Thermoluminescence (TL) Studies in KCl (Pure), KBr (Pure), KCl-KBr Mixed Crystals above Room Temperature

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Abstract: Thermoluminescence (TL) glow curves of X-irradiated KCl (Pure), KBr (Pure) and KCl-KBr mixed crystals have been studied in the different dose of X-irradiation with periods 40 minutes, 60 minutes & 120 minutes with temperature range 25-300°C. A plot of the peak height against composition shows a minimum at KCl 0.52: KBr 0.48. The glow curves were analyzed & the variation of activation energy with composition has also been studied. The variation of peak temperature and the relative intensity of the peaks with respect to the composition the addition of Br ions to the KCl lattice has been found to be more effective in enhancing the Thermoluminescence (TL) of KCl-KBr solid solution.

1. INTRODUCTION

The Phenomenon of Thermoluminescence (TL) has been known for long time. The TL being a structure-sensitive phenomenon can be used to study the structural imperfections in crystals. Densities of defects as low as 10^7 cm^-3 can give measurable Thermoluminescence (if radiative recombination is unity) while other methods e.g. ESR and optical absorption are sensitive to concentrations greater than 10^{12} cm^{-3}[1]

Thermoluminescence of KCl [2][3][4] and KBr [5] [6] in pure samples as well as samples doped with suitable impurities has been widely investigated to determine the thermal activation energy, the frequency factor and the order of kinetics of recombination of electrons and holes at trapping sites. Ausin and Alvarez Rivas [7] studied the TL and F-centre thermal annealing in heavily irradiated KCl and NaCl crystals. It was concluded by them that the TL in irradiated alkali halides is due to recombination of mobile interstitials with vacancy centres. More recent work of Mariani and Alvarez Rivas [8] on TL in alkali halides irradiated at room temperature also supports their earlier models that TL is due to the recombination of F-centres with halogen interstitial atoms which are thermally released from traps during heating. Earlier some glow curves and absorption studies were carried out on mixed alkali halide
system [9][10][11] and the peaks observed have been attributed to the destruction of F-centres by electron-hole recombination. Some investigations have been made on the luminescence centres in NaCl-NaBr [12] nakagawa et al [13] and KCl-KBr [14] systems. Recently Moharil et al [15] studied TL in KCl-KBr mixed crystals exposed to gamma rays at room temperature. They attributed the two glow peaks to F-centres in different local environments.

In this paper our attempt has been made to study the TL phenomenon in Pure KCl, Pure KBr and KCl-KBr mixed crystals exposed to X-rays above room temperature. Further, the activation energy (E) corresponding to different peaks has been calculated and its variation with the different composition of mixed crystals has been studied.

2. EXPERIMENTAL PROCEDURE

Single crystals of KCl, KBr & different composition of KCl-KBr mixed crystals were grown from principle of the solution method using GR grade starting materials. This crystals contain traces of impurities which were present in the GR grade chemicals (commercially pure); it was same for all composition. For mixed crystals were prepared for different composition such as KCl_{0.29}:KBr_{0.71}; KCl_{0.52}:KBr_{0.48}; KCl_{0.71}:KBr_{0.29}; KCl_{0.86}:KBr_{0.14}; KCl_{0.29}:KBr_{0.71}; KCl_{0.14}:KBr_{0.86}.

X-Ray Diffraction was checked for single crystals of KCl, KBr & different composition of KCl-KBr mixed crystals using Philips instrument with target material as CuKα, Voltage of 40KV, Current 30mA and angle range of 20-70°.

To measure the thermoluminescence (TL) intensity of the samples, the samples were irradiated with X-Rays from Regaku X-ray tube with copper target. X-ray tube is operated at 25KV, 7mA & filtered through Beryllium window. All samples were kept at the same distance from the window. The oven is used for heating the crystal, the power supply of the oven allows an adjustment of 15V, 20V, & 25V corresponding to low, medium & high rate of heating. Photomultiplier tube (931-A) is used, its range of 3000-6500A° with maximum 4200A°. The nanometer range of 0-100nA was selected.

