time τ (curve b) with particle size of KCl:Sr with water used as solvent, exposed to γ-dose = 5.6 × 10^3 Gy.

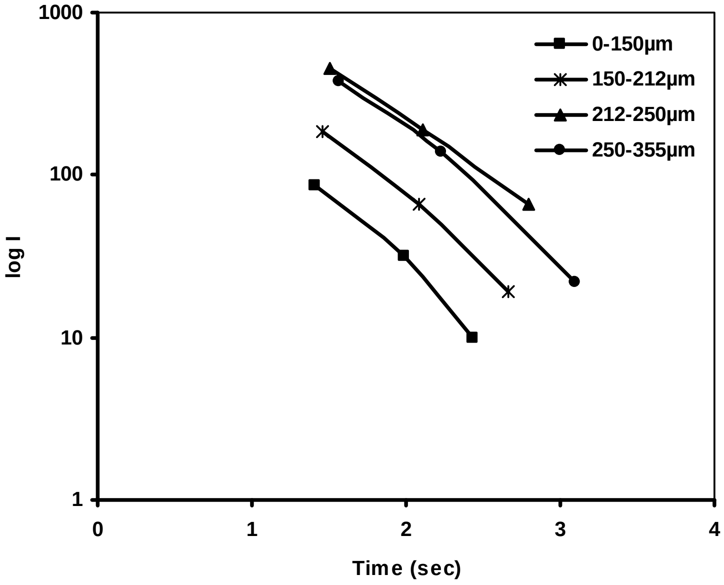

Fig. 4. Plot of log I versus t (t > t_m) of KCl:Sr microcrystalline powder for different particle sizes.

Fig. 4 shows the plot of log I of KCl:Sr powder with time. The value of log I is shows the plot of log I versus t>t_m for KCl:Sr sample for different particle sizes. In fact, there are two decay components of LL intensity. But since the Faster component does not change appreciably with particle size, hence we have plotted the curve between log I versus t>t_m for the slower component. It is seen from the curve that the plot between log I versus t>t_m is straight line with negative slope. This indicates, the relation

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

Where, τ is the decay time of LL intensity. The value of logI is increasing with particle size as more quantity of the powder is getting dissolved. The slope of the curve between log I and dissolution time is decreasing with increasing particle size, because larger sized grains dissolved slowly. This slop indicates the stability in the rate of formation of radiolysis products and dissolution of grains for the KCl:Sr powder. Therefore, decay time of LL intensity is one of the important factors for LL dosimetry.

4. Conclusions

In Fig. 2, both the curves are of increasing order with increasing size of particles due to decreasing dissolution of microcrystalline powder in water. The area between both the curves indicates the recombination of hydrated electron and hole in the surface of microcrystalline powder and recombination of radiolysis products during dissolution. This difference is very much affecting the exact energy absorption by microcrystalline powder during γ-irradiation, the LL intensity being not directly related to absorbed dose of powder. Therefore, fixed range of particle size may be permissible for KCl:Sr powder to be used as lyoluminescence dosimetry of ionizing radiations. The LL of alkali halides crystals depends on different parameters such as radiation dose, density of colour centres, rate of dissolution, temperature of the solution, mass of the dissolved sample, type of the impurity present, pH of the solvent and type of the sample. Amomg them, the most important parameter is particle size of the LL phosphor.

The application of LL on radiation dosimetry was initiated by Ettinger and co-workers. It is generally believed that the mechanism of colour centres production is similar for single crystal and microcrystalline powder. Colour centres production by γ-irradiation in NaCl, KCl and KBr is reported by Deshmukh and co-workers in crystal and microcrystalline powder. In 1997 Galand reported the LL of alkali halides and concluded that the incorporation of divalent earth alkali and transition metal cation in KCl leads to an enhancement of LL [7-11]. The mechanism of colour-centre production and annihilation in alkali halides crystals doped with divalent impurity cations is still an open question. The total LL intensity I_T increases up to a certain particle size and subsequently decreases up to 355 μm for the samples. In the present study we found that the LL intensity is optimum for the sample having particle size 212-250 μm. Besides the I_m, t_m, I_T results are identical with Ettinger [1980], Balogun and Adesanmi [1989], Reynold G. T. [1992] etc., so conclusively it may be said that correlation exists between previously reported results with present investigation.

From the results presented above, it may be concluded that the lyoluimnescence intensity cannot be directly correlated to the radiolysis product (colour centre concentration) or the dissolution rate but depends on both factors simultaneously. Such studies would be helpful in providing information for lyoluminescence dosimetry and better insight into the kinetics of reactions responsible for LL emission. It would definitely add to our knowledge of defect interactions in general and particularly in solids.

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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] R. S. Chandok, B. P.Chandra., Ind. J. Pure & appl. Phys., **44**, 519 (2006).
[10] E. Galand, C. Pagnoulle, J.Niezette, J.Garsou, J.Lum., **75**(1), 27 (1997).
[11] S. J. Dhoble, P.M. Bhujbal, N.S. Dhoble, S.V. Moharil, Nuclear Instruments and Methods in Physics Research B **192**, 280 (2002).
[12] B.P. Chandra, R.K.Tiwari, Mor R, D.P. Bisen, J Lumin. **5**, 127 (1997).
[13] R.S.Kher, S.J.Dhoble, Ind. J. Pure & App. Phys. **44**, 227 (2006)

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