Thermoluminescence in single crystals of RbBr:OH⁻ and RbBr:Ca²⁺

S B S SASTRY and S SAPRU
Department of Physics, Indian Institute of Technology, Madras 600 036, India

Abstract. Optical absorption, thermoluminescence glow and emission spectra of RbBr:Ca²⁺ and RbBr:OH⁻ have been studied and analysed. It is observed that both Ca²⁺ and OH⁻ ions enhance the F-centre concentration. F_{Z1} band in RbBr:Ca²⁺ appears at 1·55 eV. TL glow peak corresponding to F_{Z1} centre on analysis gives a trap depth of 0·84 eV. OH⁻ ions in the crystal seem to act as TL 'killers'. Spectral distribution of emission under the glow peaks shows five bands around 1·5, 1·8, 2·1, 2·5 and 2·9 eV. Probable models of TL mechanism are suggested to explain the observed TL emission bands.

Keywords. Thermoluminescence; RbBr: OH⁻; RbBr: Ca²⁺; optical absorption; emission spectra.

1. Introduction

Alkali halides have been a subject of investigation for a long time now. Their thermoluminescence (TL) characteristics have however been studied more systematically only during the last decade. Most of the work reported on these halides is on crystals grown under ordinary conditions, when the possibility of OH⁻ ions entering the lattice cannot be ruled out. The OH⁻ ions are known to influence optical absorption (e.g., Hartel 1970; Rolfe 1958), specific heat (Peressini et al 1969), dielectric constant (Kanzig et al 1964) and thermal conductivity (Chau et al 1966) of the host crystal. The effect of OH⁻ impurity on the TL properties has however not been studied.

Cationic divalent impurities when doped in alkali halides give rise to enhanced F-centre concentration and also some new optical absorption bands, called F_Z bands, on suitable optical and thermal treatments. Attempts have been made to correlate some of the TL glow peaks to these F_Z centres (Kos and Nink 1977; Radhakrishna and Chowdari 1972). However the mechanism responsible for TL emission is not yet clear. A study on spectral distribution of emission, observed under a glow peak can perhaps lead to a better understanding about the recombination processes involved.

With this in view the TL emission and optical absorption spectra of RbBr:Ca²⁺ and RbBr:OH⁻ are studied and the results reported in this paper.

2. Experimental

Single crystals of RbBr:Ca²⁺ were grown by Bridgmann technique with about 500 ppm of Ca^{2+} in our laboratory. The material used for growing these crystals was suprapure RbBr. Analar grade CaO was treated with concentrated HBr and converted to $CaBr_2$ and doped in the host material. (Even if analar grade CaO contains impurities of the order of 500 ppm the content of such impurities will be of the order of 1 ppm or less in RbBr:Ca²⁺ crystals. These can be assumed not to affect the properties drastically). Single crystals of suprapure RbBr and RbBr:OH⁻ grown from melt in nitrogen atmosphere were kindly supplied by Prof. F W Felix of the Hahn-Meitner Institute, Berlin (West) and Dr. Rolfe of NRC, Canada. Before irradiation the samples were quenched from about 700 K to room temperature. Samples were irradiated by γ-rays from a ^{60}Co source (dose rate 0·34 MR/h). All the measurements were made after γ-irradiation of about one hour. The experimental set-up for recording TL glow and emission spectra was described earlier (Sastry and Sapru 1979). Optical absorption spectra were recorded on Cary-14R spectro photometer. TL parameters were determined by the total curve fitting method and emission spectra were analysed using a non-linear least square programme on the IBM 370/155 computer.