From the temperature T_G of the peak of the curve, we can estimate the activation energy (E) approximately by using below formula;

\[ E=K_T \ln (\beta_0 T_G/\beta) \]

By taking sensitivity as \(10^{10}-10^{12}\) sec\(^{-1}\) for \(\beta_0\), we can obtain activation energy (E)

Where,

E-Activation Energy, T_G-is the temperature corresponding to the peak, \(\beta_0\)-is the Quantum mechanical constant

\(\beta\)-is the rate of heating, \(K\)-is the Boltzmann Constant

![Block Diagram of Thermoluminescence Measurement](image-url)
3. Results & Discussion

The TL measurement glow curves for Pure KCl, Pure KBr, & KCl-KBr Mixed crystals were studied with three different irradiation dose periods 40min, 60 min, & 120 min.

For KCl (Fig.1) irradiated at 40 minutes shows three peaks at 90°C, 120°C & 170 °C. For (Fig. 2) 60 minutes of irradiation shows three peaks 90°C, 105°C, & 180°C. For (Fig.3) 120 minutes of irradiation shows three peaks 90°C, 105°C & 180°C which tallies with peaks obtained by earlier workers [16][17] in the range 80-90°C, 105-135°C & 170-190°C. The peaks in the range 80-90°C could be due to the thermally released trapped holes (V -Centres), the peaks in the temperature range 105-135°C & 170-190°C could be due to the thermally released F-center electrons as mentioned by R.K.Gartia et al [18]. The activation energy for all the three peaks observed for different doses of irradiation have been calculated for first time & shown in Table 1. These activation energies are reported slightly different by earlier workers [17][18] as shown in table 1.

The plot of variation of peak height versus irradiation time for pure KCl (Fig.22) shows that at higher irradiation time the peak height saturates. This could be due to the traps getting completely filled after a certain dose of X-ray irradiation. Similar results have been reported by Brinda Subramanian et al [17].

Pure KBr (Fig. 4) irradiated at 40 minutes exhibits two peaks at 80°C and 140°C, For (Fig. 5) 60 minutes of irradiation the peaks are at 90°C and 135°C and for (Fig. 6) 120 minutes of irradiation the peaks are 75°C and 125°C which tallies with peaks obtained by earlier workers in the range 75-90°C and 125-155°C. The peak in the range 75-90°C and 125-155°C could be due to the thermally released F-Centre electrons as mentioned by earlier workers [17][19][20].

The activation energy for both the peaks observed for different doses of irradiation have been calculated and shown in table 1. These activation energies are reported slightly different by earlier workers [17][20] as shown in table 1.

The plot of variation of peak height versus irradiation time for pure KBr (Fig.23) shows that at higher irradiation time the peak height saturates. This could be due to the traps getting completely filled after a certain dose of X-ray irradiation. Similar results have been reported by Brinda Subramanian et al. [17].

For all the composition of mixed KCl-KBr crystals glow peak temperatures along with their activation energies have been shown in table 1. There are only two peaks for all the compositions and these could be due to the thermal release of trapped electrons as mentioned above. Similar results have been reported earlier by Brinda Subramanian et al [17]. For higher dose of irradiation we see a few extra peaks which are not mentioned by earlier workers and we conclude that these might have resulted due to the presence of impurities in our compounds (both KCl and KBr are GR grade having 99.5% purity).

By comparing the graphs (Fig 1-21) of all the various samples (pure and mixed), we observe that the peaks of pure KBr coincide with peaks of mixed KCl-KBr crystals. It can be seen that even with low percentage of KBr the peaks tend to be more characteristics of KBr than of KCl indicating that Br` ions play an important role in the TL of the mixed crystals. Similar results have been reported by earlier workers [17].
A plot of glow peak temperature versus concentration of KBr from (Fig.29-31) that the glow peak temperature shifts to a lower temperature as the KBr concentration increases for both high and low temperature peaks. Similar results are obtained by Brinda Subramanian et al. [17], this shows that as long as KCl concentration is more the sample shows KCl emission and after the intermediate composition (KCl$_{0.52}$: KBr$_{0.48}$) it shows KBr emission. Similar results are obtained for other dose rates.

