



PHYSICS

LUMINESCENCE STUDIES ON THALLIUM DOPED RbBr-RbI MIXED CRYSTALS

P. Eswaran^{1*}, S. Nagarajan² and R. Ravisankar³

¹Department of Physics, Vel Tech (Owned by RS Trust), Avadi, Chennai 600062, Tamilnadu, India.

²Department of Physics, Pondicherry Engineering College, Puducherry 605014, India.

³Post Graduate and Research Department of Physics, Government Arts College, Tiruvanmalai-606603, Tamilnadu, India

Abstract

Photoluminescence (PL) studies of RbBr_{1-x}I_x: Tl⁺ (0.1mol %) with x = 0.00, 0.05 and 0.10 mixed crystals grown in vacuum is reported at room temperature. PL emission spectra of the mixed crystals excited in the A-absorption band of RbBr:Tl⁺ exhibited an asymmetric emission band with peak 3.34eV, which is the characteristic emission bands of Tl⁺ ions in RbBr: Tl⁺. When excited in the low energy tail of A-band absorption, additional emission bands were observed. The photoluminescence emission bands slightly shifted towards the low energy side with increasing iodine composition x.

Keywords: Photoluminescence, complex centers, RbBr-RbI mixed crystals, A-band, ns² ions and Tl⁺ ions

Introduction

The optical properties of alkali halide crystals doped with heavy metal ions which have the ns² electronic configuration in their ground state have been studied extensively [1-3]. The impurities, substitutionally replacing cations in the lattice, induce changes in the absorption and emission spectra of the host crystals. The new absorption bands caused by ns² ions are named as A, B, C and D in order of increasing photon energy. Luminescence is observed under optical excitation in the spectral regions corresponding to the A, B, C and D absorptions. The most studied emission is that excited in the A band, consisting of one, two or even three bands depending on host crystal and temperature [4, 5]. Thallium absorption and emission mechanisms have been investigated extensively in the last few decades [1].

However, in mixed alkali halides KBr-KI doped with Tl⁺ additional absorption bands appear on the low energy side of A, B, C bands due to formation of complex Tl⁺ centres in the mixed surrounding of anions [6,7]. Kleemann and Fischer studied the optical absorption and luminescence of KBr_{1-x}I_x:Tl⁺ mixed crystals at low temperature (20K and 78K) [3]. They reported absorption bands at 4.8, 4.66, 4.55 and 4.44eV in the A-band regions. These bands were attributed to the formation of complex Tl⁺ centers of the form TlBr_{6-n}I_n. The 4.8eV band designated as A₀ band in the mixed crystals was found to have optical and luminescence characteristics similar to that of the A-band in KBr:Tl⁺ single crystals. This band was attributed to the TlBr₆ centers (i.e. a Tl⁺ ion surrounded by six Br ions as nearest neighbors) in the mixed crystals. The other additional A-absorption at 4.66,

4.55 and 4.44eV (designated as A₁, A₂ and A₃ bands respectively) which grew with x at the cost of A₀-band have been attributed to the complex TlBr_{6-n}I_n centers with n = 1, 2 and 3 respectively. Even at low temperatures (20K and 78K) these additional bands are not well resolved. The large ionic radius (1.47Å) of rubidium ions permits incorporation of a large number of cationic impurities. Optical absorption, Photoluminescence and Photo stimulated luminescence studies have been reported on RbBr doped with Tl⁺ ions. The attractive PSL characteristics of medical x-ray storage (PSL) phosphor RbBr:Tl⁺ have already been commercialized [8]. RbBr:Tl⁺ has gained renewed interest since it serves as a potential competitor to the conventionally utilized alkali earth halides BaFBr:Eu²⁺ [9,10]. But no work could be traced to Tl⁺-doped with RbBr-RbI mixed crystals, except that of the authors' work on RbBr-RbI:Tl⁺ mixed crystals. However, luminescence studies on Tl⁺ doped mixed alkali halides are still meager. In the present work, thallium doped RbBr- RbI mixed crystals with x = 0.0, 0.05 and 0.10 have been chosen for studying their luminescence behaviors are discussed for first time.

Experimental

The systems studied in the present work are (1) RbBr: TlBr (0.02 and 0.1mol %) and 2) RbBr_{1-x}I_x:Tl (0.1mol%) mixed crystals grown in vacuum with x = 0.00, 0.05 and 0.10 by slow cooling from its melt. Analytical Reagent grade RbBr and RbI (99.9%) and the dopant in the form of TlBr and TlI (99.99%) taken in the required stoichiometric proportions described in our

* Corresponding Author, Email: eswaran74@gmail.com

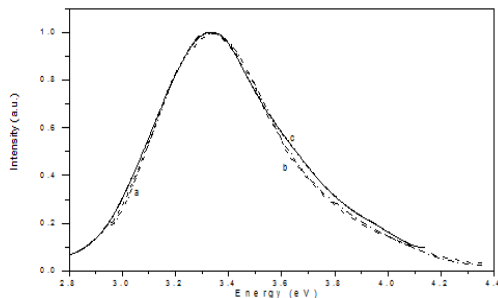
earlier work [11]. The Photoluminescence (PL) measurements were carried out using a JOBIN YVON – Spex Spectro- fluorometer (FL3-11 Modell spectrofluorometer).

