LUMINESCENCE STUDIES ON THALLIUM DOPED RbBr-RbI MIXED CRYSTALS

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Abstract
Photoluminescence (PL) studies of RbBr1-xIx: 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 and D bands due to formation of complex Ti+ centres in the mixed surrounding of anions [6,7]. Kleemann and Fischer studied the optical absorption and luminescence of KBr1-xIx: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 Ti+ centers of the form TiBr6-nIn. 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 A0-band in KBr:Tl+ single crystals. This band was attributed to the TiBr6 centers (i.e, a Ti+ 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 TiBr6-xIn 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 Ti+ ions. The attractive PSL characteristics of medical x-ray storage (PSL) phosphor RbBr:Tl+ have already been commercialized [9]. 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 Ti+-doped with RbBr-RbI mixed crystals, except that of the authors’ work on RbBr-RbI:Tl+ mixed crystals. However, luminescence studies on Ti+ 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: TiBr (0.02 and 0.1mol %) and 2) RbBr1-xIx:TlI (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 TiBr and TlI (99.99%) taken in the required stoichiometric proportions described in our
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 λ_ex = 260nm 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.

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 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 [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 $\text{Tl}^+$ 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:TiBr 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 $\lambda_{em} = 290$, 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 $\lambda_{em} = 270$nm may be due to the appearance of some additional emission bands due to some unidentified complex $\text{Tl}^+$ 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. PL emission 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 ($\lambda_{em} = 430$nm) 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).
The optical absorption spectra of RbBr$_{1-x}$I$_x$TI (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 RbBr:TIBr single crystals and RbBr:TI crystals, the changes in the absorption spectra of RbBr$_{1-x}$I$_x$TI mixed crystals are due to some complex Tl$^+$ centers involving Br$^-$ and I$^-$ ions formed in the mixed crystals (communicated).

In the case of KBr$_{1-x}$TI$^+$ mixed crystals excited in the A$_3$ absorption band 4.45eV band of the complex thallium centers (TIBr$_{6-n}$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 (TI) mixed crystals. As the behaviour of the 2.9eV shoulder of RbBr$_{1-x}$I$_x$TI mixed crystal (Present study) is found to be similar to that of the 2.95eV emission band in KBr$_{1-x}$TI mixed crystals, it is attributed to complex thallium centers involving some impurity I$^-$ ions.

The 4.45eV excitation band of RbBr:TI 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 is due to the complex thallium centers involving impurity anions. 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$_2$- 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 TIBr$_{6-n}$I$_n$ complex centers cannot 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 RbBr:TIBr 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 RbBr$_{1-x}$I$_x$TI mixed crystals excited at different wavelengths in the A-band absorption. Comparing with earlier results, the observed changes in emission of RbBr$_{1-x}$I$_x$TI mixed crystals are attributed to the formation of complex Tl$^+$ centres of the type TIBr$_{6-n}$I$_n$ involving both Br and I$^-$ ions as nearest neighbors to the Tl$^+$ ions.

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References