



RESEARCH ARTICLE

OPTICAL CHARACTERIZATIONS OF TI⁺ IONS IN RbBr_{0.95} Cl_{0.05} MIXED CRYSTALS

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ABSTRACT

In the present paper optical absorption characterizations of RbBr_{0.95} Cl_{0.05} mixed crystals doped with TI⁺ (0.02mol %) were grown under vacuum by slow cooling from its melt. The changes in the absorption spectra of mixed crystals are due to some complex TI⁺ centers. Photostimulated Luminescence observed in gamma rays irradiated crystals resembled their respective PL emissions indicating that PSL in them is due to TI⁺ ions.

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INTRODUCTION

Alkali halide single crystals doped with heavy metal ions having ns² outer electronic configuration are well known to exhibit characteristic absorption bands, namely, A, B, C and D bands. These bands are suggested to be due to the transitions from ¹S₀ (¹A_{1g}) ground state to ³P₁ (3T_{1u}), ³P₂ (3E_u or 3T_{2u}) and ¹P₂ (3T_{1u}) states respectively (Fukuda, 1964). Single crystals of alkali halides doped with small concentrations of thallium are known to exhibit excellent luminescent properties (Edgerton *et al.*, 1963; Delbec, 1966; Ranfagni, 1983). Some of the Thallium doped alkali halides exhibit excellent scintillation properties and are therefore used in the field of high energy radiation detection. Thallium doped sodium iodide and cesium iodide are well known for these applications (Moharil, 1994). Imaging Plates for X-ray radiography based on RbBr:TI, CsBr:Eu phosphors are now commercially available (Amitani *et al.*, 1986; Weidner *et al.*, 2007). Thallium doped mixed alkali halides are not studied extensively owing to many of their eutectic properties (Inaba, *et al.*, 1996; Sangster *et al.*, 1987). Recently some worker have reported that alkali halide mixed crystals doped with thallium as well as co-doped etc could be potential competitors to the conventional alkaline earth halide phosphors, BaFBr:Eu, which are used as X-ray storage phosphors (Eswaran *et al.*, 2009; 2010; 2011; Nagarajan *et al.*, 2008; 2009). In the present paper, optical absorption and Photostimulated Luminescence studies on RbBr_{0.95} Cl_{0.05}: TI⁺ (0.02mol %) mixed crystals are reported.

MATERIALS AND METHODS

RbBr_{0.95} Cl_{0.05}: TI⁺ (0.02mol %) mixed crystals (with x = 0.00, 0.05) were grown under vacuum by slow cooling from their melt. Analar Reagent Grade KBr and KI and the dopant TII (99.999%) taken in the required stoichiometric. The method of growth is briefly described in an earlier work (Eswaran, *et al.*, 2009). The solutions were dried in an oven operated at 100^oC and grounded into fine powder using. Optical absorption (OA) was carried out UV-Visible SHIMADZU 3101PC spectrophotometer at room temperature (RT). The Photoluminescence (PL) and Photo stimulated Luminescence (PSL) measurements were carried out using a JOBIN YVON – Spex Spectro- fluorometer.

RESULTS AND DISCUSSION

Optical absorption spectra of RbBr:TI (0.02mol%) can be reproduced for sake of comparison (communicated) shows a band around 4.74eV which is rather flat at its peak (Figure 1. curve a). In addition to this, a broad band around 5.6 and 5.95eV on the rising portion of the absorption on the high energy side is observed. From earlier reports, the absorption bands around 4.74eV and 5.6eV are identified as A and B bands respectively (Sharan, 1983)]. Ghosh has reported that C-band of TI⁺ ions in RbBr:TI⁺ appeared at 5.95eV (Ghosh, 1964). In the present work, C-band absorption is not well resolved. The broad absorption around 5.95eV (present study) may be related to the C-band absorption. In alkali halides heavily doped with TI⁺ ions, aggregate centers of TI⁺ ions such as TI⁺ dimers have been reported to be formed (Tajju Tsuboi, *et al.*, 1991). Two types of dimer centers have been reported in

