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Dependence on the Lyoluminescence of Divalent Impurity Doped Sodium chloride on the pH of the Solution

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Abstract-The present paper report the Dependence on the Lyoluminescence of Divalent impurity Doped Sodium chloride on			
the pH of the Solution. Luminescence is light that accompanies the transition from an electronically excited atom or molecule			
to a lower energy state. Lyoluminescence(LL) is the phenomenon of light emission ,when certain substance irradiated with			
ionizing radiation are dissolved in a suitable solvent .When Divalent impurity doped NaCl crystals are dissolved in water			
electron are released from F-centers and the formation of hydrated electron takes place. The subsequent recombination of			
hydrated electrons with its counterpart V ₂ center at the water- solid interface gives rise to luminescence. The LL intensity			
increases with increasing pH of the solution, and then it decreases with increasing pH of the solution. The LL intensity is			
optimum for a particular pH (6-7) of the solution. It has been shown that the maximum LL intensity is observed over the pH			
range in which the stability of the hydrated electron is optimum. The use of LL are in dosimetry devices.			

Index-term - Lyoluminescence, Colour Centers, Crystals, Alkalihalide

I. Introduction

When alkali halides are irradiated with ionizing radiation, colourcentres are formed within the material. These centres known as F-centres and v-centers release energy of the ionizing radiation in the form of light when dissolved in suitable solvents. The phenomenon of emission of light when dissolved in suitable solvents. The phenomenon of emission of light when a previously irradiated sample goes into solution in known as lyoluminescence (LL) [1]. weastenmark and Grapengises [2] in 1959 found the same effect in most alkali halides. Saccharides and some organic compounds. However, a more detailed study of this effect was made by Ahnstrom [3]in 1965, who proposed a mechanism for the light emission when irradiated NaCl is dissolved water. Ahnstrom [4-5] studied some physical and chemical processes accompanying the light emission. From the observed luminosity data, he determined the number of F-centres produced in a sample as function of the Y irradiated NaCl has been similarly used by Adloff [6] for measuring the growth of F- centres as a function of the Ydose. Eriksson [7] showed that the luminescence was about 10 times brighter in water saturated with N_2 than with O_2 Burns and Willians [8] reported that during the dissolution of irradiated crystals there is an evolution of H₂ and a rise in pH of the solution. In the past, the mechanism and the several workers [8-9]. In the present paper, we report the dependence of lyoluminscence of divalent impurity dope NaCl on the pHof solution.

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II. Experimental

The divalent impurity doped sodium chloride crystal weregrown from the slow cooling of their melt. The crystals were crushed into powder from and then the powders having different grain sizes were separated by using sieves of particular dimensions. Then the powders were coloured by exposing them to ⁶⁰COsource. **Fig 1 shows** the experimental set up used for LL measurements For the LL measurements, a small quality of the coloured powder was filled in a small glass test tube was placed close to a photomultiplier tube kept in a box. Then the distilled water of different ph was dropped on the powder using a syringe. The intensity of LL produced was detected by an RCA931 decreasing the pH value of distilled water H₂SO₄ is added to it and for increasing the pH value of distilled water KOH solution was added to it.

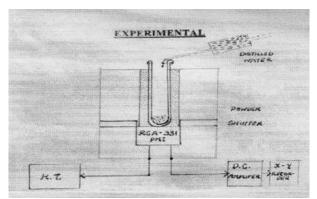


Figure 1 : Experimental setup for LL measurements

III. Result

Fig.2 shown the time dependence of the LL intensity of Yirradiated NaCl crystals for different grain sizes. It is seen from the figure that when Y-irradiated microcrystals are dissolved in affixed volume of distilled water (5 ml), then the LL intensity initially increases with time attains a maximum value, then the LL intensity initially increases with time, attains a maximum value, then it decreases and finally disappears. It found that the LL intensity is maximum for a grain size of 0.12mm.

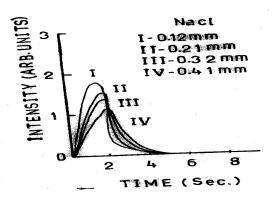


Figure 2: Time dependence of the LL intensity of Υ - irradiated NaCl crystal for different grain size .

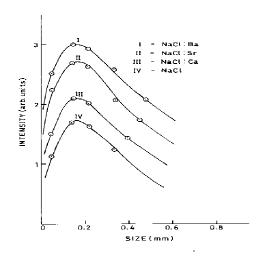


Figure 3: Dependence of the LL intensity of Υ - irradiate divalent impurity doped NaCl crystal on the different grain size .

Fig. 3 shows the size dependence of the LL intensity of Υ irradiated divalent impurity doped Nacl crystals. The LL intensity is found to be maximum for a grain size of 0.12mm. The LL intensity is Maximum for the barium doped NaCl microcrystals.

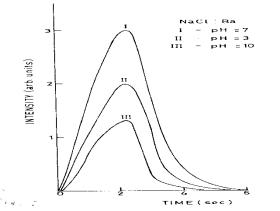


Figure 4: Time dependence of the LL intensity of Y- irradiate NaCl : Ba for different pH of the solution.