3. Results and discussion

3.1 *Thermoluminescence*

Figure 1 shows the TL glow curves of undoped (curve a) and calcium doped (curve b) RbBr recorded with a heating rate of 120 K/min. A glow peak at 413 K is observed in addition to a small glow around 500 K in the doped samples in contrast
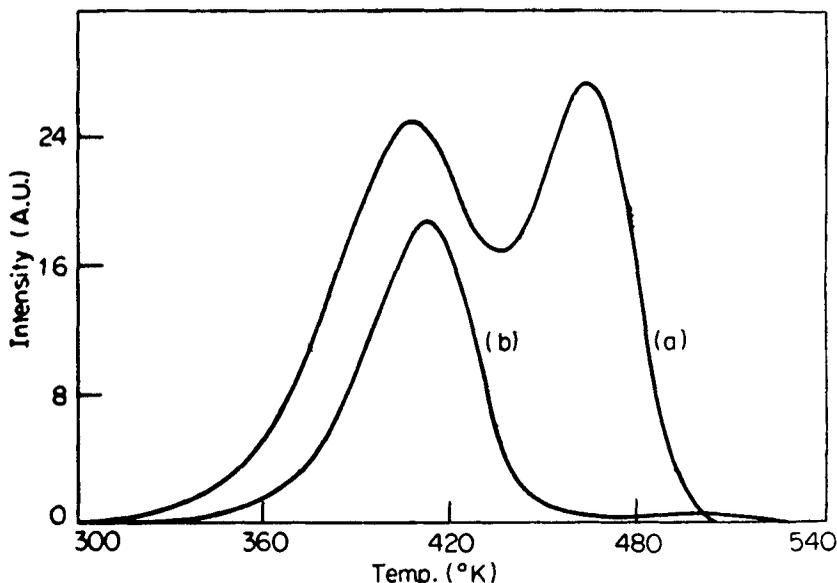

Figure 1. TL glow curves of γ-irradiated
(a) RbBr 'suprapure'. (b) RbBr:Ca²⁺ with a heating rate of 120 K/min.

to the two well-defined glow peaks at 405 and 465 K in the undoped samples. The integrated light output is also reduced in the doped samples, which contrasts with the observation in calcium doped RbCl crystals (Sastry and Sapru 1980a).

Figure 2 shows the effect of '*F*-light' bleaching on the TL glow curve of the doped sample and the inset shows the normalised line shapes of the glow peaks. Table 1 gives the relevant parameters. It is found that on *F*-light bleaching the 413 K peak falls in intensity whereas a new glow peak appears at 366 K. The intensity of 366 K glow peak increases during the initial stages of bleaching and falls off on prolonged bleaching. This behaviour suggests that, on *F*-light bleaching, electrons get redistributed in which centres responsible for 413 K glow peak get depleted and some new centres responsible for 366 K peak get filled. Since the behaviour of 413 K
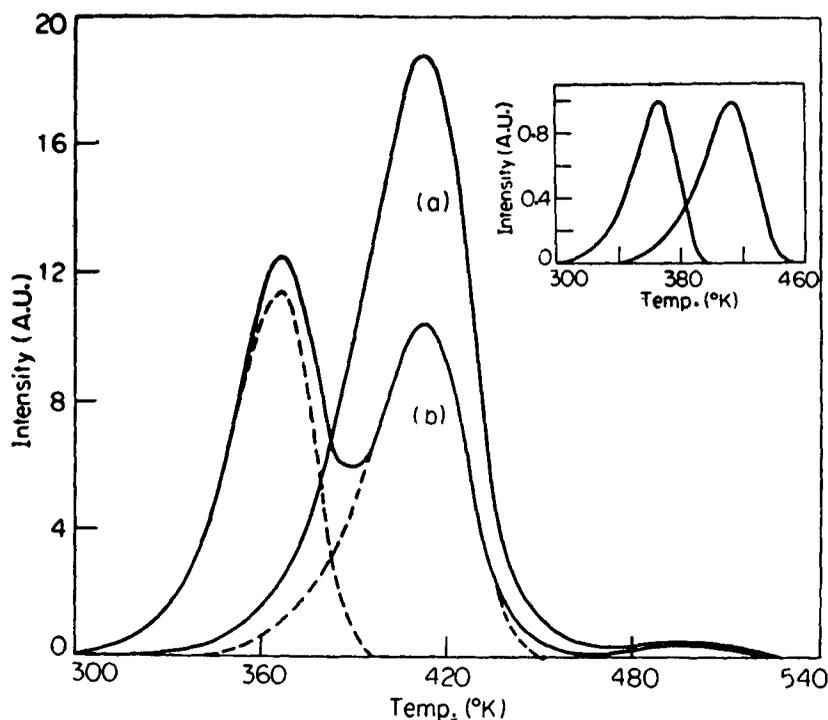

