



# Optical Studies Of Monovalent Thallium Co-Doped Mixed KBr-KI: Eu<sup>2+</sup> Mixed Crystals

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## ABSTRACT

Optical absorption spectra of KBr:TI<sup>+</sup> (0.01mol%) single crystals shows A, B and C bands around 258, 220 and 210nm respectively. An additional absorption bands are observed in KBr-KI: Eu<sup>2+</sup>, TI<sup>+</sup> (0.05, 0.01mol %) mixed crystals. These additional absorption spectra are attributed to the presence of Eu<sup>2+</sup> aggregates and complex centers involving both Eu<sup>2+</sup> and TI<sup>+</sup> ions. Inclusion of TI<sup>+</sup> ions in KBr-KI: Eu<sup>2+</sup> crystal is found to enhance the intensity of Eu<sup>2+</sup> absorption band due to an energy transfer from TI<sup>+</sup>→Eu<sup>2+</sup> ions.

**Keywords:** Optical absorption, KBr-KI mixed crystals, A-band, TI<sup>+</sup> ions, Eu<sup>2+</sup> ions, Aggregates centers

## 1. INTRODUCTION

The alkali halide crystals, pure and doped, have been extensively studied because they possess a structure which allows for simple models that can be used for interpretation of physical phenomenon in other more complex crystalline systems. Several works have been done on non-doped mixed alkali halide crystals due to the potential technological applications such as solid state laser [1], but on divalent ion doped mixed crystals the information is scarce. Currently, it is well known that this systems is completely miscible and that it can be described [2], establishing the range of anion concentration that can be mixed. The presence of their halogen impurity ions not only affects the physical properties of the crystal but also those of any impurity ions [3-7].

On other hand, much work has been done in order to characterize the optical and luminescence properties of mono and divalent TI<sup>+</sup>, Eu<sup>2+</sup> impurities alkali halide and other phosphors exhibit excellent luminescent properties and some find applications in high-energy radiation detection, imaging plates for X-ray radiography etc. [8-12]. Alkali halides with small amounts of thallium ions mainly exhibit three absorption bands, designated as A, B, C bands, in order of increasing photon energy. The absorption and emission process due to transitions between the 6s<sup>2</sup> ground state and the 6s6p first excited states depends on various factors such as the Jahn-Teller effect, spin-orbit interactions, etc. [13]. The absorption bands in alkali halide crystals containing small amount of thallium are usually attributed to TI<sup>+</sup> ions that replaces cations of the host materials. In mixed alkali halides crystals, if the composition of the base materials is changed, changes occur in the spectra of the phosphors. These changes are associated with the appearance of new bands that differ from the component phosphors bands. There is no doubt that the new bands are due to centers formed by an activator in the mixed surroundings. It is noted that there is not a possibility that the appearance of additional A- bands is caused from the Jahn-Teller effect. It was clearly shown that the appearance of the new bands

depends strongly on the composition [14, 15] In the present work, the influence of co-doping thallium ion in KBr-KI:Eu<sup>2+</sup> mixed crystals is reported for the first time.

## 2. EXPERIMENTAL

KBr: TI<sup>+</sup> and KBr-KI:Eu<sup>2+</sup>, TI<sup>+</sup> (0.05, 0.01mol%) mixed crystals were grown from the melt. Prior to measurements the crystals were quenched from 500 °C to room temperature. The method of growth is briefly described in an earlier work [7]. Optical absorption measurements were carried out using UV-Visible Shimadzu 3101PC spectrophotometer at room temperature (RT).

## 3. RESULTS AND DISCUSSIONS

The optical absorption spectrum of a single crystal of KBr:TI<sup>+</sup> (0.01mol%) can be reproduced for sake of comparison [15] exhibits an absorption band at 258 nm shown in (Figure.1). On the shorter wavelength side of this band at least two overlapping bands around 220 and 210 nm are observed. As the undoped alkali halides are usually transparent in these wavelength ranges these absorption bands are attributable to the doped impurity TI<sup>+</sup> ions.