Results and discussions

PL emission in RbBr:TlBr (0.02 and 0.10mol%) excited in various absorption bands shows a single asymmetric emission band at 3.34eV with different relative intensities.

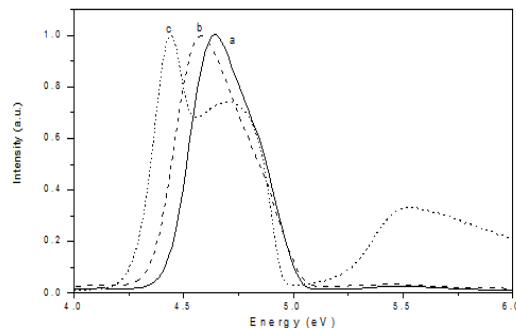
In Figure.1, the PL emission spectra of RbBr:TlBr (0.02 and 0.10mol%) and RbBr:TlI (0.1mol%) for $\lambda_{ex} = 260\text{nm}$ are compared. Each spectrum in Figure.1 is normalized to unity at its maximum. These spectra show a single emission band with spectral peak position at 3.34eV. However, the emission of RbBr:TlI single crystal (curve c) appeared to be slightly wider than the emission bands of RbBr:TlBr single crystals.

Figure.1. PL emission spectra of (a) RbBr: TlBr (0.02mol %), (b) RbBr: TlBr (0.10mol %) and (c) RbBr: TlI (0.1mol %) for 260nm excitation. Each spectrum is normalized to unity at its maximum



The PL excitation spectra for the 3.34eV emission in RbBr:TlBr (0.02 and 0.10 mol%) and RbBr:TlI (0.10mol%) are shown in Fig.2. RbBr:TlBr (0.02mol%) single crystals shows a band at 4.6eV with a shoulder around 4.8eV (curve a). In RbBr:TlBr (0.10mol%) single crystals, the 4.6eV excitation band appears to have slightly shifted to 4.56eV (Figure.2, curve b). Comparing with earlier reports, the 4.8eV shoulder is related to the A-band of monomer Tl^+ ions while the band around 4.6eV is attributed to aggregates of Tl^+ ions [12]. However, excitation in the 4.6eV band does not produce any additional emission band. Excitation spectrum for 3.34eV emission in RbBr:TlI (0.1mol%) shows a broad band around 265nm (4.67eV) and a sharp band around 279nm (4.44eV) (Figure.2, curve c). In all these cases weak overlapping excitation bands in the region between 200-250nm are observed. They show a peak around 225nm (5.5eV) which corresponds to the B-band of Tl^+ ions in RbBr [8, 13]. The overlapping band on the short wavelength side (around 5.90eV) is not resolved, which may be attributed to C-band of Tl^+ ions [12].

Figure.2. PL excitation spectrum of (a) RbBr:TlBr (0.02mol%), (b) RbBr:TlBr (0.1mol%) and (c) RbBr:TlI (0.1mol%) grown in vacuum for emission at 3.34eV. Each spectrum is normalized to unity at its maximum



The observation of new excitation band around 4.44eV in RbBr:TlI may be attributed to the complex thallium centers involving both Br- and I- ions. Exciting the RbBr:TlI (0.10mol%) crystals by radiation of wavelength around 280nm (4.43eV) produces an emission band which is slightly broadened towards the high energy side (Figure. not shown).

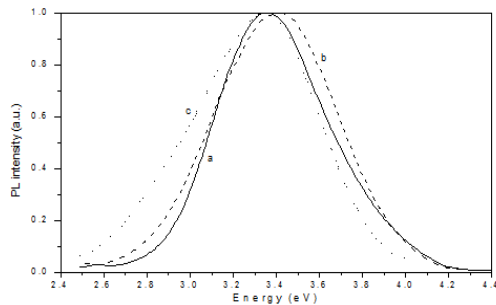
PL emission of RbBr: Tl^+ excited in the A-band is reported to produce two emission bands at 330 and 390nm (3.76 and 3.18eV) respectively [8]. At RT, the 330nm band appeared only as a weak shoulder to the 390nm emission band. Sharan has observed a single asymmetric emission band in RbBr:TlBr powder phosphors which was resolved into two gaussian components peaking at 317nm (3.9eV) and 365nm (3.4eV) [12]. The absorption and emission bands of Tl^+ ions in alkali halides are ascribed to be due to transitions between the ground $^1\text{S}_0$ and excited $^3\text{P}_1$ 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 $^3\text{P}_1$ excited state of the s^2 ions [2]. In the present study, A_T and A_X emission bands are not resolved in the PL emission spectra of RbBr:TlBr and RbBr:TlI crystals. 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^+ [12]. 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 [13]. Thus, comparing with the earlier reports, the excitation bands in the 4.5-4.6eV 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 [14]. The observation of the same emission band around 3.34eV in the $RbBr:TlBr$ crystals as well as in the $RbBr_{1-x}I_x:TlI$ mixed crystals (present study) for excitation in different absorption bands may also be an indication that, the excitation and emission processes take place on different centers and they are separated by some intermediate processes (such as energy relaxation and transfer) leading to the same emission spectra [15].

