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Optical absorption of Tl^+ ions in $KBr_{1-x}I_x$:TlI mixed crystals

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Abstract Optical absorption spectra of the mixed crystals of $KBr_{1-x}I_x:Tl^+$ crystals studied at room temperature are reported. The absorption spectra indicated 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. Comparing with earlier reports, the additional bands were attributed to the complex Tl^+ centers in the mixed configuration surrounded by Br^- and I^- ions as nearest neighbors. The absorption spectra of gamma irradiated mixed crystals showed F band, which shifts towards low energy side with the composition of iodine ions in the mixed crystals.

Key words F-centers, KBr_{1-x} I_x:TlI mixed Crystals, Optical absorption, Tl^+ ions, Mixed halides, A-absorption band

1 Introduction

The absorption spectrum of alkali halides activated by Tl^+ like ions exhibit characteristic bands, i.e. the A, B, C and D bands in the order of increasing energy. While the A, B and C bands are connected with the excited levels of activator ion $^3P_1$, $^3P_2$ and $^1P_1$, the D band is related to the excitation of the anion excitation perturbed by the activator[1]. The behavior of A-band absorption and luminescence, which has been treated by a number of experimental and theoretical works, is strongly influenced by the local symmetry around the impurity, temperature, concentration of the activator, alloying of the host, etc[2–6]. Alkali halide and other phosphors doped with Tl^+ ions ($6s^2$ ground state configuration) exhibit excellent luminescent properties[7], and some of them find their applications in the fields of high-energy radiation detection, imaging plates for X-ray radiography, etc[8,9].

In recent times, luminescence studies on mixed alkali halides doped with activators (such as Eu^{2+} doped KCl-KBr, CsBr-CsCl, etc) have gained importance for potential applications of X-ray imaging, UV dosimetry, etc[10,11]. However, the work reported on impurity-doped mixed crystals of KBr-KI system is still meagre[12–14]. These mixed crystals have a limited solid solubility because of their eutectic properties[15]. In $KBr_{1-x}I_x:Tl^+$-mixed crystals, the formation of complex Tl^+ ion centers in the mixed surrounding of anions has been reported[12]. This is manifested by the appearance of new absorption bands on low energy side of A, B and C bands of Tl^+ ions with iodine composition x in the $KBr_{1-x}I_x:Tl^+$ mixed crystals. Photo-excitation at the wavelengths corresponding to the additional A-bands resulted in emission spectra, which were similar in temperature behavior but red shifted relative to the A-band emission of $KBr:Tl^+$ system[12]. The abovementioned studies have been carried out at low temperatures.

To the best of our knowledge, optical absorption and luminescence studies at RT on KBr_{1-x} $I_x:Tl^+$ mixed crystals have not been reported. KBr system seems to be attractive in view of the spectral peak position of its F-band (around 630 nm) since it lies close to the He-Ne laser wavelength (633 nm), which is used for photo-stimulation in X-ray radiography employing imaging plates based on $BaFBr:Eu^{2+}$ Photo Stimulated Luminescent (PSL) phosphors[16]. With this view in mind, as a complementary study to photoluminescence (PL) and PSL in gamma irradiated KBr-KI mixed crystals doped with thallium[17], optical absorption of

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$KBr_{1-x}I_x$: Tl^+ mixed crystals has been studied at room temperature and reported in this paper. The results are interpreted comparing with earlier reports. The F-band absorption in gamma irradiated $KBr_{1-x}I_x$:Tl^+ mixed crystals is reported for the first time.

2 Experimental

$KBr_{1-x}I_x$ mixed crystals doped with (0.01 and 0.05 mol%) of thallium (with x=0.0, 0.05, 0.1, 0.15) were grown under vacuum or in atmosphere by slow cooling from their melt. Analytical reagent grade KBr and KI (99.9%) and the dopant of TlI (99.99%) in the required stoichiometric proportions were completely dissolved in triple-distilled water. The solutions were dried in at 100℃. The dried material was ground into a fine powder using mortar and pestle, and packed into a quartz ampoule. Prior to this, melting point of each powder samples of different composition was determined with DTA analysis using a Linseis – model L-70 DTA unit. For growth under vacuum conditions, the quartz ampoule filled with the powder was evacuated to less than 0.13 Pa (10^{-3} Torr) and sealed under vacuum. The powder sample was melted in a furnace operated at about 20℃ above the melting temperature of the sample. After maintaining the melt for several hours at this temperature for thorough mixing and homogeneity, it was slowly cooled to RT in 40 h. Transparent single crystals were obtained from the ingot which were about 5mm×5mm×8mm. Samples in thickness of about 1mm cleaved from the middle portion were used for the measurements, after the samples were quenched from 500℃ to RT for 1 h.

