Thermoluminescence Studies in Divalent Activated Potassium Chloride Single Crystals

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Abstract— We have grown pure and doped potassium chloride single crystals by Czochralski technique. They were irradiated with X-ray at room temperature. Care has been taken so that there is uniform irradiation of the sample and therefore, both the surfaces of the crystals were allowed to expose to X-rays for equal interval of time. Thus, on an average each sample was kept for about 40 minutes to get exposed with x-rays in a uniform manner. The irradiated samples were heated in a furnace. Thermo-luminescence glow curves were recorded using thermo-luminescence set-up. It is observed that on adding the dopant and subsequently increasing its concentration in pure KCl the number of peaks increases. The results of present investigation indicate that the F-center generated due to the vacancies present in the system due to thermo-dynamical requirement give rise the peak at lower temperature side. Small shift in their position on doping can be attributed to the small perturbation around the location of F-centers caused by the presence of dopant ions.

Keywords— Dopant, Irradiation, F-Center, X-Rays, Thermo-Luminescence

I. INTRODUCTION

Thermo luminescence is considered to be an effective method for getting information about the nature of trap centers. When crystal are exposed at lower temperature to high-energy radiation like x-rays, γ-rays and later warmed at constant rate in dark, they exhibit luminescence. This type of luminescence is called thermo luminescence. This phenomenon is strictly sensitive to the structure of imperfections. The considerable amount of thermo luminescence intensity was observed [1] from a crystal having defects only of the order of 10 per cm whereas other methods viz. ESR and optical absorption demands a concentration of defects much greater than this number. Thus a better understanding of this phenomenon can provide a powerful tool for the study of imperfections in solid-state materials. Various workers have reported a lot of literature in the field of TL shown by different materials. Large number of dielectric materials, minerals, rocks, inorganic single crystals, polycrystalline materials, semiconductors and insulators exhibits TL emission [2].

In alkali halide crystals on heating, x-ray or γ-ray irradiated samples, over a temperature range of 25°C to 300°C, thermal glow curves were observed. The stability of color center was studied [3] extensively in proton irradiated KCl-KBr mixed crystal in the temperature range 25°C to 225°C. Two luminescence peaks having different thermal ionization, one at around 100°C where as another at around 160°C were observed. Mixed crystals were found to show high luminescence. The position of second peak shifts towards high temperature. This shows that in mixed crystals more F-centers destroyed thermally at higher temperatures than in separate KCl and KBr component.

Calcium Sulphide (CaS) phosphors has been described as an efficient photo luminescent and thermo luminescent material [4-7]. Randall and Wilkins [8] have developed a theory for the calculation of various TL parameters such as, the activation energy E, escape frequency factor S and the order of kinetics. The glow curve can provide valuable information about the role of various impurities present in the sample. Research activities in the area of TL over the years have led the scientist in three different directions. The first approach was concentrated on the determination of trapping parameters such as activation energy E, frequency factor S and order of kinetics relevant to the TL glow curves [9]. The second approach was related to study of defect centers in insulators and semiconductor [10]. The third approach makes use of the capability of deep traps in insulating materials to store charge carriers above room temperature for a longer time. This approach has lead two main applications of thermo-luminescence one in the field of dosimetry and another dating [11]. The multiple glow peak curves can be analyzed by well known initial rise method and careful monitoring of the thermal cleaning process [12]. Thermo luminescence in pure KCl and KBr crystal has drawn attention of several workers [13-19]. The doped alkali halide crystals have received much more attention in the past [20-25]. Two TL peaks were observed by Jain and Mahendru [13], one at 135°C while the other at 190°C in pure crystals while in doped KCl crystal one additional peak at 85°C was observed.
It was suggested that 85°C peak is due to the presence of background impurity in the crystal whereas peak at 135°C & 190°C corresponds separately to the bleaching of first and second stage F-center, respectively. Normally, the first stage F-center are formed by the vacancies present in the crystals prior to irradiation and are distributed uniformly throughout the crystal whereas the second stage F-centers are formed by the vacancies generated during the process of irradiation and thus remains present in small regions with high local concentrations. Later on, an additional peak at 270°C in deformed KCl crystal was also observed. It was also observed that the rate of growth of peaks observed at 190°C was reduced. In irradiated KCl crystals TL peaks at 47°C, 68°C, 113°C, 194°C, 247°C and 268°C were observed by Amin [15]. To explain these observations, a simple model was proposed which is based on the assumption that the mobile entity is neither an electron nor a hole in the thermo luminescent process but it is the halogen ions, which remain stabilized at interstitial position during irradiation. On heating the irradiated sample, they are thermally released and migrate until they recombine with F-centers. In Ba⁺⁺ doped KCl crystal it was observed that TL intensity as well as position of glow peaks was affected by the state of dispersion of impurities in the lattice [26]. Two TL peaks were observed, one at 110°C while other at 190°C. The former peak was attributed to the presence of background impurities while later to the F-centers. In highly pure KBr crystals also, two peaks were observed [19], one at 90°C, while other at 150°C. These two peaks were also considered to be associated with two types of F-centers. Thermal bleaching of F-band in X-ray irradiated KBr crystals takes place in two stages and each stage has a separate well defined peak as in KCl crystal. In X-ray irradiated KBr crystal in the temperature range 300K to 510K four glow peaks respectively at 359K, 377K, 392K and 499K were observed [18]. Later on the Mariani [27] has studied thermoluminescence and thermal stability of F-center in pure KBr single crystal irradiated with X-ray and also that of γ-rays at room temperature. They concluded that the observed TL peaks were due to the recombination of halogen interstitial atoms with F-centers. Thermo luminescence in KCl-KBr mixed crystals irradiated with γ-ray at room temperature was also studied by Moharil [28] et al. Glow peaks were observed in the temperature range 409K to 427K, the exact temperature depending upon the composition. The F-band bleaching studies have shown the emergence of peak on low temperature side, which grew at the cost of high temperature peak.