Figure 2. TL glow curves of RbBr:Ca²⁺ with a heating rate of 120 K/min. (a) After *γ*-irradiation. (b) *γ*-irradiated and subsequently *F*-light bleached for 2 min. The broken lines show the analysis of curve b and inset shows the normalized line shapes of the glow peaks.

Table 1. TL parameters of RbBr:Ca²⁺ recorded with a heating rate of 120 K/mt.

	Peak temperature K	Peak intensity A.U	Trap depth eV	Frequency factor $S(S^{-1})$	Order of kinetics
Before	413	18·85	0·86	$2·0 \times 10^9$	I
Bleaching	500⁺	0·50	—	—	—
After	366	11·40	0·84	$5·3 \times 10^{10}$	I
Bleaching	413	10·35	0·88	$6·5 \times 10^9$	I
	500⁺	0·40	—	—	—

⁺The parameters of 500 K glow peak could not be determined in view of its very low intensity.

glow peak under F-light bleaching is similar to the 465 K glow peak of the undoped sample (Sastry and Sapru 1979), this peak is attributed to the involvement of F-electrons.

3.2 *Optical absorption*

Figure 3 shows the optical absorption spectra of RbBr:Ca^{2+} after irradiation with respect to the unirradiated sample (curve a) and the effect of F-light bleaching (curve b). A broad absorption region is observed from 3·9 to 5·6 eV in addition to a sharp F-band at 1·78 eV. The V-centres reported in RbBr absorb around 4·35, 4·42 and 4·76 eV (V_4, V_2 and V_3 centres respectively). The broad absorbtion indicates that all the V-centres may be present even at room temperature though with different intensities (Winter *et al* 1969).

On F-light bleaching the F-band intensity falls and so does the intensity in the region of V-bands. There is an increase in the absorption on the low energy wing of F-band, indicating the appearence of a new band. Inset of figure 3 shows the analysis of the bleached F-band region, wherein a band is clearly seen at 1·55 eV. This absorption band is identified to be F_{Z1} band, since alkaline earth and rare earth impurities are known to give rise to F_{Z1} band on F-light bleaching of an irradiated sample at such temperatures. The position of F_{Z1} band does not vary much with different impurities but depends on the host crystal. F_{Z1} band reported in RbBr doped with Sr^{2+} is located at 1·635 eV (Kenntner and Paus 1971).

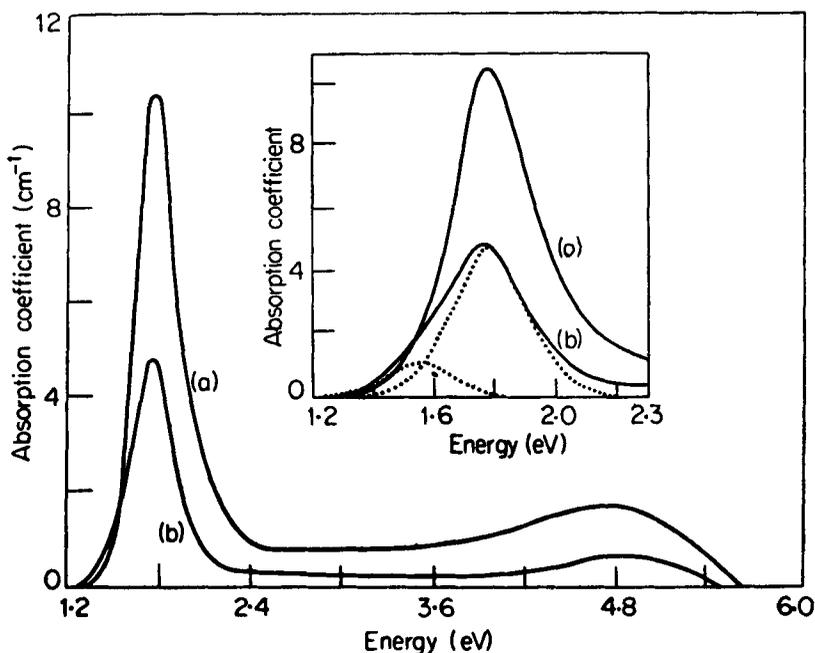If the optical absorption spectrum is recorded after thermally cleaning the 366 K