Optical absorption measurements were carried out using UV-*vis* (Shimadzu 3101PC) at RT. Powder diffraction patterns were recorded at RT using Rigaku X-ray diffractometer (Cu K_α). A ^{60}Co source was used to irradiate the samples with a dose rate of 500 Gy/h.

3 Results and discussion

Mixed crystals of $KBr_{1-x}I_x$:Tl (y mol%), with x=0.0, 0.05, 0.10 and 0.15 mole fraction, and y=0.01 and 0.05 mol%, grown from their melt in vacuum or atmosphere, were studied. In this paper, the composition of iodine x and the Tl^+ ion concentration (y) refer to the proportionate amounts of potassium iodide and thallous halide added to the melt. Powder XRD was used to study the crystal structure of the mixed crystals grown in vacuum and open air (Fig.1). All the diffraction peaks are indexed and the lattice parameter refined. The results are comparable with standard data (JCPDS 73-0389). The analysis of diffraction patterns confirmed the formation of single phase FCC cubic structure. The lattice parameter was found to increase with iodine composition x (from 6.616 Å for x=0.05 to 6.652 Å for x=0.15). The increase in the lattice parameter with x is due to the substitutional replacement of bromine ions by iodine ions having larger ionic radii.

All the samples showed the presence of some OH^- ions as indicated by the characteristic IR band of OH^- ions at 3442 cm^{-1} observed in the FTIR spectra (figure not shown). It is slightly higher in the case of air grown crystals.

Optical absorption spectra of $KBr_{1-x}I_x$:Tl^+ (0.01 and 0.05 mol %) mixed crystals with x=0.0, 0.05, 0.10 and 0.15 grown in vacuum and open air measured at RT are shown in Fig.2a–2d. The absorption spectra exhibit complex absorption bands, showing wide variations in their structure with the iodine composition. For the sake of convenience in explaining the results, each absorption spectrum is considered to have two parts; the absorption region of 4.0–5.0 eV on the low energy side (denoted as A-band region) and the region above 5.0 eV on the high-energy side (denoted as B and C bands 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 a KBr:TlI (0.01 mol%) single crystal sample grown in air shows absorption bands around 4.8, 5.6 and 5.95 eV (Fig.2a, Curve a) which are the well known A, B and C bands of Tl^+ ions in KBr respectively[19].

Optical absorption spectra of $KBr_{1-x}I_x$:TlI (0.01 mol%) mixed crystals grown in air exhibit a broad and asymmetrical absorption band in the A-band region whose peak position shifts to low energy side with iodine composition (x) from 4.8 eV for x=0 (Fig.2a, Curve a) to 4.72, 4.66 and 4.64 eV for x=0.05, 0.10 and 0.15, respectively (Fig.2a, Curves b, c and d). These bands are wider than the A-band of Tl^+ ions in KBr:Tl^+ single crystals and extend to lower energies.

The observed shift of peak position of A-band and its broadening towards the low energy side could be attributed to the appearance of some additional bands on its low energy side at the cost of the A-band absorption at 4.8 eV.