A plot of Relative intensity ($I_2/I_1$) versus concentration of KBr in KCl (Fig.32-34) (where $I_2$ is intensity of the high temperature peak and $I_1$ is the intensity of the low temperature peak) indicates that Relative intensity decreases with addition of KBr to KCl but after the intermediate concentration it increases towards KBr. While a plot of activation energy versus concentration increases towards KBr.

While a plot of activation energy versus concentration of KBr and KCl (Fig 35-37) shows that the activation energy decreases with addition of KBr to KCl but after the intermediate concentration it increases towards KBr. This could be either due to the change in the configuration of the trap as a result of the presence of Br$^-$ ions in KCl or due to a change in trap depth, this could be due to difference in size of anions in KCl-KBr (that is Cl$^-$ ion having 18 electrons while Br$^-$ ion having 36 electrons). Similar results have been reported by Brinda Subramanian et al. [17].

X Ray Diffraction pattern of our pure KCl & Pure KBr we notice that there is an extra peak for KBr just before the principle peak, the same is absent in KCl. This is because in KCl the number of electrons of K$^+$ & Cl$^-$ are equal, and also the scattering amplitudes F(K$^+$) & F(Cl$^-$) are almost exactly equal. Our mixed KCl-KBr crystals we see that as the concentration of KBr increases in KCl, the intensity of the extra peak before the principle peak increases linearly in (fig.38). Hence, we can almost be certain that our concentrations have mixed properly.

**TABLE 1: Activation energy & TL glow peak temperature for different Irradiation periods for 40 min, 60 min & 120 minutes.**

<table>
<thead>
<tr>
<th>SAMPLES</th>
<th>PEAKS FROM A CTIVATION ENERGY FROM PAPERS (eV)</th>
<th>PEAKS (°C)</th>
<th>ENERGY (eV)</th>
<th>PEAKS (°C)</th>
<th>ENERGY (eV)</th>
<th>PEAKS (°C)</th>
<th>ENERGY (eV)</th>
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<tr>
<td>KCl (Pure)</td>
<td>88 115 180</td>
<td>90</td>
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<td>90</td>
<td>1.059</td>
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<tr>
<td>KBr (Pure)</td>
<td>75 125</td>
<td>80</td>
<td>1.024</td>
<td>90</td>
<td>1.059</td>
<td>75</td>
<td>1.013</td>
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<tr>
<td>KCl (0.86):</td>
<td>105 151</td>
<td>85</td>
<td>1.038</td>
<td>90</td>
<td>1.063</td>
<td>90</td>
<td>1.066</td>
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<tr>
<td>KBr (0.14)</td>
<td></td>
<td>125</td>
<td>1.157</td>
<td>100</td>
<td>1.09</td>
<td>120</td>
<td>1.146</td>
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<tr>
<td>KCl (0.71):</td>
<td>90 145</td>
<td>90</td>
<td>1.055</td>
<td>110</td>
<td>1.129</td>
<td>100</td>
<td>1.088</td>
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<td>KBr (0.29)</td>
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<td>140</td>
<td>1.202</td>
<td>130</td>
<td>1.187</td>
<td>140</td>
<td>1.214</td>
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<tr>
<td>KCl (0.52):</td>
<td>75 130</td>
<td>77</td>
<td>1.013</td>
<td>75</td>
<td>1.011</td>
<td>75</td>
<td>1.015</td>
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<tr>
<td>KBr (0.48)</td>
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<td>125</td>
<td>1.154</td>
<td>130</td>
<td>1.181</td>
<td>92</td>
<td>1.061</td>
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<tr>
<td>KCI (0.29):</td>
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<td>85</td>
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<td>KBr (0.71)</td>
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<td>1.128</td>
<td>115</td>
<td>1.18</td>
<td>115</td>
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**Table:**

