CHAPTER-IV

LYOLUMINESCENCE IN $\gamma$-IRRADIATED Ce, Dy AND Eu DOPED BORATE BASED PHOSPHORS
4.1 INTRODUCTION

The luminescence produced due to recombination process during dissolution of irradiated materials to certain suitable solvent is known as lyoluminescence (LL). The quantum of light yield produced is proportional to absorbed dose in the solid. The lyoluminescence phenomenon, owes its origin to the transfer of energy from the radiation-induced free radicals to the solvent molecules, a part of which gets transposed to visible light. The lyoluminescence is a quite general phenomenon occurring with very different materials but most of the systematic studies turned to the dosimetric application have been concentrated on alkali halides and on two classes of organic compounds regarded as tissue equivalents, saccharides and amino acids. Recent work in this field appears to deal more with improvement of techniques, both of detection and preparation of materials, aimed at achieving more reliable dosimetry (Ettinger and Puite, 1982). However there are number of various factors that influence the light yield during the dissolution of γ-irradiated phosphors in solvent which have not been investigated in detail. Mass of the sample, pH of the solvent, temperature of the solvent, irradiation dose etc. are some example of parameters that influence the LL intensity. For the purpose of developing LL dosimetry material, these factors require detail investigation.

The word lyoluminescence was coined by Wiedemann and Schamidt (1895) who first observed the phenomenon on dissolving NaCl irradiated with cathode rays in water. In the same year they reported a further observation with MgSO₄·Cd. There were no further reports until 1959 when Ahnstron and Ehrenstein (1959) observed persistent luminescence on dissolving glucose irradiated with X-rays, γ-rays and
neutrons to absorbed doses of several MGy. Westermark et al (1960),
investigated the lyoluminescence of both inorganic and organic materials,
and also observed light emission from irradiated polystyrene dissolved in
liquid scintillator. Subsequent studies included those of Ahnstrom (1961),
Eriksson (1962) and Ahnstrom (1965). Observations of inorganic
lyoluminescence were reported by Lelievre and Adloff (1964); Avotinsh
termed the phenomenon aquoluminescence for dissolution in water and
sololuminescence as the more general term to include solvents other than
water (Arnikar et al, 1971).

The application of lyoluminescence to radiation dosimetry was
discussed by Atari et al (1973). Investigations of the lyoluminescence of
inorganic materials both for the possible application to dosimetry and to
understand the mechanism of light production were continued by Atari,
Ettinger and co-workers (1974, and 1977) and by Arnikar and colleagues
(1975, 1977a, and 1977b). However, greater emphasis has been put on
the lyoluminescence of organic materials, particularly saccharides, in
view of their similarity of elementary composition to tissue (Atrari and
Ettinger, 1973). The possibility of the development of a fairly true tissue
equivalent dosimeter was presented by Atari and Ettinger (1974).

Organic materials other than saccharides have also been studied,
namely amino acids, amino sugars, proteins and nucleic acid (Ettinger
and Atari, 1974; Thwaites et al, 1976; Ettinger et al, 1977 and Puite et al,
1980); but in general, the lyoluminescence phosphors of choice have been
saccharides (Ettinger et al, 1977; Chazhoor and Mishra, 1979; Bartlett,
1979; Bartlett, 1982; Busuoli and Monteventi, 1982 and Puite et al,
1977). Puite and co-workers (1977) have reported the application of
lyoluminescence of mannose to the dosimetry of low energy X-rays and fast neutrons for application to radio-biology and radiotherapy, and of glutamine (1980) for high dose intercomparisons. Ettinger et al (1977) and Puite (1977) have also considered the application of lyoluminescence dosimetry in commercial irradiation of foodstuffs. Ziemer et al (1978), reviewed lyoluminescence dosimetry and investigated the lower limit of detection using trehalose dehydrate. The effect of storage on the lyoluminescence response of mannose was investigated and the dependence of the change in response on observed dose has been determined by Bartlett (1979). Kundu and his co-workers (1984 and 1992) have studied LL of certain organic solids. The mechanism of radical generation, peroxide formation and light emission has been summarized by Chatterjee et al (1993), giving a comprehensive calculation of kinetics and the light yield.

