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Optical absorption behavior of Thallium co-doped RbBr_{0.95} I_{0.05}:Eu²⁺ mixed crystal

P. Eswaran^a, S. Nagarajan^b and R. Ravisankar^c

 *a Department of Physics, Vel Tech (Owned by RS Trust), Chennai, Avadi- 600062, India.
^b Department of Physics, Pondicherry Engineering College, Puducherry 605 014, India.
^c Post Graduate and Research Department of Physics, Government Arts College, Tiruvanamalai-Tamilnadu, India

ABSTRACT

In the present paper optical absorption (OA) studies of RbBr_{0.95} $I_{0.05}$: Eu^{2+} , Tl^+ mixed crystal are reported. Optical absorption spectrum of RbBr: Tl^+ (0.02mol %) can be reproduced for sake of comparison (communicated) shows a band around 4.8eV which is rather flat at its peak. In addition to this, a broad band around 5.6 and 6.0eV on the rising portion of the absorption in the high energy side is observed. In the case of mixed crystal showed that the characteristic Aabsorption band of Tl^+ ions in RbBr_{0.95} $I_{0.05}$: Tl^+ (0.02mol %) mixed crystal broadened towards the low energy side with iodine composition. The change in the absorption spectrum of mixed crystal is suggested to be due to complex centers involving Br⁻ and Γ ions formed in the mixed crystal. But in the case of Tl^+ co-doped RbBr_{0.95} $I_{0.05}$: Eu^{2+} mixed crystal exhibits structured absorption band in the range between 2.8 to 4.0eV in addition with a shoulder around 4.2 and 5.07eV are observed. The broad and structured bands from 2.8 to 4.0eV may contain several absorption bands due to Eu^{2+} and Tl^+ ions and their aggregates.

Keywords: Mixed crystals; ${\rm Tl}^+$ doped KBr-KI Mixed crystals, absorption band, and co-doped KBr-KI:Eu^{2+} .

INTRODUCTION

In alkali halides doped with Tl^+ type impurities several prominent absorption bands originating from intraionic transition a_{1g}^2 to $a_{1g} t_{1u}$ appear below the energy of an intrinsic absorption edge of host materials and the lowest one is denoted the A band [1]. The band is strongly affected by the local structure around the impurity and by the alloying of the host materials [2, 3]. In such a lattice, a substitutional Tl^+ impurity is expected to replace a Rb⁺ ion because of both its electric charge and ionic size (ex. RbBr:Tl⁺). On the other hand, there have been few investigations for

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impurities in mixed crystals of alkali halides [4-7]. In our previous work [8], we reported KBr_{1-x} I_x :Tl⁺ mixed crystals doped with Tl⁺ impurities and studied the appearance of additional bands on the low energy side of the characteristic A, B and C absorption bands of KBr:Tl⁺ single crystals with increasing iodine composition. It was found that, the additional bands are attributed to Tl⁺ ions of the complex centers of the type TlBr_{6-n} I_n (n = 1, 2, 3...). Mixed alkali halides are not studied extensively owing to many of their eutectic properties [9]. Recently KCl:Eu²⁺ powder phosphors co-activated with Tl⁺ ions showed some interesting results [10, 11]. The enhancement of luminescence due to the Eu²⁺ ions was attributed to energy transfer from Tl⁺ to Eu²⁺ ions in KCl: Eu²⁺, Tl⁺ phosphors. To best of our knowledge no work reported in thallium co-doped with mixed crystals of rubidium halides. In the present work, RbBr_{0.95} I_{0.05}:Eu²⁺, Tl⁺ mixed crystals have been studied at room temperature.

MATERIALS AND METHODS

The systems studied in the present work are (1) RbBr: TlBr (0.02mol %) and 2) RbBr $_{0.95}$ I $_{0.05}$:Tl⁺, Eu²⁺ (0.02 and 0.05mol%)mixed crystals grown in vacuum 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 earlier work [8]. The Optical Absorption (OA) measurements were carried out using a Systronics-2101 UV-Visible-Spectrophotometer