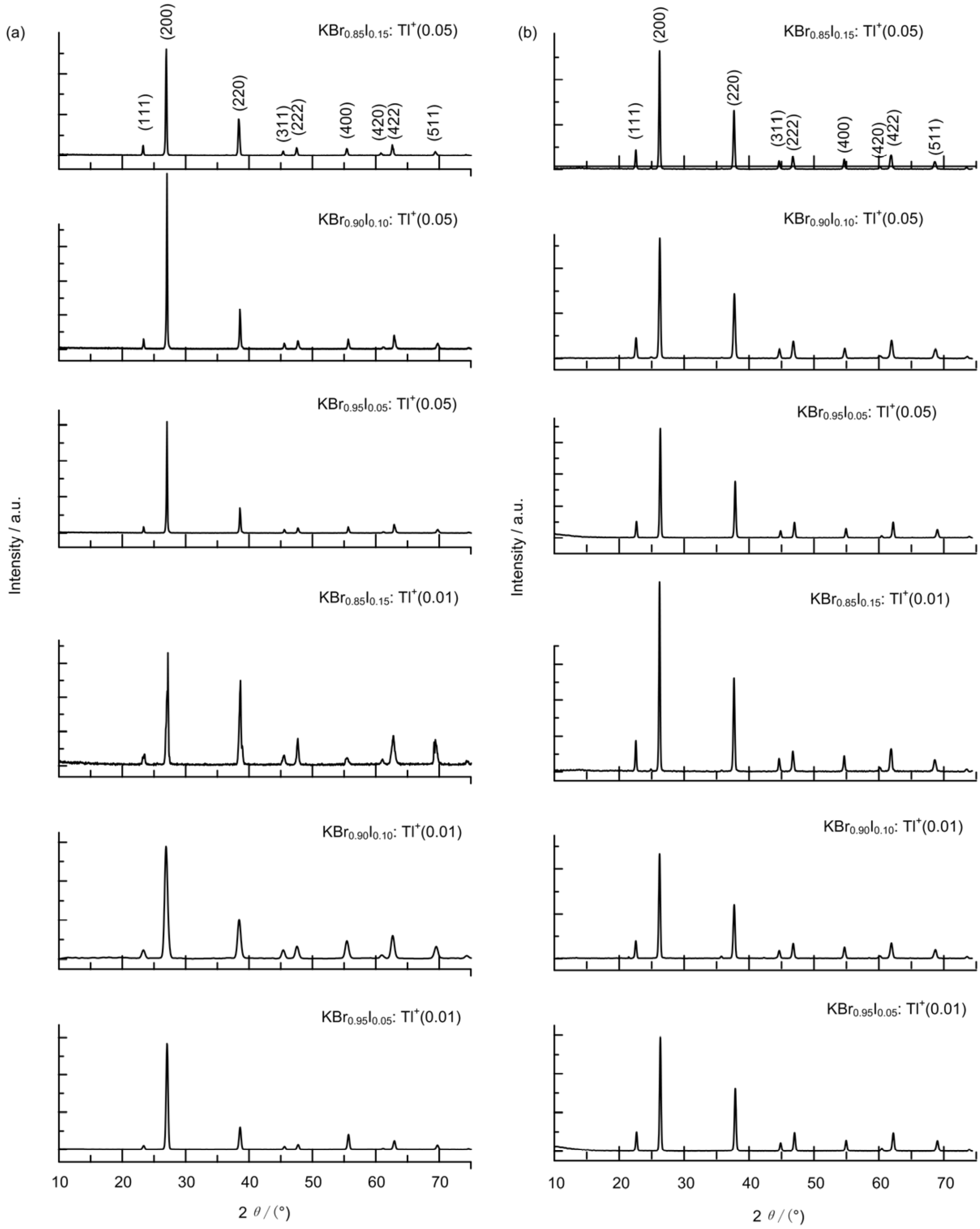

Fig.1 XRD patterns of $KBr_{1-x}I_x$:TlI (0.01 and 0.05 mol%) grown in vacuum (a) and open air (b).

Similar to the absorption in the A-band region, the low energy tail of absorption in the B- and C bands region of the mixed crystals also extends to lower photon energies (around 5 eV in mixed crystals against 5.4 eV in KBr:Tl^+ single crystals). In this region, mixed crystals with x=0.05 show a band at 5.74 eV while the crystals with x=0.10 show a band at 5.6 eV. The 5.95 eV absorption band (C-band) is not prominent. In the case of mixed crystals with $x = 0.15$, the absorption in the high-energy region is not well defined but it remains broad and flat. Usually, the amount of Tl^+ ions that has entered into a particular alkali halide host crystal is less than the amount of Tl^+ added to the melt in the form of thallous halide[19,20]. This is mainly because of the fact that thallium is volatile at the melting point of most of the alkali halide hosts and hence some of the thallium may be lost by evaporation[8]. A similar loss of iodine from the melt by evaporation is also likely in the mixed crystals. The concentration of Tl^+ ions in the KBr:Tl^+ (0.01 mol%) single crystals of the present study estimated by using the Wanger's formula using absorption coefficient at the A-band maximum (μ_A^{max}) measured at RT[20] is found to be around 0.0002 mol%. The concentrations of Tl^+ ions in the mixed crystals of the present study are not calculated since the spectral peak position and structure of the A-band and its composition are influenced significantly by the iodine anion doping.