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Tl⁺ doped crystals; In D_{4h} dimers, two Tl⁺ ions located along <100> direction are separated by an anion and in D_{2h} dimers, two Tl⁺ ions occupy nearest neighbor positions along <110> direction. At low temperatures, weak absorption bands due to Tl⁺ dimers appear on the tail regions of A, B and C band absorptions. However, at RT, the A-band absorption of Tl⁺ dimers are seen only as an inhomogeneous broadening of A-band towards low energy side (Halperin *et al.*, 1978). Considering the above earlier results, the broadening of the absorption bands towards low energy side of A, B and C bands with increasing TlBr content in RbBr:TlBr single crystals may be attributed to the formation of such aggregates of Tl⁺ ions. In the case of RbBr_{0.95}Cl_{0.05}:Tl⁺ (0.02mol %) mixed crystals, shows A-band around 4.8eV (Figure.1. curve b). In addition to this, two overlapping bands around 5.8eV and 6.0eV are observed on the B and C bands region. The shift of the A-band absorption in RbBr_{0.95}Cl_{0.05}:Tl⁺ towards high energy side relative to the RbBr:TlBr single crystals is an indication it is likely that complex Tl⁺ centers with Br⁻ and Cl⁻ ions in the mixed configuration as the nearest neighbor to Tl⁺ ions formed modify the A-band as well as the B and C bands absorption (Kleemann *et al.*, 1966). The valley of absorption bands between 5.0 to 5.5eV broadened/ shifted slightly towards the high energy side. This may be attributed to some additional amount of Chlorine ions incorporated into the mixed crystals. The shifting of absorption bands on the higher energy side with increasing chlorine composition is, perhaps, due to the appearance of new absorption bands. From these reports it is clear that even the addition of a small amount of chlorine has a profound effect on the absorption spectra of heavy metal ions in alkali halide crystals also cannot be ruled out dimer centers (Kleemann *et al.*, 1966). PL emission in RbBr_{0.95}Cl_{0.05}:Tl⁺ (0.02mol %) mixed crystals, excited in various absorption bands shows a long tail single asymmetric emission band at 3.34eV with different relative intensities shown in Figure 2.

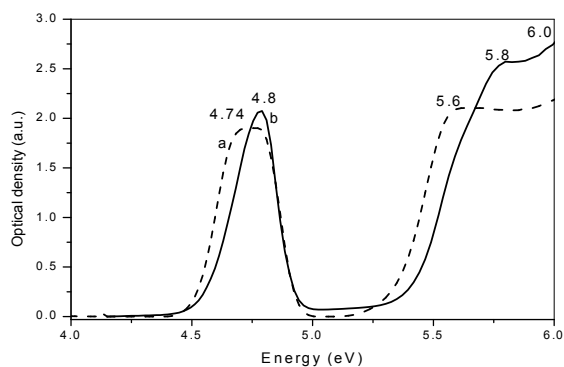


Fig. 1. Optical absorption spectra of RbBr_{0.95}Cl_{0.05}:Tl⁺ (0.02mol %) grown in vacuum mixed crystal

However, the emission spectra of mixed crystal appeared to be slightly wider of than the emission bands of RbBr:TlBr single crystals (Figure not shown). PL emission of RbBr:Tl⁺ excited in the A-band is reported to produce two emission bands at 330 and 390nm (3.76 and 3.18eV) respectively (Von Seggern, *et al.*, 1989). At RT, the 330nm band appeared only as a weak shoulder to the 390nm emission band. (Sharan, *et al.*, 1983) observed a single asymmetric emission band in RbBr:TlBr powder phosphors which was resolved into two gaussian components peaking at 317nm (3.9eV) and 365nm (3.4eV).

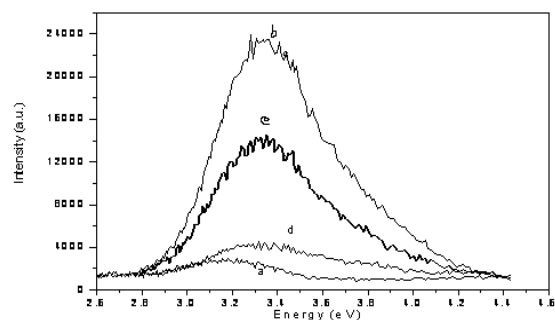


Fig. 2. PL Emission spectrum of RbBr_{0.95}Cl_{0.05}:Tl⁺ (0.02mol %) mixed crystal excited at (a) 244, (b) 258, (c) 270 and (d) 280nm

The absorption and emission bands of Tl⁺ ions in alkali halides are ascribed to be due to transitions between the ground ¹S₀ and excited ³P₁ states of the Tl⁺ ion. The appearance of two emission bands (designated as A_T and A_X emission in the order of decreasing energy) upon A-band excitation and the temperature dependence of their intensity have been explained by Jahn-Teller splitting of the ³P₁ excited state of the s² ions (Ranfagni, *et al.*, 1983). In the present study, A_T and A_X emission bands are not resolved in the PL emission spectra of RbBr:Tl⁺ (0.02mol %) mixed crystals (Figure not shown). However, the asymmetric emission band around 3.34eV has a long tail on the high energy side. In heavily doped RbBr:Tl⁺ powder phosphors, Sharan reported the appearance of additional emission bands in the visible region at 440 and 530nm (around 2.82 and 2.34eV respectively) with corresponding excitation bands at 267 (4.64eV) and 278nm (4.46eV) in their excitation spectra respectively. These additional emission and excitation bands were attributed to the Tl⁺ dimers in heavily doped RbBr:Tl⁺ (Sharan *et al.*, 1983). However, in the present study, these additional visible emissions attributed to Tl⁺ dimers are not observed. This behavior is similar to that observed in Tl⁺ doped single crystals like KBr:Tl⁺ etc where the visible dimer emission together with monomer-like emission is observed only at low temperatures and on increasing the temperature towards RT the dimer emission is drastically suppressed (Taiju Tsubo *et al.*, 1991). Thus, comparing with the earlier reports, the absorption bands in the 4.5-4.7eV region observed in the present study could be tentatively attributed to some Tl⁺ aggregate centers. Excitation in these bands at RT results in monomer like emission only (Taiju Tsubo *et al.*, 1991).