The study of LL investigation of inorganic phosphors yielded useful results. Inorganic LL phosphors other than alkali halides were investigated in the beginning of nineties. Copty Wergles et al (1990) investigated LL during dissolution of calcite and aragonitesnail irradiated with $^{60}$Co gamma ray in HCl. LL induced by the dissolution of UV irradiated Tb doped potassium peroxodisulphate in aqueous solution was reported by Kulama and Haapakka (1994). Matachescu et al (1997) have reported the mechanism of analytical application of luminol-specific extrinsic LL of UV irradiated potassium peroxidisulphate. LL phenomenon in the super molecular aggregation of antinuclear gold complex was studied by Vickery et al (1997). Chattopadhyay et al (2000) developed a nonlinear differential equation and analyzed it by a dynamic system analysis as well as exact numerical integration. Raman et al (2001) reported the LL of trehalose dihydrate. They observed that LL
shows linear gamma sensitivity in the dose range $0.1 \times 10^2$ to $5 \times 10^2$ Gy. LL property of gamma irradiated Eu activated KNaSO$_4$ and K$_3$Na(SO$_4$)$_2$ phosphors were reported by S.J. Dhoble (2002). He observed linear response of absorbed gamma dose from $0.06$ to $10$ Ckg$^{-1}$. He also studied the fading of LL intensity and found that this phosphor is suitable for LL dosimetry. Dependence of the lyoluminescence of divalent impurity doped NaCl on temperature was studied by Gour et al (2004). The effect of pH of solution on the lyoluminescence of divalent impurity doped sodium chloride was studied by Chourasia et al (2004). Particle size dependence of lyoluminescence of gamma irradiated sodium bromide was reported by Banerjee et al (2005). Hakansson et al (2006) studied the lyoluminescence of aluminium induced by lanthanides chelates in alkaline aqueous solution.

Lyoluminescence (LL) of MgSO$_4$:Dy phosphors has been studied by Kher et al.(2008). The maximum LL intensity was observed for 0.05 mole% of Dy in MgSO$_4$. Thermoluminescence (TL) glow curves of MgSO$_4$:Dy phosphors are complex and peaks around $110^0$C, $150^0$C and $220^0$C were observed. The effect of post-irradiation annealing on the LL shows that with removal of $220^0$C TL peak, the LL intensity decreases markedly.

KNaSO$_4$:Tb$^{3+}$ phosphors were synthesized by melt technique with different concentration of Tb$^{3+}$ ions and MgSO$_4$:Dy$^{3+}$ phosphor were prepared by solid state diffusion method by Upadhyay et al (2008). Lyoluminescence and photoluminescence (PL) characterization of KNaSO$_4$:Tb and MgSO$_4$:Dy$^{3+}$ phosphors were reported in this paper.
They showed that $\text{KNaSO}_4: \text{Tb}^{3+}$ and $\text{MgSO}_4: \text{Dy}^{3+}$ phosphors are suitable as a lyoluminescence dosimetry phosphor for ionizing radiations.

The lyoluminescence (LL) intensity of gamma irradiated KCl:Sr microcrystalline powder of different particle sizes have been investigated by Sahu et al. (2009). They found that in the mesh range of 150-355 $\mu$m, the peak LL intensity initially increases with increasing particle size, attains an optimum value for particular size and then it decreases with further increase in particle size of the sample.

The temperature and mass dependence of lyoluminescence intensity of $\gamma$-irradiated colored potassium chloride powder were studied by Nayar et al. (2010). They found that peak lyoluminescence intensity increases with increasing amount of solute added up to 50 mg and then tends to saturate. Further they reported the dependence of decay time on mass and dependence of LL intensity on temperature. They found that initially the peak LL intensity increases with temperature up to 60°C, then decreases with further increase in temperature and decay time tends to decrease with increasing temperature.

Rare earth Ce and Dy doped polycrystalline $\text{Li}_2\text{BPO}_5$ phosphors were prepared by high temperature solid state reaction by Puppalwar et al. (2011). They reported that LL emission of $\text{Li}_2\text{BPO}_5: \text{Ce}, \text{Dy}$ phosphor occurs in blue – yellow region of the spectrum and response curve of LL with gamma rays exposure upto 3.5 kGy is linear.

Lyoluminescence and mechanoluminescence of Cu activated $\text{LiKSO}_4$ phosphors for radiation dosimetry is studied by Dhoble et al.
(2011). Synthesis of Cu$^{2+}$ activated LiKSO$_4$ phosphor and its possible use as lyoluminescence (LL) and mechanoluminescence (ML) dosimeter were discussed. Cu activated LiKSO$_4$ phosphor showed less fading in LL and ML over a long time, linear gamma-ray dose response up to 1 kGy, emission around 455 nm, and simple glow curve. These properties make this phosphor a useful candidate for LL and ML dosimetry.

Survey of literature show that no systematic investigation has been made on the lyoluminescence of borate based phosphors. Borates are good candidate for thermoluminescence dosimetry and many thermoluminescence materials also show LL when dissolved in suitable solvent. The present chapter reports the systematic investigation of LL of borate based phosphors. The objective is to find suitability of these phosphors for dosimetry and to use this for understanding of other luminescence phenomena.