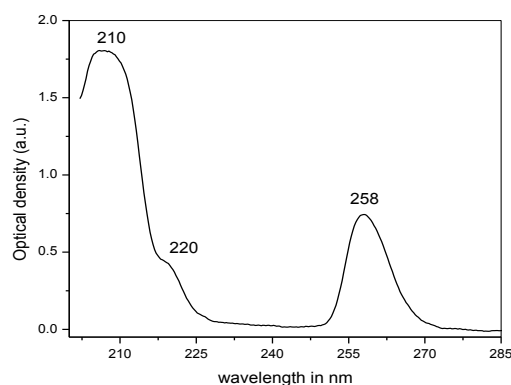
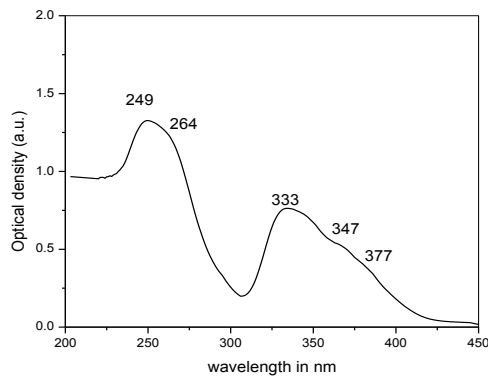
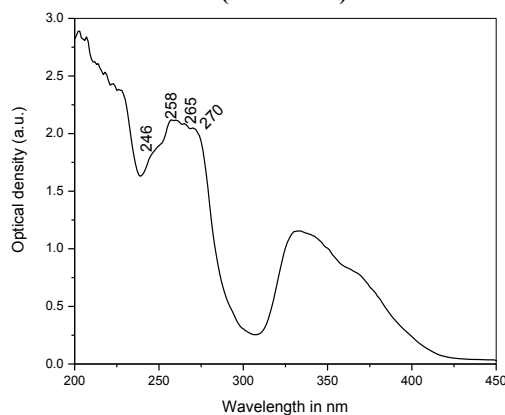


Figure.1. Optical absorption spectrum of KBr:TI<sup>+</sup> (0.01mol%)

Tsuboi and Jacobs [4] have observed the optical absorption bands due to  $Tl^+$  ions in KBr at 258.2, 221.7 and 209.7nm. These bands were attributed to the well known A, B and C bands respectively of the  $Tl^+$  ions. Comparing the optical absorption bands observed in the present study with those reported in the literature [4], it is clear that these bands are due to A, B, C bands of the  $Tl^+$  ions which have replaced substitutionally the host cations.



**Figure 2: Optical absorption spectrum of  $KBr_{0.95}-KI_{0.05}:Eu^{2+}$  (0.05mol %)**



**Figure 3: Optical absorption spectrum of  $KBr_{0.95}-KI_{0.05}:Eu^{2+}, Tl^+$  (0.05, 0.01mol %)**

Optical absorption spectra of  $KBr_{0.95}-KI_{0.05}:Eu^{2+}$  (0.05mol %) mixed crystal and co-doped  $KBr_{0.95}-KI_{0.05}:Eu^{2+}, Tl^+$  (0.05, 0.01mol %) mixed crystals are shown in Fig. 2 & 3 respectively. The optical absorption spectrum of a  $KBr_{0.95}-KI_{0.05}:Eu^{2+}$  (0.05mol %) mixed crystal (shown in Fig.1) exhibits an absorption band at 249 nm as well as a structured band from 310 to 400 nm due to the transitions of  $Eu^{2+}$  ions from  $4f^7$  ground state to the  $t_{2g}$  and  $e_g$  components of its  $4f^65d$  excited state respectively [11]. The absorption band at 249 nm, observed in  $KBr_{0.95}-KI_{0.05}:Eu^{2+}$  (0.05mol %) mixed crystal is replaced by a relatively stronger band with a composite bands centered around 265 nm with shoulder at 258, 246 and 270nm in  $KBr_{0.95}-KI_{0.05}:Eu^{2+}, Tl^+$  mixed crystals. In addition to this, a broad absorption with unresolved bands in the wavelength range between 200-220 nm is observed. Further, an increase in the relative intensity of characteristic  $Eu^{2+}$  absorption bands (310- 400 nm) in doubly doped  $KBr_{0.95}-KI_{0.05}:Eu^{2+}, Tl^+$  mixed crystal are observed when compared to  $KBr_{0.95}-KI_{0.05}:Eu^{2+}$  crystals.