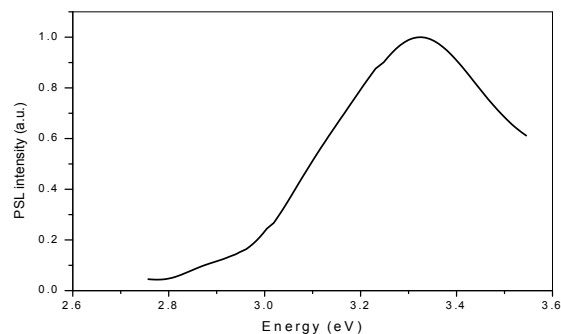


Fig. 3. PSL Emission spectrum of RbBr_{0.95}Cl_{0.05}:Tl⁺ (0.02mol %) mixed crystal grown in vacuum

In the present study, the observation of the broad emission band around 3.34eV in the RbBr_{0.95}Cl_{0.05}:Tl⁺ mixed crystals

for excitation in different absorption bands may also be an indication that, the emission processes take place on different centers (complex centers) and they are separated by some intermediate processes (such as energy relaxation and transfer) leading to the same emission spectra (Eswaran *et al.*, 2010). The PSL emission spectrum of X-irradiated $\text{RbBr}_{0.95}\text{Cl}_{0.05}:\text{Tl}^+$ mixed crystal stimulated at 690 nm shows PSL emission around 3.34eV (Fig.3.). This PSL emission spectrum is more or less similar to the PL emission spectrum of $\text{RbBr}_{0.95}\text{Cl}_{0.05}:\text{Tl}^+$. Von Seggern *et al.*, 1989, studied the PSL emission and stimulation spectra of $\text{RbBr}:\text{Tl}$ at 206 K and at RT. Stimulation spectrum was observed at 695 nm. This wavelength agrees well with the published data for F-absorption band maximum of RbBr . Due to quantitative agreement between the stimulation spectrum and the F-centre absorption band the nature of the electron trap was attributed to the F- centres in $\text{RbBr}:\text{Tl}$.

From the above results it may be suggested that during X-irradiation, Tl^+ ions trap holes becoming Tl^{2+} ions while the corresponding electrons are trapped at anion vacancies forming F- centres. Trapping of some holes by Tl^+ dimers or Tl^+ ion complexes may also happen. During PSL, stimulation at F-band may result in the release of F-centre electrons into the conduction band, which are mobile. When these mobile electrons recombine with Tl^{2+} ions, they are converted into Tl^+ ions in the excited state ($^3\text{P}_1$). When they relax to the ground state ($^1\text{S}_0$) they emit the characteristic Tl^+ emission. Recombination of electrons with hole trapped Tl^+ aggregates may also result in monomer like emission as observed in PL. A similar mechanism was proposed by Von Seggern *et al.*, in $\text{RbBr}:\text{Tl}^+$. However they observed in a later study that the temperature dependence of PSL was solely determined by lifetime of Tl^+ ions in the range 50-500 K and that there was no decrease in PSL below 80K where release of electrons into conduction band becomes less probable (Von Seggern *et al.*, 1989). This observation prompted them to propose a tunneling mechanism. The plot of PSL emission intensity (370nm emission) of $\text{RbBr}_{0.95}\text{Cl}_{0.05}:\text{Tl}$ (0.02mol%) mixed crystals against radiation dose is shown in Figure.4.

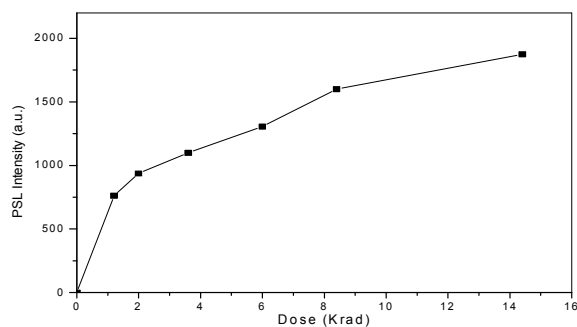


Fig. 4. PSL emission intensity of $\text{RbBr}_{0.95}\text{Cl}_{0.05}:\text{Tl}^+$ (0.02mol %) mixed crystal as function of irradiation dose

The intensity of PSL emission of gamma irradiated mixed crystal increase with increasing gamma ray dose in two stages.

Conclusion

Optical absorption spectra of $\text{RbBr}_{0.95x}\text{Cl}_{0.05}:\text{Tl}$ mixed crystals slightly shifted towards higher energy side due to influence of Cl^- ions. It may be the formation of some complex centers,

though in small numbers, cannot be ruled out. PSL emission spectra of gamma irradiated $\text{RbBr}_{0.95}\text{Cl}_{0.05}:\text{Tl}$ mixed crystals under F-band stimulation show PSL emission band around 3.34eV. The PSL emission bands are comparable to the PL emission bands observed in them. Comparing the results with earlier reports, a mechanism for PSL emission is suggested.

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