4.2 EXPERIMENTAL

Ce, Dy and Eu doped MB$_4$O$_7$ (M= Ba, Ca, Sr) and LnCa$_4$O(BO$_3$)$_3$ (Ln= Gd, La, Y) phosphors were prepared by the methods described in chapter-II. Gamma irradiation was carried out using $^{60}$Co source. The LL read out system fabricated for lyoluminescence measurements consists of a lyoluminescence cell, a light detector, signal processor and signal recorder. Fig. 4.1 shows the schematic diagram of the LL reader system. The lyoluminescence cell and the photomultiplier tube (PMT) are kept in the light-tight box. A circular hole was cut on the top surface of the box into which a glass tube (8 mm diameter and 4 cm length) was fitted. This glass tube is acted as the dissolution vessel. It rests just in front of the
window of the PMT. The solvent is injected into the vessel with the help of a conventional hypodermic syringe.

The light emitted during the dissolution was detected by RCA-931 photomultiplier tube. For biasing the various dynodes of the PMT, a high voltage power supply was used. The output of PMT was fed to storage CRO. All the experiments have been conducted in a dark room at room temperature. The mass of the samples used for recording LL data is kept approximately (~1mg) in each case and dilute HCl has been used as the solvent to dissolve the sample. The volume of the solvent was 2.5 ml in each case. For reading LL spectra filters were placed between LL cell and the PMT. For each point at least three observations were recorded in identical experimental conditions to ensure the reproducibility.

Fig. 4.1 Experimental setup used for LL measurement
4.3 RESULTS

It is observed that when Ce, Dy and Eu doped MB$_4$O$_7$ (M = Ba, Ca, Sr,) and LnCa$_4$O(BO$_3$)$_3$ (Ln = Gd, La, Y) phosphors exposed to gamma dose were dissolved in solvent, MB$_4$O$_7$ did not show any measurable intensity in solvent while LnCa$_4$O(BO$_3$)$_3$ (Ln = Gd, La, Y) phosphors showed prominent peaks when it was dissolved in dilute HCl.

Figure 4.2a, 4.2b and 4.2c shows the time dependence of LL intensity of $\gamma$-irradiated Ce, Dy and Eu doped GdCa$_4$O(BO$_3$)$_3$, LaCa$_4$O(BO$_3$)$_3$ and YCa$_4$O(BO$_3$)$_3$ phosphors respectively. It is seen that on dissolving gamma irradiated samples in to dilute HCl, initially the LL intensity increases with time, attains maximum value $I_m$ at a particular time $t_m$ (i.e. time corresponding to LL peak) then it decreases and finally disappears. Similar pattern was observed for all the samples, however relative intensity is different.

Figure 4.3a, 4.3b and 4.3c show the dependence of total LL intensity on concentration of dopant for Ce, Dy and Eu doped GdCa$_4$O(BO$_3$)$_3$, LaCa$_4$O(BO$_3$)$_3$ and YCa$_4$O(BO$_3$)$_3$ phosphors respectively. It is observed that undoped phosphors show very weak LL intensity. LL intensity initially increases with increasing dopant concentration attains maximum value for a particular concentration, and then decreases with further increase in concentration. It is also observed that $t_m$ i.e. time corresponding to LL peak does not change significantly with change in concentration of dopant. It is also observed that Ce is more effective dopant for the enhancement of LL intensity in borate based phosphors.
Figure 4.4a, 4.4b and 4.4c show the total LL intensity as a function of gamma ray dose given to the samples for Ce, Dy and Eu doped GdCa$_4$O(BO$_3$)$_3$, LaCa$_4$O(BO$_3$)$_3$ and YCa$_4$O(BO$_3$)$_3$ phosphors respectively. It is observed that the LL intensity increases with gamma ray dose given to the samples and attains saturation for higher values of gamma doses.

Figure 4.5a shows LL emission spectrum of Ce doped $\gamma$-irradiated LnCa$_4$O(BO$_3$)$_3$ (Ln = Gd, La, Y) phosphors. It is observed that all the studied phosphors emit LL mainly at 455 nm (in blue region).

Figure 4.5b shows LL emission spectrum of Dy doped $\gamma$-irradiated LnCa$_4$O(BO$_3$)$_3$ (Ln = Gd, La, Y) phosphors. Two peaks were observed in the range 470-480 nm and 570-580 nm for all the samples.

Figure 4.5c shows LL emission spectrum of Eu doped $\gamma$-irradiated LnCa$_4$O(BO$_3$)$_3$ (Ln = Gd, La, Y) phosphors. A single peak around 606 nm was observed for LnCa$_4$O(BO$_3$)$_3$ phosphors.