Figure 3. Optical absorption spectra of RbBr:Ca^{2+} with respect to the uncoloured sample. (a) γ-irradiated. (b) Bleached with F-light for 2 min. Inset shows the resolution of curve 'b'.

glow peak, the absorption on the low energy wing of F-band does not appear. Thus the 366 K glow peak can be related to F_{Z1} centres.

The optical absorption spectra of undoped and doped samples are compared in figure 4. In the doped samples the intensity of F-band is higher as is expected due to the presence of charge compensating cationic vacancies (Ikeya *et al* 1966). There is an increase in the absorption region of V-bands. Ca^{2+} doping enhances the F-centres concentration and gives rise, at times, to Hayes-Nichols bands in the UV region (Hayes and Nichols 1960). An IR absorption spectrum taken on these samples showed a band though weak) around 3450 cm⁻¹, characteristic of OH⁻ ions. This indicates that part of the increase in absorption in the UV region may be due to OH⁻ ions as known from the work of Rolfe (1958) in some of the alkali halide crystals and more recently from the studies of Guckelsberger and Zelsmann (1979). Hayes-Nichols bands, which are normally observed below room temperature may not be contributing to the increased absorption in the UV region observed in this case. Thus there is enough evidence to show the presence of OH⁻ ions in these crystals. It is not, however, possible to separate the contribution of V-bands and OH⁻ bands because of the overlap of the very intense fundamental absorption of the crystal.

On first thought one fails to understand the cause of the suppressed TL intensity despite the enhanced F-centre concentration. However, OH⁻ is suspected to be responsible for such an effect. In order to confirm this view KOH was deliberately doped in the crystal. Inset of figure 4 shows the F-bands of undoped, Ca^{2+} doped and OH⁻ doped RbBr. Obviously, samples of RbBr:OH⁻ show higher F-centre concentration. Since KOH was mixed with RbBr material to dope OH⁻ ions one expects the F-centre enhancement to be due to OH⁻ ions and/or the involve-
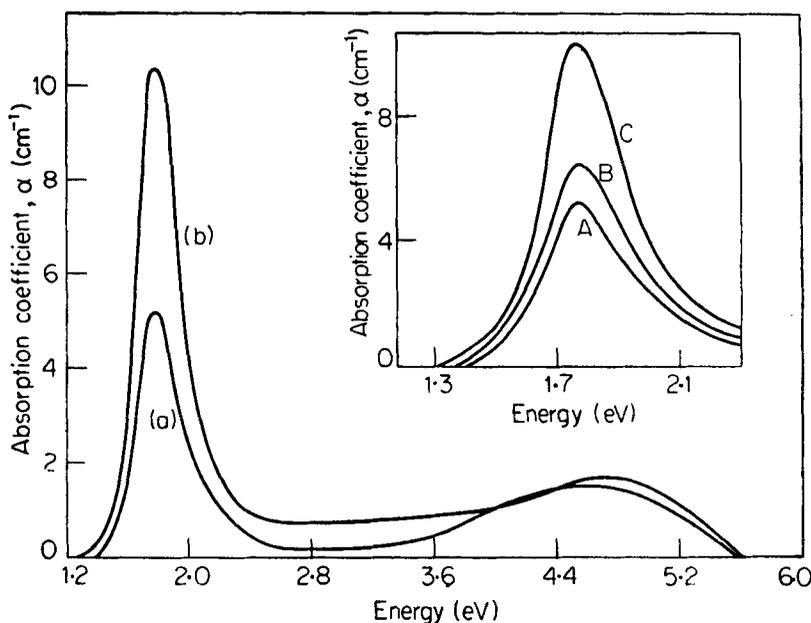