Fig. 4 shows the time dependence of the LL intensity for different pH of the solution for NaCl : Ba crystals. It is seen from the figure that LL intensity initially increases with increasing the ph value of the solvent and then it decreases with increasing the pH value of the solvent.

Fig.5 shows the exponential decay of LL versus $(t-t_m)$ is a straight line with a negative slope. This fact shows $(t-t_m)$ plot depends on the pH of the solvent and it is minimum for the a particular pH of the solution for which the LL intensity is optimum.

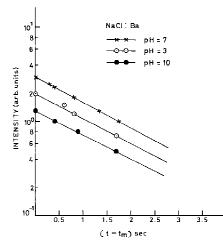


Figure 5: Plot of in I versus (t-t_m) for different pH the solution.

IV. Discussion

When coloured alkali halide crystals are dissolved in water, then electron releases from F- centres and the formation of hydrated electrons (e_{aq}) take place. The subsequent recombination of hydrated electrons with its counterpart (v₂-centres) at the water solid interface gives rise to luminescence. Schematically the mechanism of LL may be described by following equations

Hydration _____ F-center e_{aq}^{-}

 $e_{aq}^{-}+V_2$ - center (Water -solid interface) Recombination h v

Chandra et al [12] have shown that the LL intensity depends on different parameters and it can be expressed as

$$I = \frac{\eta \beta \alpha \Upsilon n_F N_o}{(\beta - \alpha)} \{ exp(-\alpha t) - exp(-\beta t) \} \dots (1)$$

Where

 η = probability of radioactive recombination

- β = rate constant for the recombination of hydrated electrons with holes
- Υ =factor correlating the number of hydrate electrons and the number of dissolved F- centres
- A = rate of dissolution of solute in the solvent
- n_F= density of F- centres
- N_o = initial number of the molecules of solute
- t = time of dissolution

The above equation shows that when water will be dropped into the solute then initially the LL intensity should increase linearly with time, attain a maximum value and then it should decrease exponentially with time. This fact is supported by the result illustrated in fig. 2

It is evident from fig.3 that I_m initially increases and then decreases with increasing grain size of the crystals. Equation (2) indicates I_m should decrease with increasing grain size of the crystals, firstly due to the formation of less density of colourcentres in larger grain as compared to that in the crystallites of smaller grains, and secondly due to the decreases rate of dissolution α with increasing grain size of crystallites. For smaller grain size Immay decrease with decreasing grain size because of the less stability of colourcentres in the crystallites of smaller dimensions, where the significant bleaching of colourcentres may take place [13].

Fig. 4 show the dependence of LL intensity on the pH of the solution. It is seen that the LL intensity is optimum for a particular pH of the solvent [4-5]. It has been shown that the maximum intensity in lyoluminescence is observed the pH range in which the stability of the hydrate electron is optimum [10-11]. Equation (2) shows that the LL intensity depends on different parameters. The factors Υ ,n_F,N_oand α are independent of the pH value of the solution , however η changes with the pH of the solution .

We know that pH means negative logarithms of hydrogen ion concentration i.e. pH = -log [H+], pure water is essentially a covalent compound. It ionises very slightly and the following equilibrium is established;

$$H_2O \longrightarrow H^+ + OH$$

Where H^+ is a hydrogen ion and OH^- is a hydroxyl ion. The removal of one orbital electron from a hydrogen atom yields the positive hydrogen ion or hydrogen cation, which is in fact a bare proton. The bare proton has no separate existence in solution and owes its stability to salvation by a water molecule to give the hydronium ion, H_3O^+ The ionisation equilibrium of water is thus respresented more accurately as

$$2H_2OH_3O^+ + OH^- \longrightarrow$$

The pH m of neutral solution is 7. In asidic solution $[H^+] > 10^{-7}$ or $[H^+] > [OH^-]$ or $[H_3O^+] > [OH^-]$. In basic solution $[OH^-] > 10^{-7}$ or $[OH^-] > [H^+]$ or $[OH^-] > [H_3O^+]$. In water $[H^+] = [OH] = 10^{-7}$

It has been found that for low value of pH, the LL intensity decreases with decreasing pH of the solution. The decreasing pH means the increase in the hydrogen ion concentration or $[H_3O^+]$ concentration. For lower pH the existence of more hydrogen ions may cause decreases in the number of hydrogen ions. Because the electron of the hydrated electron may combine with the hydrogen ions. Thus the probability of non-radiative recombination of hydrate electron may decrease with decreasing pH of the solution and consequently the LL intensity may decreases with decreasing pH of the solution.

It has been found that for higher pH , the LL intensity decreases with increasing pH of the solution . As the increasing pH means the increasing concentration of [OH] ions .consequently the number of holes responsible for luminescence may decrease with increasing pH of the solution .As a matter of the fact, for higher pH value, the LL intensity may decrease with increasing pH of the solution. In this way, the LL intensity should be optimum for a particular pH of solution.

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