Maximum LL intensity observed in GdCa$_4$O(BO$_3$)$_3$:Ce(0.5mol%) as compared to other borate based phosphors. Therefore, the LL glow curves of GdCa$_4$O(BO$_3$)$_3$:Ce(0.5mol%) sample have been shown in further results.

Fig. 4.6 shows the dependence of total LL intensity on mass of dissolved $\gamma$-irradiated GdCa$_4$O(BO$_3$)$_3$:Ce(0.5mol%) sample. It is seen that initially the LL intensity increases with the mass of the crystallites added in a fixed volume of dilute HCl and then it seems to attain a saturation value for higher mass of the crystallites dissolved. It is also seen that time corresponding to LL peak shifted towards higher value side with increasing the mass of solute.
**Figure 4.2 (a):** Time dependence of LL intensity of $\gamma$-ray-irradiated GdCa$_4$O(BO$_3$)$_3$:RE phosphors dissolved in dilute HCl. ( $\gamma$-ray dose 1.1 kGy, amount of solute 1 mg, amount of solvent 2.5 ml, pH 4, particle size 90-120 $\mu$m)

**Figure 4.2 (b):** Time dependence of LL intensity of $\gamma$-ray-irradiated LaCa$_4$O(BO$_3$)$_3$:RE phosphors dissolved in dilute HCl. ( $\gamma$-ray dose 1.1 kGy, amount of solute 1 mg, amount of solvent 2.5 ml, pH 4, particle size 90-120 $\mu$m)
Figure 4.2 (c): Time dependence of LL intensity of $\gamma$-ray-irradiated $\text{YCa}_4\text{O}(\text{BO}_3)_3$:RE phosphors dissolved in dilute HCl. ($\gamma$-ray dose 1.1 kGy, amount of solute 1 mg, amount of solvent 2.5 ml, pH 4, particle size 90-120 $\mu$m)

Figure 4.3 (a): Relative total LL intensity of $\gamma$-ray-irradiated $\text{GdCa}_4\text{O}(\text{BO}_3)_3$:RE phosphors dissolved in dilute HCl as a function of dopant concentration ( $\gamma$-ray dose 1.1 kGy, amount of solute 1 mg, amount of solvent 2.5 ml, pH 4, particle size 90-120 $\mu$m)
Figure 4.3 (b): Relative total LL intensity of $\gamma$-ray-irradiated LaCa$_4$O(BO$_3$)$_3$:RE phosphors dissolved in dilute HCl as a function of dopant concentration ( $\gamma$-ray dose 1.1 kGy, amount of solute 1 mg, amount of solvent 2.5 ml, pH 4, particle size 90-120 $\mu$m)

Figure 4.3 (c): Relative total LL intensity of $\gamma$-ray-irradiated YCa$_4$O(BO$_3$)$_3$:RE phosphors dissolved in dilute HCl as a function of dopant concentration ( $\gamma$-ray dose 1.1 kGy, amount of solute 1 mg, amount of solvent 2.5 ml, pH 4, particle size 90-120 $\mu$m)
Figure 4.4 (a): Relative total LL intensity of $\gamma$-ray-irradiated GdCa$_4$O(BO$_3$)$_3$:RE phosphors dissolved in dilute HCl as a function of gamma ray doses given to the sample (amount of solute 1 mg, amount of solvent 2.5 ml, pH 4, particle size 90-120 $\mu$m).

Figure 4.4 (b): Relative total LL intensity of $\gamma$-ray-irradiated LaCa$_4$O(BO$_3$)$_3$:RE phosphors dissolved in dilute HCl as a function of gamma ray doses given to the sample (amount of solute 1 mg, amount of solvent 2.5 ml, pH 4, particle size 90-120 $\mu$m).
**Figure 4.4 (c):** Relative total LL intensity of $\gamma$-ray-irradiated YCa$_4$O(BO$_3$)$_3$:RE phosphors dissolved in dilute HCl as a function of gamma ray doses given to the sample (amount of solute 1 mg, amount of solvent 2.5 ml, pH 4, particle size 90-120 $\mu$m)

**Figure 4.5 (a):** LL emission spectra of $\gamma$-ray-irradiated Ce doped oxyborate phosphors dissolved in dilute HCl ($\gamma$-ray dose 1.1 kGy, amount of solute 1 mg, amount of solvent 2.5 ml, pH 4, particle size 90-120 $\mu$m)
Figure 4.5 (b): LL emission spectra of $\gamma$-ray-irradiated Dy doped oxyborate phosphors dissolved in dilute HCl ($\gamma$-ray dose 1.1 kGy, amount of solute 1 mg, amount of solvent 2.5 ml, pH 4, particle size 90-120 $\mu$m)