Optical absorption and luminescence studies on  $KBr_{1-x}I_x:Tl^+$  mixed crystals have been reported by a few authors [7,14, 16]. Kleemann and Fischer [16] found that, at RT, the spectral peak position of the asymmetrical A-band absorption in  $KBr_{1-x}I_x:Tl^+$  (with  $0 < x < 0.17$ ) mixed crystals grown from the melt in air shifted towards Higher wavelength side while its half width increased with iodine composition (x). However, at 20K, Kleemann 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  $Tl^+$  cation 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 appearing and growing (one after the other) at the cost of  $A_0$  band at 258nm were designated as  $A_1, A_2$  and  $A_3$  bands and they were attributed to the  $TlBr_{6-n}I_n$  centers formed by gradual replacement of  $Br^-$  ions with one, two and three  $I^-$  ions respectively as nearest neighbors to the  $Tl^+$  ions. The appearance of these additional A-bands was attributed to the non-uniform distribution of  $I^-$  ions in the mixed crystal lattice [7, 14, 16]. Taiju Tsuboi has reported the appearance of additional absorption bands around 270 nm on the long wavelength side of the 258 nm band (A- band) in heavily doped alkali halides phosphors [4]. These additional bands were attributed to  $Tl^+$  dimers with  $D_{4h}$  symmetry [4] can not be ruled out.

Among the A, B and C bands of  $ns^2$  ions in alkali halide single crystals, the C-absorption band is the strongest since it is associated with the symmetry and spin-allowed transition  $^1A_{1g} \rightarrow ^1T_{1u}$  [17, 18]. The A-absorption band due to  $^1A_{1g} \rightarrow ^3T_{1u}$  is relatively weak when compared to the C-band since it is made partially allowed through mixing of  $^1T_{1u}$  excited state with  $^3T_{1u}$  excited state by the spin-orbit interaction. Hence, in  $ns^2$  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 [17].

Comparing with earlier reports, the composite absorption bands in  $KBr_{0.95}-KI_{0.05}:Eu^{2+}, Tl^+$  mixed crystal (present study) may be attributed to the appearance of additional absorption bands due to the formation of such complex  $Tl^+$  centers at the cost of  $TlBr_6$  complexes [16] as well as their aggregates [4]. While the unresolved absorption bands between 200 -220 nm may be related to their B and C bands.

Influence of europium aggregates in alkali halides have been reported by several authors [19, 20]. It was found that the formation of different types of europium aggregates (such as Suzuki type, metastable  $EuCl_2$  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 [19, 20]. It is well known that the 10Dq splitting of 5d orbitals (i.e, the difference between 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 [19, 20].

Since the 246 nm  $Eu^{2+}$  absorption band observe in  $KBr_{0.95}-KI_{0.05}:Eu^{2+}, Tl^+$  mixed crystal is not observed separately in  $KBr_{0.95}-KI_{0.05}:Eu^{2+}$  mixed crystal it is likely that aggregates involving  $Tl^+$  and  $Eu^{2+}$  are also formed whose absorption bands may be within the envelope of the composite band around 265 nm. The composite of the A-band of monomer  $Tl^+$  ions may be due to the formation of such aggregates cannot be ruled out.



In  $\text{KBr}_{0.95}\text{-KI}_{0.05}:\text{Eu}^{2+}, \text{Tl}^{+}$  mixed crystal, the enhancement of  $\text{Eu}^{2+}$  absorption with inclusion of  $\text{Tl}^{+}$  ions is due to an energy transfer from  $\text{Tl}^{+}$  ions to  $\text{Eu}^{2+}$  ions. As suggested in the case of  $\text{KCl}:\text{Eu}^{2+}, \text{Mn}^{2+}$  crystals [21], the distribution of  $\text{Eu}^{2+}$  and  $\text{Tl}^{+}$  ions in the complex and aggregate centres formed in  $\text{KBr}_{0.95}\text{-KI}_{0.05}:\text{Eu}^{2+}, \text{Tl}^{+}$  mixed crystal (present study) is random so that  $\text{Eu}^{2+}$  and  $\text{Tl}^{+}$  ions are close enough for the energy transfer to take place.

#### 4. CONCLUSION

Influence of  $\text{Tl}^{+}$  activators on the optical absorption of  $\text{KBr}_{0.95}\text{-KI}_{0.05}:\text{Eu}^{2+}$  mixed crystals were investigated. Optical absorption studies of  $\text{KBr}_{0.95}\text{-KI}_{0.05}:\text{Eu}^{2+}, \text{Tl}^{+}$  mixed crystal exhibited characteristic absorption bands of  $\text{Eu}^{2+}$  ions and their aggregates. Some additional bands corresponding to  $\text{Tl}^{+}$  ions and complex centres involving  $\text{Tl}^{+}$  observed in the doubly doped crystals. An enhancement in intensity of absorption bands is observed in  $\text{Tl}^{+}$  co-doped  $\text{KBr}_{0.95}\text{-KI}_{0.05}:\text{Eu}^{2+}$  mixed crystal. This enhancement is attributed to an energy transfer from  $\text{Tl}^{+} \rightarrow \text{Eu}^{2+}$  ions.

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