Figure 4. Optical absorption spectra after γ-irradiation. (a) RbBr—'suprapure' sample with respect to uncoloured sample. (b) RbBr:Ca^{2+} with respect to uncoloured sample. Inset shows the F-band intensities of (a) Undoped RbBr (b) RbBr:OH⁻ (c) RbBr:Ca^{2+}.

ment of K⁺ ions. If K⁺ ions are involved then $F_A(K)$ centres should be formed in the lattice. F_A centres in turn enhance the F-excited states (Lüty 1968). No F_A-centres or enhancement of F-excited states were observed in these samples. Even the undoped suprapure RbBr crystals did not show the presence of F_A-centres (Sastry and Sapru 1979). This is in contrast to the observation on suprapure RbCl crystals where F_A-centres were observed both by TL and optical absorption techniques (Sastry and Sapru 1980d). Such a behaviour is expected because of the instability of F and other electron excess centres at and above room temperature which increases as one passes on from alkali flourides to iodides (Pooley 1966). In view of the absence of any evidence of the involvement of K⁺ ions the enhancement of F-centre concentration is attributed to the presence of OH⁻ ions in these samples.

These KOH doped samples did not show any TL even after much higher irradiation doses. Similar results were observed in RbCl doped with KOH (Sastry and Sapru 1980b). This clearly indicates that OH⁻ acts as a TL poison. Normally most of the samples grown under ordinary conditions do contain some traces of OH⁻ and as such one can say that TL results in such cases do not reveal the complete picture.

3.3 *Thermoluminescence emission*

Figure 5 shows the TL emission spectra of RbBr : Ca²⁺. On analysis we observe emission bands around 1.5, 1.8, 2.1, 2.5 and 2.9 eV. Four of these bands (1.5, 2.1, 2.5 and 2.9 eV) are very close to those found in the undoped samples and thus have to be due to the host crystal (Sastry and Sapru 1979). In addition to these emission bands, a weak band is observed around 1.8 eV in the calcium-doped sam-
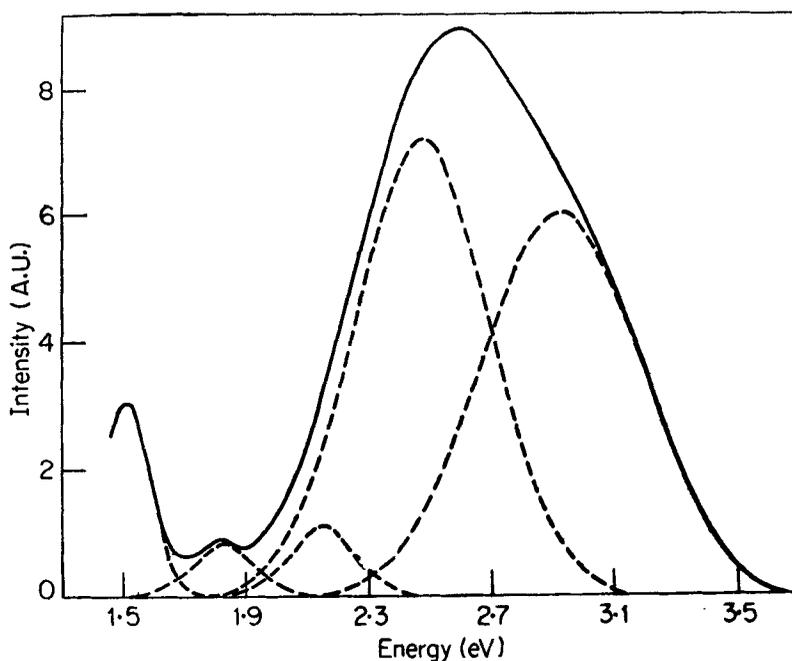