Figure 4.5 (c): LL emission spectra of $\gamma$-ray-irradiated Eu doped oxyborate phosphors dissolved in dilute HCl ($\gamma$-ray dose 1.1 kGy, amount of solute 1 mg, amount of solvent 2.5 ml, pH 4, particle size 90-120 $\mu$m)
Figure 4.6: Time dependence of LL intensity of γ-ray-irradiated GdCa₄O(BO₃)₃:Ce(0.5 mol%) phosphors dissolved in dilute HCl for different mass of solute. (γ-ray dose 1.1 kGy, amount of solvent 2.5 ml, pH 4, particle size 90-120 µm)

Figure 4.7: Relative total LL intensity of γ-ray-irradiated GdCa₄O(BO₃)₃:Ce(0.5 mol%) phosphors dissolved in dilute HCl as a function of pH value of the solvent (amount of solute 1 mg, amount of solvent 2.5 ml, particle size 90-120 µm)
Figure 4.8: Time dependence of LL intensity of $\gamma$-ray-irradiated GdCa$_4$O(BO$_3$)$_3$:Ce(0.5 mol%) phosphors dissolved in dilute HCl for different temperature of solvent ($\gamma$-ray dose 1.1 kGy, amount of solvent 2.5 ml, mass of solute 1 mg, pH 4, particle size 90-120 $\mu$m)

Figure 4.9: Relative total LL intensity of $\gamma$-ray-irradiated GdCa$_4$O(BO$_3$)$_3$:Ce(0.5 mol%) phosphors dissolved in dilute HCl as a function volume of solvent ($\gamma$-ray dose 1.1 kGy, mass of solute 1 mg, pH 4, particle size 90-120 $\mu$m)
Figure 4.10: Time dependence of LL intensity of $\gamma$-ray-irradiated GdCa$_4$O(BO$_3$)$_3$:Ce(0.5 mol%) phosphors dissolved in dilute HCl for different particle size ($\gamma$-ray dose 1.1 kGy, amount of solvent 2.5 ml, mass of solute 1 mg, pH 4)

Figure 4.11: Relative total LL intensity of calcium oxy borate phosphors dissolved in dilute HCl. ($\gamma$-ray dose 1.1 kGy, amount of solvent 2.5 ml, mass of solute 1 mg, pH 4)
Fig. 4.7 shows the dependence of total LL intensity on the pH of dilute HCl for γ-irradiated GdCa₄O(BO₃)₃:Ce(0.5mol%) sample. It is seen that the LL intensity is optimum for a particular pH value of the solvent. Results show that the LL peak intensity increases from a nearly zero value at a pH of 1 to a maximum value of 4 and then it decreases rapidly to nearly zero again at a pH of about 7.

Fig. 4.8 shows the LL glow curve of γ-irradiated GdCa₄O(BO₃)₃:Ce(0.5mol%) sample for different temperature of the solvent (dilute HCl). It is observed that LL intensity increases with time, attains an optimum value and then decreases and finally disappears. It is also seen that peak intensity Iₘ increases with increasing temperature of the solvent, attains an optimum value at 75°C and then decreases with increasing temperature of the solvent. It is also observed that tₘ shifted towards shorter time value with temperature of the solvent.

Fig. 4.9 shows the dependence of the total LL intensity of γ-irradiated GdCa₄O(BO₃)₃:Ce(0.5mol%) sample on volume of the solvent (dilute HCl). It is seen that LL intensity increases with increase in volume of the solvent and attain an optimum value for a particular volume of solvent without any appreciable change in tₘ.

Fig. 4.10 shows the time dependence of the LL intensity for different grain size of γ-irradiated GdCa₄O(BO₃)₃:Ce(0.5mol%) sample. It is seen that on dissolving the γ-irradiated sample of a particular grain size to a fixed volume (2.5ml) of dilute HCl, initially the LL intensity increases with time, attains a maximum value Iₘ at a particular time tₘ, then it decreases and finally disappears. It is also observed that tₘ shifts towards higher value with the increase of grain size.
Fig. 4.11 shows the effect of storage on LL (at room temperature in dark) of $\gamma$-irradiated GdCa$_4$O(BO$_3$)$_3$:Ce(0.5mol%), LaCa$_4$O(BO$_3$)$_3$:Ce (2mol%), and YCa$_4$O(BO$_3$)$_3$:Ce(2mol%). It is clear that fading in LL intensity of the entire sample is very low.