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<th>Temp2</th>
<th>Glow1</th>
<th>Glow2</th>
<th>Temp3</th>
<th>Glow3</th>
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<tr>
<td>KCl (0.15): KBr (0.85)</td>
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<td>77</td>
<td>1.013</td>
<td>75</td>
<td>1.011</td>
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<td></td>
<td>130</td>
<td>----</td>
<td>125</td>
<td>1.154</td>
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<td>1.188</td>
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</table>

**Figures:**

- **Fig 1:** Graph of Intensity (nA) V/S Temp(OC)  
  Sample: PURE (KCl), Irradiation Time: 40 Min  
  Glow Peak: 90°C, 120°C, 170°C

- **Fig 2:** Graph of Intensity (nA) V/S Temp(OC)  
  Sample: PURE (KCl), Irradiation Time: 60 Min  
  Glow Peak: 90°C, 120°C, 170°C

- **Fig 3:** Graph of Intensity (nA) V/S Temp(OC)  
  Sample: PURE (KCl), Irradiation Time: 120 Min  
  Glow Peak: 85°C, 105°C, 180°C

- **Fig 4:** Graph of Intensity (nA) V/S Temp(OC)  
  Sample: PURE (KBr), Irradiation Time: 40 Min  
  Glow Peak: 80°C, 140°C

- **Fig 5:** Graph of Intensity (nA) V/S Temp(OC)  
  Sample: PURE (KBr), Irradiation Time: 60 Min  
  Glow Peak: 90°C, 125°C

- **Fig 6:** Graph of Intensity (nA) V/S Temp(OC)  
  Sample: PURE (KBr), Irradiation Time: 120 Min  
  Glow Peak: 75°C, 125°C
Fig 7: Graph of Intensity (nA) V/S Temp(OC)
Sample: KCl$_{0.14}$:KBr$_{0.86}$, Irradiation Time: 40 Min
Glow Peak: 70°C, 105°C

Fig 8: Graph of Intensity (nA) V/S Temp(OC)
Sample: KCl$_{0.14}$:KBr$_{0.86}$, Irradiation Time: 60 Min
Glow Peak: 70°C, 105°C

Fig 9: Graph of Intensity (nA) V/S Temp(OC)
Sample: KCl$_{0.14}$:KBr$_{0.86}$, Irradiation Time: 120 Min
Glow Peak: 70°C, 90°C, 107°C, 140°C

Fig 10: Graph of Intensity (nA) V/S Temp(OC)
Sample: KCl$_{0.29}$:KBr$_{0.71}$, Irradiation Time: 40 Min
Glow Peak: 80°C, 114°C
Fig 11: Graph of Intensity (nA) V/S Temp(OC)
Sample: KCl<sub>0.29</sub>:KBr<sub>0.71</sub>, Irradiation Time: 60 Min
Glow Peak: 90°C, 115°C.

Fig 12: Graph of Intensity (nA) V/S Temp(OC)
Sample: KCl<sub>0.29</sub>:KBr<sub>0.71</sub>, Irradiation Time: 120 Min
Glow Peak: 85°C, 115°C, 140°C.

Fig 13: Graph of Intensity (nA) V/S Temp(OC)
Sample: KCl<sub>0.52</sub>:KBr<sub>0.48</sub>, Irradiation Time: 40 Min
Glow Peak: 77°C, 125°C.