Bhimashankaran [29] has studied thermo luminescence in X-ray irradiated NaCl-NaBr mixed crystal and observed that as the percentage of NaBr in NaCl increases the number of peaks decreases. Two prominent peaks were observed in mixed crystals having chloride concentration up to 36%. Above this concentration these mixed crystal show single prominent peak. It was suggested that centers responsible for first peak are more stable that those responsible for second peak. Subramaniam [30] has also observed thermo luminescence in KCl-KBr mixed crystal and observed peaks whose number, both at lower and higher temperature, varies with temperature. In the present paper the results of thermo luminescence studies in pure and doped KCl single crystals are reported. The dopants used Ba⁺⁺, Ca⁺⁺ and Mg⁺⁺. Their concentrations kept at 0.1% and 0.5% by weight.

II. EXPERIMENTAL

Samples of size 5mm × 5mm × 3mm were cleaved from as-grown crystals grown by Czochralski technique. They were irradiated with X-ray at room temperature. All the crystals were exposed to X-rays for about 40 minutes. Care has been taken so that there is uniform irradiation of the sample and therefore, both the surfaces of the crystals were allowed to expose to X-rays for equal interval of time. Thus, on an average each sample was kept for about 40 minutes to get exposed with X-rays in a uniform manner. The irradiated samples were heated in a furnace and the supply was so adjusted that rate of increase of temperature was around 5°C-10°C per minute. Thermo luminescence glow curves were recorded using thermo luminescence set-up.

III. RESULTS & DISCUSSIONS

The TL intensity (in arbitrary unit-au) v/s temperature (T in Kelvin) was plotted for both undoped and doped KCl crystals are shown in figure 1 to 3. It is observed that on adding the dopant and subsequently increasing its concentration in pure KCl the number of peaks increases. The results shown in figure 1 to 3 clearly reflects that there is only one peak observed in pure KCl crystal at about 120°C. On doping with 0.1% concentration of dopant ions this peak get shift slightly towards lower temperature side in case of Mg⁺⁺ and higher temperature side in case of Ca⁺⁺. On the other hand with Ba⁺⁺ no shift in the position of peak is observed. In addition to this, an additional peak has appeared towards higher temperature side. The width of these high temperature peaks is observed to be higher than that of lower temperature peak.
On increasing the dopant concentration to 0.5% both the peaks which were appeared at 0.1% concentration get further shift towards higher temperature side in case of Mg$^{++}$ doped crystals. In Ba$^{++}$ doped crystal the original peak get shift towards lower temperature and an additional peak appeared towards higher temperature side. On the contrary in Ca$^{++}$ doped crystals three peaks were observed viz one at the same temperature at which it was observed at 0.1% dopant concentration while the other towards higher temperature side. A third peak clearly appeared in between these two peaks. The luminescence intensity corresponding to all the three peaks was smaller than that of corresponding peaks observed at 0.1% dopant concentration.

Where $k$ is Boltzman’s constant in eV, $T_g$ is Temperature corresponding to the peak in Kelvin and $B_0$ is the Quantum mechanical constant for the system; generally in the range of $10^{10}$ to $10^{12}$ for alkali halide family, (since E is not very sensitive to this factor so in calculation it is taken to be equal to $10^{11}$). Thus, $E = 8.6 \times 10^{-5} T_g \times 2.3026 \log_{10} \left(10^{11} \times T_g / \beta\right)$

Where $\beta$ is the rate of heating in $^\circ$C/sec.; the activation energy so calculated are shown in table 1.