4.4 DISCUSSION

The phenomenon of the emission of light on dissolution of irradiated samples to the solvent is known as lyoluminescence, and has been investigated by a number of workers for dosimetric applications. Several inorganic and organic samples possess LL properties. In inorganic materials such as alkali halides the release of trapped electrons from F centers is responsible for the light emission. In case of some organic materials such as saccharide, trapped free radicals are involved in process of LL.

It is observed that the LL intensity of LnCa$_4$O(BO$_3$)$_3$ phosphors may depends on different parameters in the following way:

i. Radiation dose: The intensity of LL emission initially rises with the increase in radiation dose given to the sample and then attains a saturation value for higher values of the radiation dose.

ii. Density of defect centres ($n_F$): The intensity of LL emission depends linearly on the density of defect centres.

iii. Time of dissolution (t): The LL intensity initially increases attains an optimum value and then decreases exponentially with the time of dissolution of the sample.

iv. Temperature of the solvent (T): LL intensity initially increases with temperature, attain optimum value then decrease with further increase in temperature.
v. **Mass of the dissolved sample:** The LL intensity initially increases and then tends to attain a saturation value for higher mass of the solute added to the solvent.

vi. **Type of the sample:** The LL intensity is different for different sample.

vii. **pH of the solvent:** The LL intensity attains an optimum value for a particular value of pH of the solvent.

viii. **Volume of the solvent:** The LL intensity is optimum for a particular volume of the solvent.

ix. **Type of impurity present:** This causes increase in LL intensity.

x. **Particle size of the sample:** The LL intensity depends on the particle size of the sample.

4.4.1 **Mechanism of the LL in borate based phosphors**

Borates under γ-rays irradiation are known to produce various defect centers such as $\text{B}^{2+}$, $\text{BO}_3^{2-}$, $\text{O}^{-}$, $(\text{B}_3\text{O}_6)^{3-}$, $\text{O}_3^{-}$, $\text{O}_2^{-}$ etc (Porwal et al, 2005; Lochab et al, 2007). On dissolving such borates in suitable solvent the LL is observed due to release of trapped energy during dissolution as per mechanism suggested by Arinkar et al (1971). Schematically, the mechanism of LL in $\text{LnCa}_4\text{O(BO}_3)\text{_3}$ may be described by the following equations:

\[
\begin{align*}
\text{e}^-_{\text{trapped}} + \text{Aqueous Solvent} & \rightarrow \text{e}^-_{\text{aq}}, \\
\text{e}^-_{\text{aq}} + X & \rightarrow X_{\text{aq}}^*, \\
X_{\text{aq}}^* & \rightarrow X_{\text{aq}} + \hbar\nu,
\end{align*}
\]

where, $X =$Radicals generated due to γ-rays irradiation.

It is possible that steps (b) and (c) occur together without the intermediate state $X_{\text{aq}}^*$. A similar mechanism was also suggested by Ahnstrom (1965).
Generally, in the lyoluminescence experiment, X- or γ-irradiated crystallites of a given mass are dissolved in a given volume of a solvent. If the solute contains N molecules at any time t and α is the rate of dissolution in the solvent, then the rate of decrease in the number of solute atoms may be written as

\[ -\frac{dN}{dt} = \alpha N. \]  \hspace{1cm} (4.1)

For \( N=N_0 \) at \( t = 0 \), the integration of Eq. (4.1) gives

\[ N = N_0 \exp (-\alpha t). \]  \hspace{1cm} (4.2)

Assuming the linear dependence of the rate of generation \( g \) of the hydrated electrons on \( n_F \) and \((-dN/dt)\), we get

\[ g = \gamma n_F (-dN/dt) \]

or

\[ g = \gamma n_F N_0 \alpha \exp (-\alpha t), \]  \hspace{1cm} (4.3)

where, \( \gamma \) is a factor correlating the number of hydrated electrons with the number of dissolved defect-centres of the crystal.

The number of hydrated electrons will increase due to the dissolution of the crystallites and it will decrease due to the recombination of hydrated electrons with the holes present on the surface of the crystallites. In this way, the rate equation may be written as

\[ \frac{dn}{dt} = g - \sigma_r N_r \nu n, \]  \hspace{1cm} (4.4)

where, \( n \) is the number of hydrated electrons at any time \( t \), \( \sigma_r \) is the capture cross-section of holes, \( N_r \) is the density of recombination centres i.e. holes and \( \nu \) is the average velocity of the hydrated electrons.
Now, substituting the value of $g$ from Eq. (4.3) into Eq. (4.4), we have

$$\frac{dn}{dt} = \gamma N_0 n_F \alpha \exp(-\alpha t) - \sigma_r N_r v n$$

or

$$\frac{dn}{dt} = \gamma N_0 n_F \alpha \exp(-\alpha t) - \beta n, \quad (4.5)$$

where, $\beta = \sigma_r N_r v$, is the rate constant for the recombination of hydrated electrons with holes.