PL emission spectra of $RbBr_{0.95}I_{0.05}:TlI$ (0.1mol %), mixed crystals is excited at 260nm shows, an emission band at 3.35eV is observed while the excitation of the crystal by 270nm radiation results in an emission at 3.4eV (Figure.3).

Figure.3. PL emission spectra of $RbBr_{0.95}I_{0.05}:TlI$ (0.1mol %) grown in vacuum for different excitation wavelengths 260nm a), 270nm b) and 280nm c). Each spectrum is normalized to unity at its maximum



PL emission spectra of these crystals for $\lambda_{ex} = 290, 280$ and $240nm$ show an emission band around 3.35eV with an additional shoulder around 2.9eV. The slight shifting of the emission band for $\lambda_{ex} = 270nm$ may be due to the appearance of some additional emission bands due to some unidentified complex Tl^+ centers.

In $RbBr_{0.9}I_{0.10}:TlI$ mixed crystals; similar emission bands are observed (Figure.4). However, the peak position and half width of emission bands change slightly with the wavelength of excitation in the A-band. When excited around 4.4eV (280-290nm), these mixed crystals show the presence of a broad shoulder around 2.9eV on the low energy side of the emission as in the case of $RbBr_{0.95}I_{0.05}:TlI$ mixed crystals.

Figure.4. PL emission spectra of $RbBr_{0.9}I_{0.10}:TlI$ (0.1mol%) grown in vacuum for different excitation wavelengths 260nm a), 280nm b) and 290nm c). Each spectrum is normalized to unity at its maximum

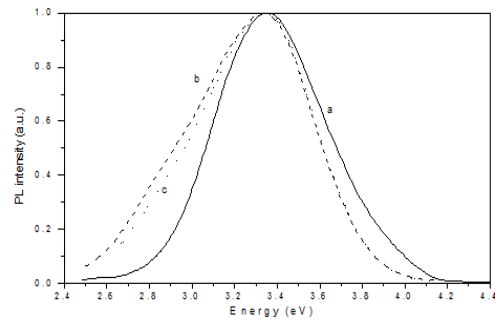
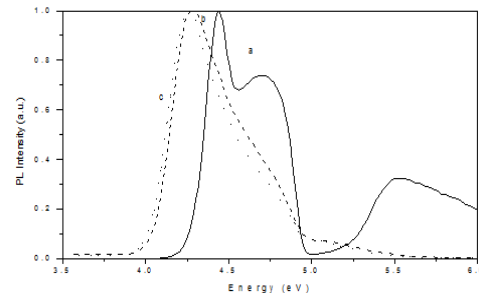


Figure.5. shows the PL excitation spectra of $RbBr_{1-x}I_x:TlI$ (0.1mol%) mixed crystals for the 3.35eV emission. The PL excitation spectrum of $RbBr:TlI$ (0.1mol%) for this emission shown in Figure.2, curve c is reproduced as curve a in Figure.5 for the purpose of comparison.

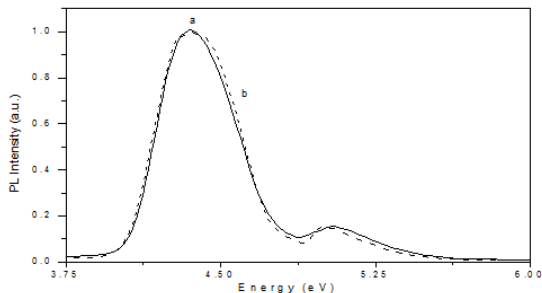
Figure.5. PL excitation spectra of $RbBr_{1-x}I_x:TlI$ (0.1mol%) mixed crystals grown in vacuum for emission wavelengths 370nm a) $x = 0.00$, b) $x = 0.05$ and c) $x = 0.10$. Each spectrum is normalized to unity at its maximum



The excitation spectrum for the 370nm (around 3.35eV) emission in $RbBr_{0.95}I_{0.05}:TlI$ (0.1mol %) mixed crystals shows a sharp band at 4.27eV with a shoulder around 4.8eV and a weak band around 5.2eV (Figure.5. curve b). The structure of PL excitation spectrum for the A-band emission in the case of $RbBr_{0.9}I_{0.10}:TlI$ (0.1mol %) mixed crystals is found to be similar to that of $RbBr_{0.95}I_{0.05}:TlI$ (0.1mol %) mixed crystals. However, the sharp peak at 4.27eV is slightly shifted towards low energy side (4.26eV) (Figure.5. curve c).