Thermo-luminescence (TL) glow curves in alkali halide crystals show several peaks. These peaks were assumed to arise due to the depopulation of traps on account of thermal energy available at corresponding temperatures. The depopulation of centers causes the recombination of electrons and holes in the vicinity of luminescence centers. The annealing of F-centers with interstitials may also be possible cause for these glow curves [15]. In both these processes the light is emitted during electron hole recombination. The mobility of charge carries was taken into consideration above the room temperature [31]. Mitchell [32] et al has proposed a theory for generation of F-centers in x-ray irradiated alkali halide crystals. According to Mitchell theory F-centers are created in two stages. The vacancies which are present in the crystal due to the thermodynamical requirement contribute in first stage whereas the vacancies which are created during the irradiation plays important role in the generation of F-centers in second stage. When an electron gets trapped at the site of any of these vacancies then F-centers are formed. The basic difference in the generation of F-centers in these two stages lies in their distribution within the crystal. F-centers generated in the first stage remains uniformly distributed whereas those generated in the second stage remains localized.
It has also been suggested that dislocations do play an important role in the generation of F-centers in alkali halide crystal [33, 34]. Asthana [35] have reported that on addition of Br⁻ ion into the NaCl lattice, the lower temperature peak get shifted towards lower temperature side whereas the higher temperature peak shifted towards the higher temperature side. The shift in higher temperature peak was not as marked as the shift in lower temperature peak. These observations were interpreted by assuming the fact that the centers responsible for the emission occurring at higher temperature are associated with background impurities whereas those responsible for lower temperature peak are due to the centers free from the influence of these impurities. It has also been observed that the TL glow curve peak in NaBr crystals usually occurs at lower temperature. Therefore, the shift in the lower temperature peak towards lower temperature side on addition of Br⁻ ion can be associated with the presence of more Br⁻ ion in the lattice. Moreover, the lower temperature peaks can be said to have characteristics more of NaBr than of NaCl. Thus the Br⁻ ions seem play an important role in modifying the thermo luminescence of these systems. The luminescence and absorption phenomenon in NaCl-NaBr solid solution was studied by Nakai [36] et al and Nakagawa [37] et al. Nakai et al attributed the emission of 4.0 eV energy to the Br⁻ center whereas the emission of 5.15 eV energy to the Br²⁻ center in NaCl crystal. Nakagawa et al have suggested that 4.0 eV luminescence can be enhanced linearly by increasing the Br⁻ ion concentration. Subramaniam [30] has also observed that the glow curve peak in KCl-KBr solid solution shift towards lower temperature on increasing the concentration of Br⁻ ion in the lattice. It was also suggested that the nature of variation of peak temperature with composition does not depend upon the method of growth of crystals. Moreover, the densities of dislocation were observed having no influence on the TL properties of these crystals.

It has been observed that the intensity of the low temperature peak was more as compared to that of high temperature in KCl crystals whereas in KBr crystals the situation was exactly reverse [30]. For mixed system the intensity of the low temperature peak decreases whereas high temperature peak increases as one move from KCl to KBr. The variation of relative intensity of two peaks with composition of the crystal was observed to have minima at intermediate composition and increases on both sides i.e. towards KBr as well as KCl end. It was suggested that the minima at about intermediate composition might be due to the following reasons -

i. Change in the configuration of traps due to the presence of bromide ion in the KCl lattice.
ii. Change in trap depth.