Now, the lifetime of hydrated electrons is given by

$$\tau = \frac{1}{\beta} = \frac{1}{\sigma_r N_r v}. \quad (4.6)$$

For $n = 0$ at $t = 0$ the integration of Eq. (4.5) gives

$$n = \frac{\gamma \alpha n_F N_0}{(\beta - \alpha)} \{\exp(-\alpha t) - \exp(-\beta t)\}. \quad (4.7)$$

If $\eta$ is the probability of radiative recombination, then the LL intensity may be given by

$$I = \frac{\eta \beta \gamma \alpha n_F N_0}{(\beta - \alpha)} \{\exp(-\alpha t) - \exp(-\beta t)\}. \quad (4.8)$$

It is evident from the above equation that the LL intensity $I$ is zero, at $t = 0$, and $t = \infty$. Thus, the LL intensity should be maximum at a particular value of time, $t_m$. The value of $t_m$ can be determined by differentiating $I$ with respect to $t$ and then equating it to zero. This gives

$$\alpha \exp(-\alpha t_m) = \beta \exp(-\beta t_m) \quad (4.9)$$
The value of intensity $I_m$ corresponding to the peak of LL intensity versus time curve, may be given by

$$I_m = \frac{\eta \beta \gamma \alpha n_F N_0}{(\beta - \alpha)} \left\{ \frac{\beta}{\alpha} - 1 \right\} \exp(-\beta t_m)$$

or

$$I_m = \frac{\eta \beta \gamma \alpha n_F N_0}{(\beta - \alpha)} \left\{ \frac{\beta}{\alpha} - 1 \right\} \exp\{-\beta/\beta - \alpha\} \log(\beta/\alpha)\}. \quad (4.11)$$

As the dissolution of a solute in a solvent is a slow process as compared to the process of recombination of hydrated electrons with holes, we may assume $\beta \gg \alpha$, and thus Eq. (4.11) may be written as

$$I_m = \eta \gamma n_F N_0 \alpha. \quad (4.12)$$

The total LL intensity $I_T$ i.e. the total area below the LL intensity versus time curve may be given by

$$I_T = \int_0^\infty I dt$$

or

$$I_T = \int_0^\infty \frac{\eta \beta \gamma \alpha n_F N_0}{(\beta - \alpha)} \times \left[ \exp(-\alpha t) - \exp(\beta t) \right] dt$$

or
\[ I_T = \eta \gamma n_F N_0. \]  \hfill (4.13)

The above equation shows that the value of \( I_T \) will be directly proportional to \( n_F \) and \( N_0 \).

### 4.4.1.1 Rise and decay of LL intensity

For low value of \( t \), Eq. (4.8) may be written as

\[ I = \eta \beta \gamma \alpha n_F N_0 t. \]  \hfill (4.14)

The above equation shows that when the solute will be added to the solvent then initially the LL intensity will increase linearly with time.

Since \( \beta >\alpha \), for higher values of \( t \), Eq. (4.8) may be expressed as

\[ I = \eta \gamma \alpha n_F N_0 \exp(-\alpha t). \]  \hfill (4.15)

The above equation shows that the LL intensity should decrease exponentially with time. Thus, by plotting a curve between log \( I \) and \( t \), one will be able to determine the value of \( \alpha \) from the slope of the curve.

As \( \alpha \) increase with temperature, an increase in the values of \( I \) with temperature is expected. However, at higher temperature the thermal bleaching of defect-centres takes place and the LL intensity may decrease with temperature. Thus, the LL intensity should be optimum for a particular temperature of the solvent.
4.4.1.2 LL glow curve

It is found that when $\gamma$-irradiated LnCa$_4$O(BO$_3$)$_3$ sample of a given mass is dissolved in a fixed volume of dilute HCl, then the LL intensity initially increases linearly with time, attains an optimum value, then it decreases and finally disappears. These results are in accordance with Eqs. (4.8), (4.14) and (4.15).

4.4.1.3 Dependence of LL on dopant concentration

It is observed that the LL intensity depends on the concentration of the activators (Impurity) in the crystallites. Initially the LL intensity increases with the concentration of activator, attains an optimum value for a particular concentration and then it decreases with further increase in concentration of the dopant. When the concentration of the dopant is increased, initially the number of luminescent centre and the formation of defect centre increase, thereby increasing the LL intensity. Later on when the concentration exceeds a particular level, the concentration quenching starts and the efficiency of radiative transition decreases. The critical concentrations of different activators for optimum LL intensity are different in the present investigation. It may be speculated that the factors leading to an increase in the probability of non-radiative transitions results as a decrease in the optimum luminescence efficiency.