RESULTS AND DISCUSSIONS

Optical absorption spectra of RbBr: TlBr (0.02mol %) can be reproduced for sake of comparison (communicated) and RbBr_{0.95} $I_{0.05}$: Tl⁺, Eu²⁺ (0.02, 0.05 mol %) mixed crystals grown in vacuum measured at RT are shown in Fig. 1. The absorption spectra exhibit complex absorption bands, showing wide variation in the structure with iodine composition (RbBr_{0.95} $I_{0.05}$). For the sake of convenience in explaining the results, absorption spectrum considered to have two regions; the absorption region of 4.0 - 5.0eV on the low energy side (denoted as A- band region) and the region from 5.0 - 6.0eV on the high energy side (denoted as B and C region). Optical absorption bands in both regions of the spectra of the mixed crystals appear to be broadened with additional structures when compared to those of single crystals. The optical absorption spectrum of RbBr: TlBr (0.02mol %) single a crystal shows a broad absorption bands around 4.8eV which is rather flat at its peak. In addition to this, a broad band around 5.6 and 6.0eV on the rising portion of the absorption in the high energy side is observed (Fig. 1, curve a) which are the well known A, B and C bands of Tl⁺ ions in RbBr respectively [12]. Ghose has reported that C-band of Tl⁺ ions in RbBr respectively [12]. Ghose has reported that C-band of Tl⁺ ions in RbBr: Tl⁺ appeared at 5.95eV [13]. In the present work, C-band absorption is not well resolved, these broad absorption band 6eV (present study) may be related to the C-band absorption.



Figure 1. Optical absorption spectra of (a) RbBr:TlBr (0.02mol%), (b) RbBr_{0.95}I $_{0.05}$:TlBr (0.02mol%) and (c) RbBr $_{0.95}$ I $_{0.05}$:Tl⁺, Eu $^{2+}$ (0.02 and 0.05mol%)

In alkali halides heavily doped with Tl^+ ions, aggregate centers of Tl^+ ions such as Tl^+ dimers have been reported to be formed [14]. Two types of dimer centers have been reported in 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 is seen only as an inhomogeneous broadening of A-band towards low energy side [15]. Considering the above earlier results, the broadening of the absorption bands towards low energy side of A, B and C bands in RbBr:TlBr single crystals may be attributed to the formation of such aggregates of Tl^+ ions cannot be ruled out.

In the case of RbBr_{0.95} I_{0.05}: TlBr (0.02mol %) mixed crystals shows the A-band around 4.8eV is found to broadened towards the low energy side with increasing iodine composition x = 0.05 and broad overlapping bands around 5.3 and 5.9eV in the B and C-bands regions (Fig. 1, Curve b). Comparing with earlier reports [16], the broadening of A-band could be due to the appearance of new absorption bands on its low energy side at the cost of A-band absorption at 4.8eV. Similar to the absorption in the A-band region, the low energy tail of absorption in the B and C bands regions of the mixed crystals also extends to low energy side indicate the formation of new thallium centers involving Γ ions in the Tl doped mixed crystals of RbBr-RbI.

Kleeman and Fischer observed additional structures due to overlapping bands on the long wavelength side of A, B and C bands in their $KBr_{1-x}I_x:Tl^+$ mixed crystals due to complex Tl^+ centres of the form $TlBr_{6-n}$ I_n (n = 1, 2, 3) formed in them by the selective and preferential association of I anions with Tl^+ cations as its nearest neighbors. The absorption bands of the mixed crystals with their peak positions corresponding to the A, B and C bands in KBr: Tl^+ single crystals were designated as A_0 , B_0 and C_0 bands respectively. They were assumed to be associated with the configuration of six Br. ions around each Tl^+ ion (i.e., $TlBr_6$ complex) in the

mixed crystals. The additional bands 4.66, 4.55 and 4.44eV appearing and growing (one after the other) at the cost of A_0 band at 4.8eV were designated as A_1 , A_2 , and A_3 bands and they were attributed to the TlBr_{6-n} I_n centres formed by gradual replacement of Br⁻ ions with one, two and three I⁻ respectively as nearest neighbors to the Tl⁺ ions [8, 16, 17]. Similar to A-band absorption, the absorption in the B and C band region between 5-6eV is also modified significantly due to overlapping absorption bands in this region also are not well resolved. At RT, the A-band absorption was found to get broadened inhomogeneously towards the low energy side with x due to the formation of these complex centers [16, 17]. The broadening of the A-band absorption (as well as B and C bands) in RbBr_{0.95} I_{0.05}:TlBr mixed crystals (present study) is also similar to that observed in KBr_{1-x} I_x :TlI mixed crystals [18]. Hence the broadening of the absorption bands of Tl⁺ ion towards low energy side in the mixed crystals of the present study is attributed to the appearance of some new bands due to the complex Tl⁺ centers in the mixed configuration with both Br⁻ and I⁻ ions as nearest neighbours to the Tl⁺ ions.

From these reports it is clear that even the addition of a small amount of iodine has a profound effect on TlBr doped RbBr-RbI mixed crystals of the present study. The peak positions of the additional absorption bands could not be fixed with certainty due to their overlapping at RT. But in any particular series of the mixed crystals, broadening of the absorption bands in both regions towards the low energy side with iodine composition is attributable to the formation of different complex Tl^+ centers involving Γ ions at the cost of $TlBr_6$ complexes. The formation of aggregate centers of Tl^+ ions also produces a similar shift towards low energy side; the broadening may also be partially due to the formation of such Tl^+ aggregate centers cannot be ruled out [19].