The calculation of activation energy corresponding to the peaks and their variation with composition of the crystal indicates to a situation where the configuration and depth of the traps also varied with composition and may have different value at about equimolar composition. The TL glow curve in NaCl-NaBr solid solution grown by Kyropoulos technique was studied by Bhimashankaram [29]. It was observed that in pure crystal two peaks remains present along with a shoulder at lower temperatures. As Br⁻ ion concentration in the lattice increases, initially the peaks become more and more sharp (74:26), and thereafter the high temperature peak grows at the expense of the lower temperature peak and finally after 50:50 composition only a single peak was observed even in case of pure NaBr crystal. An attempt has been made to explain these observations in the light of theory proposed by Mitchell [32] et al and Frohlich [38] et al. Their observations indicate that the centers responsible for high temperature peak in mixed crystals having NaBr are more stable compared to those present in NaCl crystal. The center responsible for lower temperature peak gets bleached with ease in mixed crystal. It has further been observed that a NaBr crystal is exceedingly difficult to color but on addition of NaCl to NaBr crystal a single prominent peak which is a characteristics of NaBr crystal, prominently observed. This fact points to a possibility that the addition of NaCl to NaBr makes F-center more stable. TL glow curve in undoped NaCl crystal and NaCl-NaBr mixed crystals having composition 60:40 show the presence of two prominent luminescence peaks, one at lower temperature whereas other at higher temperature. Three peaks are seen at equimolar composition and thereafter. This clearly shows that not only the addition of NaBr to NaCl lattice modifies the TL characteristics of the system but also the addition of NaCl into the NaBr lattice affects the TL characteristics in a prominent manner. On doping, surprisingly, in all the crystal whether it is pure or mixed, only a single peak was observed to be present that too at high temperature side. To explain the observed nature of glow curves a modification in the theory proposed by Mitchell [32] et al and Frohlich [38] et al is needed. The presence of single glow curve clearly indicates that only one type of environment remains present in the crystals of all the compositions.
The addition of bromide ion into the NaCl lattice simply has their influence in modifying the trap depth and thereby changing the activation energy needed for depopulating the available luminescence centers [35]. Only the vacancies present in the crystal as a result of thermo-dynamical requirement significantly contributes in deciding the luminescence characteristics of doped NaCl-NaBr mixed crystal. The effect of irradiation only seems to release free electrons and holes in the system and even if a small number of vacancies are created in the process, their number appears to be insignificant in comparison to those already present in the lattice as a result of thermo dynamical requirement. The effect of doping with divalent cation not only strains the lattice but also create equal number of vacancies to maintain the charge neutrality condition intact. Therefore a doped crystal is expected to have a higher concentration of luminescence centers than an undoped crystal. Therefore the intensity of luminescence emitted from that of a doped crystal would be more in comparison to that emitted from the corresponding to undoped crystals. Helperin [39] has measured the Tl intensity in NaCl, KCl, KBr etc irradiated by x-rays and get valuable information’s. Bonfiglioli [40] et al have suggested that all glow peaks in the glow curve are of same activation energy. Pre-heat treatment of synthetic quartz was observed to influence Tl glow curve pattern. Moreover, duration of thermal pre-treatment influences the glow curve pattern quite differently then temperature of annealing [41]. Mishra [42] has observed Tl in ZnS : Pr and ZnS ( Cu, Pr) phosphors and reported that the peak maxima shifted to higher temperature side at higher rate of heating. Kher [43] has observed the luminescence in divalent impurity activated LiF single crystal and reported that the Tl glow curve peaks around 380K, 425K and 500K are produced irrespective of the impurity added. No doubt the relative intensity of these glow peaks varies for different dopants. The results of present investigation indicate that the F-center generated due to the vacancies present in the system due to thermodynamical requirement give rise the peak at lower temperature side. Small shift in their position on doping can be attributed to the small perturbation around the location of F-centers caused by the presence of dopant ions. The peak observed at higher temperature side might correspond to the more stable centers. Their larger width further indicates that centers responsible for these peaks exist under the perturbing influence of dopant ions. The presence of an additional peak in between lower and higher temperature peak clearly reflect to a situation where different local environment may exist in a system which give rise varying stability to these centers.

The variation in Tl intensity on increasing the dopant concentration can be attributed to the nature of dopant ions. Moreover, from these results we can infer that the nature of dopant ions plays a vital role in modifying the luminescence properties of alkali halides. There are basically three factors such as vacancies already existed, vacancies generated on irradiation and the dopant ions which act as back ground impurities, are the controlling parameters of thermo luminescence in this alkali halide system.

Table 1
Showing Peak Position, Activation Energy and Tl Intensity in pure and Doped KCl Single Crystals

<table>
<thead>
<tr>
<th>S. NO.</th>
<th>SAMPLE</th>
<th>PEAK POSITION (ºC)</th>
<th>ACTIVATION ENERGY (eV)</th>
<th>INTENSITY (au)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>PURE KCl</td>
<td>120</td>
<td>1.13</td>
<td>0.27</td>
</tr>
<tr>
<td>2.</td>
<td>Ba” DOPED (0.1%)</td>
<td>120</td>
<td>1.13</td>
<td>0.30</td>
</tr>
<tr>
<td>3.</td>
<td>Ba” DOPED (0.5%)</td>
<td>100</td>
<td>1.07</td>
<td>0.16</td>
</tr>
<tr>
<td>4.</td>
<td>Ca” DOPED (0.1%)</td>
<td>130</td>
<td>1.16</td>
<td>0.34</td>
</tr>
<tr>
<td>5.</td>
<td>Ca” DOPED (0.5%)</td>
<td>130</td>
<td>1.16</td>
<td>0.25</td>
</tr>
<tr>
<td>6.</td>
<td>Mg” DOPED (0.1%)</td>
<td>110</td>
<td>1.10</td>
<td>0.20</td>
</tr>
<tr>
<td>7.</td>
<td>Mg” DOPED (0.5%)</td>
<td>190</td>
<td>1.26</td>
<td>0.26</td>
</tr>
</tbody>
</table>

REFERENCES