4.4.1.4 Dependence of LL on $\gamma$-ray dose

In the observation of the dependence of LL intensity on the $\gamma$-irradiation dose given to the LnCa$_4$O(BO$_3$)$_3$ crystal, It is seen that
initially the LL intensity increases with the radiation dose and then it attains a saturation value for higher radiation doses given to the crystallites. This can be understood as follows:

When a LnCa₄O(BO₃)₃ crystal is exposed to high energy radiation like γ-rays or X-rays, excitation of electrons of borate atoms from valence band to conduction band takes place. Some of the excited electrons return immediately from the conduction band to the valence band, however, some of the electrons in the conduction band get trapped in the negative ion vacancies during their movement and consequently the formation of defect centres takes place. Initially the number of defect centres increases with the radiation dose given to the crystals and thereby, the LL intensity increases with the radiation dose. However, for long duration of the irradiation of the crystals the recombination between electrons and holes takes place and consequently the density of defect centres in the crystals attains a saturation value.

As a matter of the fact, the LL intensity also attains a saturation value for high radiation dose given to the crystallites.

4.4.1.5 LL Spectroscopy

Spectroscopic studies of the LL emission indicate that rare earth impurity doped in the borate based phosphors act as luminescence centers. It can be assumed that energy released shown in equation (c) is transferred non-radiatively to the rare earth ions present in host lattice
which excites that rare earth ions and the de-excitation of the rare earth ions give rise the luminescence.

4.4.1.6 Dependence of LL on mass of solute

It is observed that initially the LL intensity increases with the mass of the crystallites added in a fixed volume of dilute HCl and then it attains a saturation value for higher mass of the crystallites added. Such results are predicted from Eq. (4.13), where \( N_0 \) is related to mass of the sample added into the solvent. When higher mass of the crystallites are added to the solution, a saturation will occur and only a fixed amount of the solute will be dissolved, hence, the LL intensity will attain a saturation value beyond a particular mass of the solute.

4.4.1.7 Dependence of LL on pH of the solvent

In the observation of the dependence of LL intensity on the pH of the solvent it is seen that the LL intensity is optimum for a particular pH value of the solvent. The effect of pH on the intensity of lyoluminescence of irradiated LnCa₄O(BO₃)₃ has been studied by varying the pH of the medium in which the sample were dissolved by adding to it a calculated amount of HCl. Results show that the peak height increases rapidly from a nearly zero value at a pH of 1 to a maximum value of 4 and then it decreases rapidly to nearly zero again at a pH of about 7. It has been shown that the maximum intensity in lyoluminescence is observed over the pH range in which the stability of the hydrated electrons is optimum.
4.4.1.8 Dependence of LL on temperature

As the probability of radiative recombination increases with increasing temperature, the LL intensity should increase with increasing temperature. When the temperature of the solvent was increased LL intensity increased with temperature attained an optimum value at 75°C then decreased with further increase in temperature. The decrement of LL at higher temperature is because of thermal bleaching (eq.4.15).

4.4.1.9 Dependence of LL intensity on volume of the solvent and particle size of the sample

It is observed that the LL intensity initially increases with increase in the volume of the solvent, attains an optimum value for a particular volume and then decreases with further increase in the volume. This can be interpreted as the rate of dissolution increases with the increase in the volume of the solvent and consequently LL intensity increases initially. For a higher volume of the solvent in which a particular mass of the solute is dissolved, the average distance between the hydrated electron and holes on the surface of solute will increase. It seem that this quenches the occurrence of radiative recombination between the hydrated electrons and holes near the surface of the solute, and therefore resulting in a decrease in LL intensity with increasing volume of the solvent.

It is found that LL intensity initially increases with increasing particle size of the sample. This may be due to greater stability of defect centres in crystallites of large dimensions whereas in the case of smaller dimensions there is a rapid decay of defect centre resulting in poor radiolysis products. Above a certain particle size, the LL intensity
decreases with increase in particle size. This is in accordance with equation (4.12) which clearly indicates that $I_m$ should decrease firstly due to the formation of less density of defect centres in larger grain, and secondly due to decrease in the rate of dissolution with increasing grain size of crystallites. It is also observed that the time $t_m$ corresponding to the peak of the LL intensity increases with increasing particle size. This may be due to longer time duration needed for dissolving the samples of larger particle size. Since the dissolution rate decreases with increasing particle size, Equation (4.10) indicates that $t_m$ should increase linearly with particle size of the sample.

Conclusively, it may be said that there is a good qualitative correlation between the experimental and theoretical results.

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REFERENCES


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