The absorption band around 4.8eV, observed in RbBr_{0.95} $I_{0.05}$: TlBr mixed crystals is replaced by a relatively stronger band with a flattened peak centered around 4.70eV in RbBr_{0.95} $I_{0.05}$:Tl⁺, Eu²⁺ mixed crystals shown in (Fig.1, Curve c). In addition, a broad absorption with unresolved bands in the range between 2.8-4.0eV and a shoulder around 4.2eV are observed. Furthermore, an increase in the relative intensity of absorption, especially, in the A-band region when compared to single doped mixed crystals. The 4.70eV main absorption band in RbBr_{0.95} $I_{0.05}$: Tl⁺, Eu²⁺ mixed crystals is a composite and it is slightly shifted towards high energy side with additional band appeared around 5.07eV. The shift of the A-band absorption in RbBr_{0.95} $I_{0.05}$:Tl⁺, Eu²⁺ mixed crystals towards high energy side relative to the RbBr_{0.95} $I_{0.05}$:Tl⁺, Eu²⁺ crystals are of different nature from those formed in RbBr_{0.95} $I_{0.05}$:Tl⁺ crystals. In the former case, it is likely that complex Tl⁺ centers with Br⁻ and I⁻ 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 [17].

Comparing with these results, the flattened peak around 4.70eV in RbBr_{0.95} $I_{0.05}$:Tl⁺, Eu²⁺ mixed crystals (present study) due to the complex Tl⁺ centers in the mixed configuration with both Br⁻ and Γ ions as nearest neighbors to the Tl⁺ ions [17]. The unresolved structured band from 2.8-4.0eV due to the transition of Eu²⁺ ions from the 4f⁷ ground state to the t_{2g} components of its 4f⁶ 5d excited state, respectively [20,11] while the broad overlapping band in the B and C-band region from 5.0 to 6.0eV, its may be due to combine effect of Eu²⁺ and Tl⁺ ions and their aggregates. The influence of europium aggregates in alkali halides has been reported [21, 22]. It was found that the formation of different types of europium aggregates (such as Suzuki type, metastable EuCl₂-type precipitates, etc) result in some additional absorption bands as well as

shifting of characteristic absorption bands of Eu^{2+} monomer ions to the long wavelength side in alkali halides [21, 22]. It is well known that the 10 Dq splitting of 5d orbitals (i.e. difference between the centers of gravity of high energy and low energy absorption bands of Eu^{2+} ions) gives information about the characteristics of different Eu^{2+} aggregates formed in alkali halides [21, 22]. Since the additional absorption bands around 4.2 and 5.07eV is observed in RbBr_{0.95} I_{0.05}:Tl⁺, Eu²⁺mixed crystals not observed separately in RbBr_{0.95} I_{0.05}:Tl⁺mixed crystals it is likely that Eu^{2+} aggregates formed. The intensity enhancement of optical absorption attributed to the transfer of energy from Tl⁺ to Eu^{2+} ions in RbBr_{0.95} I_{0.05}:Tl⁺, Eu^{2+} mixed crystals [23].

Among the A, B and C bands of ns² ions in alkali halides single crystals, the C-absorption band is the strongest since it is associated with the symmetry and spin-allowed transition ${}^{1}A_{1g}$ to ${}^{1}T_{1u}^{*}$ [24, 25]. The A-absorption band due to ${}^{1}A_{1g}$ to ${}^{1}T_{1u}^{*}$ is relatively weak when compared to the Cband since it is made partially allowed through mixing of ${}^{1}T_{1u}$ excited state with ${}^{3}T_{1u}$ excited state by the spin-orbit interaction. Hence, in ns² ions doped alkali halide phosphors; the C-band absorption is always stronger than the A-band absorption depending on the value of the dipole strength ratio R of the phosphor which depends on spin-orbit interaction, Jahn-Teller effect, etc [24].

CONCLUSION

The absorption spectrum of $RbBr_{0.95} I_{0.05}$: Tl^+ mixed crystal broadened towards low energy side with iodine composition. The change in the absorption spectrum is suggested to be due to complex centers involving Br⁻ and Γ ions formed in the mixed crystal. But in the case of Tl^+ codoped $RbBr_{0.95} I_{0.05}$: Eu^{2+} mixed crystal exhibits structured absorption band may contain several absorption bands due to Eu^{2+} and Tl^+ ions and their aggregates. The intensity enhancement of optical absorption attributed to the transfer of energy from Tl^+ to Eu^{2+} ions in $RbBr_{0.95} I_{0.05}$: Tl^+ , Eu^{2+} mixed crystals.

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