Figure 5. TL emission spectra of RbBr:Ca²⁺. The broken lines show the analysis.

ples. A similar band was observed in $RbCl : Ca^{2+}$ and was suggested to be due to the involvement of calcium (Sastry and Sapru 1980a). The present studies also indicate that 1·8 eV band may be due to the calcium involvement. This emission is observed under all the glow peaks suggesting that calcium ion may be acting as a recombination centre, in which case the process may be that an electron released during heating recombines with a calcium ion. If this is the case then Ca^{2+} should have become Ca^{3+} on irradiation. This conversion requires about 50 eV energy. Much higher energies are however available in the ionizing radiations; thus the conversion can be envisaged. Some cases where ions like Sn^{2+} and Pb^{2+} do convert to higher valence states requiring about 40 and 32 eV energy respectively have been reported (Murin and Seregin 1970; Schoemaker and Kolopus 1970).

From our work on $RbCl : Eu^{2+}$ and $RbBr : Eu^{2+}$ systems we observed that Eu^{2+} converts to Eu^{3+} and into Eu^{4+} ions as well on irradiation (Sastry and Sapru 1980c).

The ionic radii of Ca^{2+} and Eu^{2+} are close to each other (1·09 and 1·03Å respectively), offering perhaps a similar cross-section for the ionizing radiations. In the absence of any direct evidence (since calcium ions do not have any characteristic absorption bands), one can only tentatively suggest the conversion of Ca^{2+} to Ca^{3+} on irradiation and Ca^{3+} acting as a recombination centre during a TL run.

The comparison between Ca^{2+} and Eu^{2+} ions from the results of our earlier work on similar systems ($RbCl : Eu^{2+}$ and $RbBr : Eu^{2+}$) cannot be really stretched too far as these ions belong to different categories. However, their presence in alkali halide crystals is known to lead to the formation of similar centres like F_z-centres (Radhakrishna and Chowdari 1972), indicating a comparable behaviour.

Alternatively, one can think of Ca^{2+} converting to Ca^+ on irradiation and regaining a hole on heating thereby emitting 1·8 eV energy. If such be the case then one should say that electrons and holes become mobile simultaneously during a TL run.

A tentative band model is proposed (figure 6) to indicate the TL processes in this system as in the case of other ionic crystals proposed earlier (Hagaseth 1972; Sastry and Sapru 1980a).

4. Conclusions

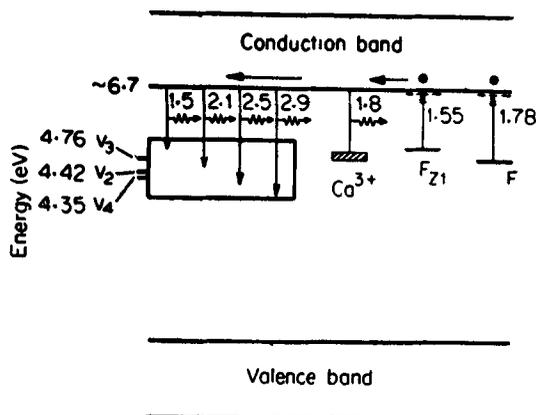From these results we are led to the conclusion that if intrinsic TL properties of

Figure 6. Tentative energy level diagram for TL processes in RbBr:Ca²⁺.

RbBr crystals are to be studied they must be grown under careful conditions especially to avoid OH⁻ radicals entering the crystal. Although the presence of OH^- enhances electron excess centres like F-centres it reduces or even 'kills' the TL glow depending on its concentration. Ca^{2+} enhances the F-centre concentration and also changes the TL glow and emission patterns. Calcium involves itself perhaps as a recombination centre in this system emitting around 1·8 eV.

Acknowledgements

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