Excitation spectra for the 2.9eV emission ($\lambda_{em} = 430nm$) in both $RbBr_{1-x}I_x:TlI$ mixed crystals with $x = 0.05$ and 0.10 (Figure.6, curves a and b respectively) show a rather flat and broad band around 4.34eV along with a weak band around 5.2eV for $x = 0.05$ which shifts to 5.1eV for $x = 0.10$. The 4.8eV shoulder is not prominent. The 5.2eV excitation band may be related to the B-band of some complex thallium centers in the mixed surrounding of anions (Br⁻ and I⁻ ions).

Figure.6. PL excitation spectra of $\text{RbBr}_{1-x}\text{I}_x:\text{TlI}$ (0.1mol%) grown in vacuum for 2.9eV emission for a) $x = 0.05$ and b) $x = 0.10$. Each spectrum is normalized to unity at its maximum



The optical absorption spectra of $\text{RbBr}_{1-x}\text{I}_x:\text{TlI}$ (0.1mol%) mixed crystals exhibited an inhomogeneous broadening of the A-band towards low energy side with increases of I⁻ ion composition. Compared with the absorption spectra of $\text{RbBr}:\text{TlBr}$ single crystals and $\text{RbBr}:\text{TlI}$ crystals, the changes in the absorption spectra of $\text{RbBr}_{1-x}\text{I}_x:\text{TlI}$ mixed crystals are due to some complex Tl^+ centers involving Br⁻ and I⁻ ions formed in the mixed crystals (communicated).

In the case of $\text{KBr}_{1-x}\text{I}_x:\text{Tl}^+$ mixed crystals excited in the A_3 -absorption band 4.45eV band of the complex thallium centers ($\text{TlBr}_{6-n}\text{I}_n$ centers with $n = 3$), a prominent additional emission appeared around 2.95eV [16]. At RT, this emission band was found to grow with KI content in the KBr-KI (TII) mixed crystals. As the behaviour of the 2.9eV shoulder of $\text{RbBr}_{1-x}\text{I}_x:\text{TlI}$ mixed crystal (Present study) is found to be similar to that of the 2.95eV emission band in $\text{KBr}_{1-x}\text{I}_x:\text{TlI}$ mixed crystals, it is attributed to complex thallium centers involving some impurity I⁻ ions.

The 4.45eV excitation band of $\text{RbBr}:\text{TlI}$ and the 4.27 and 4.26eV excitation bands of mixed crystals with $x = 0.05$ and 0.10 may be related to the complex thallium centers involving impurity anions. The shift of the additional excitation band towards low energy side with iodine ion composition implies that it is not fundamental to the $\text{RbBr}:\text{Tl}^+$ system. Also, the decrease of the relative intensity of 4.8eV excitation band with I⁻ ion composition indicates that the centers responsible for the additional excitation bands are formed at the cost of those responsible for the 4.8eV excitation band (viz, A_0^- centers). Thus comparing with earlier reports [6], the additional excitation bands may be related to some complex Tl^+ centers involving both Br⁻ and I⁻ ions. Although the exact number of I⁻ ion neighbors to the Tl^+ ion in the $\text{TlBr}_{6-n}\text{I}_n$ complex centers could not be fixed, tentatively it may be suggested that the complex centers responsible for the 4.45eV excitation band involve less number of I⁻ ion neighbor than those responsible for the 4.27 or 4.26eV excitation bands.

Conclusions

The $\text{RbBr}:\text{TlBr}$ single crystals are excited at different wavelengths in A-band same asymmetric emission band (3.34eV) is observed. An additional emission band around 2.9eV is observed in $\text{RbBr}_{1-x}\text{I}_x:\text{TlI}$ mixed crystals excited at different wavelengths in the A-band absorption. Comparing with earlier results, the observed changes in emission of $\text{RbBr}_{1-x}\text{I}_x:\text{TlI}$ mixed crystals are attributed to the formation of complex Tl^+ centres of the type $\text{TlBr}_{6-n}\text{I}_n$ involving both Br⁻ and I⁻ ions as nearest neighbors to the Tl^+ ions.

Acknowledgements

The authors would like to acknowledge Dr. M. T. Jose, Dr. A. R. Lakshmanan and Dr. V. MeenakshiSundaram, Safety Division (RSD), IGCAR, Kalpakkam, India for extending their experimental facilities for this work.

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