Fig 14: Graph of Intensity (nA) V/S Temp(OC)
Sample: KCl<sub>0.52</sub>:KBr<sub>0.48</sub>, Irradiation Time: 60 Min
Glow Peak: 75°C, 130°C.
Fig15: Graph of Intensity (nA) V/S Temp(°C)
Sample: KCl_{0.3}:KBr_{0.4}, Irradiation Time: 120 Min
Glow Peak: 75°C, 92°C, 130°C

Fig16: Graph of Intensity (nA) V/S Temp(°C)
Sample: KCl_{0.3}:KBr_{0.4}, Irradiation Time: 40 Min
Glow Peak: 90°C, 140°C

Fig17: Graph of Intensity (nA) V/S Temp(°C)
Sample: KCl_{0.3}:KBr_{0.4}, Irradiation Time: 60 Min
Glow Peak: 110°C, 130°C

Fig18: Graph of Intensity (nA) V/S Temp(°C)
Sample: KCl_{0.3}:KBr_{0.4}, Irradiation Time: 120 Min
Glow Peak: 100°C, 110°C, 140°C

Fig19: Graph of Intensity (nA) V/S Temp(°C)
Sample: KCl_{0.3}:KBr_{0.4}, Irradiation Time: 40 Min
Glow Peak: 85°C, 125°C

Fig20: Graph of Intensity (nA) V/S Temp(°C)
Sample: KCl_{0.3}:KBr_{0.4}, Irradiation Time: 60 Min
Glow Peak: 90°C, 100°C, 145°C
Fig 21: Graph of Intensity (nA) VS Temperature (°C)
Sample: KClₐₐ : KBr₀.₁₄ Irradiation Time: 120 Min
Glow Peak: 90°C, 100°C, 120°C, 140°C,

Fig 22: Graph of Peak Height VS Time of Irradiation Sample: KCl (Pure)

Fig 23: Graph of Peak Height VS Time of Irradiation Sample: KBr (Pure)

Fig 24: Graph of Peak Height VS Time of Irradiation Sample: KCl 0.29: KBr 0.71

Fig 25: Graph of Peak Height VS Time of Irradiation Sample: KCl 0.52: KBr 0.48

Fig 26: Graph of Peak Height VS Time of Irradiation Sample: KCl 0.14: KBr 0.86
Fig 27: Graph of Peak Height V/S Time of Irradiation
Sample: KCl 0.71: KBr 0.29

Fig 28: Graph of Peak Height V/S Time of Irradiation
Sample: KCl 0.85: KBr 0.15

Fig 29: Graph of Glow Peak temp V/S Conc. of KBr
Time of Irradiation: 40 min

Fig 30: Graph of Glow Peak temp V/S Conc. of KBr
Time of Irradiation: 60 min

Fig 31: Graph of Glow Peak temp V/S Conc. of KBr
Time of Irradiation: 120 min

Fig 32: Graph of Relative Intensity (I2/I1) V/S Conc. of KBr (mol %)
Time of Irradiation: 40 min
Fig 33: Graph of Relative Intensity (I2/I1) V/S Conc. of KBr (mol %) Time of Irradiation: 60 min

Fig 34: Graph of Relative Intensity (I2/I1) V/S Conc. of KBr (mol %) Time of Irradiation: 120 min

Fig 35: Graph of Activation Energy V/S Conc. of KBr (mol %) Time of Irradiation: 40 min

Fig 36: Graph of Activation Energy V/S Conc. of KBr (mol %) Time of Irradiation: 60 min

Fig 37: Graph of Activation Energy V/S Conc. of KBr (mol %) Time of Irradiation: 120 min

Fig 38: Graph of Intensity V/S Conc. of KBr in KCl(XRD)
4. Conclusions

TL glow curves recorded for single crystals of KCl, KBr and KCl-KBr mixed systems show that the intensity of the high temperature peak increases at the cost of a decrease in the low – temperature peak intensity to give glow curves characteristic of KBr.

The variation of peak temperature as well as the activation energy of the traps with composition reveals the fact that the addition of Br\(^-\) ions to KCl is more effective than the addition of Cl\(^-\) ions to a KBr lattice.

5. Acknowledgement

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References

1. Fieschi & Paracchini, 1970