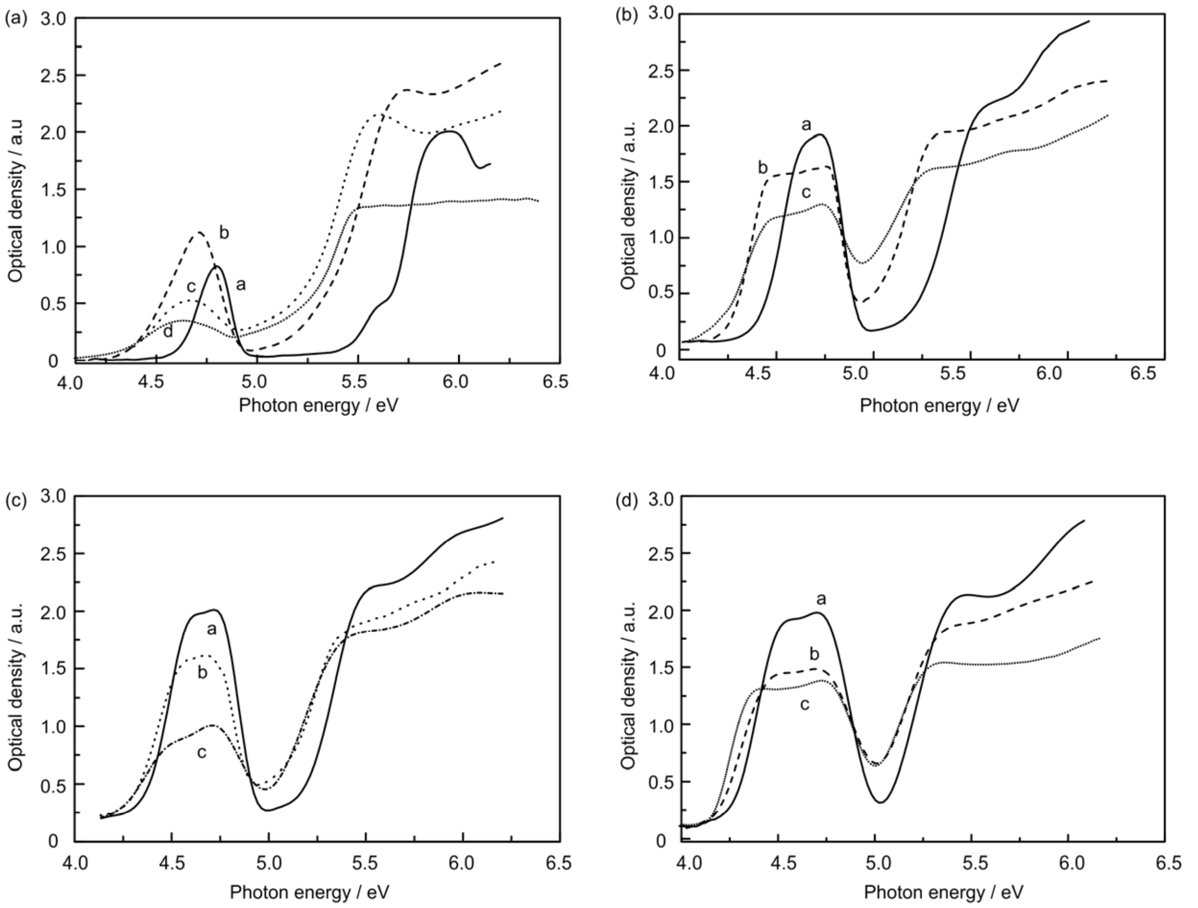

Fig.2 Optical absorption spectra of KBr_{1-x} I_x :TlI (0.01 mol% and 0.05 mol%) grown in open air and vacuum, (a) x=0.05, (b) x=0.10, (c) x=0.15 and (d) x=0.

Fig.2b shows the optical absorption spectra of mixed crystals of $KBr_{1-x}I_x$:Tl^+ (0.01mol%) grown in vacuum. In these spectra, there is an enhancement in the intensity of absorption, especially, in the A-band region when compared to the air-grown crystals.

A sample of $KBr_{0.95}I_{0.05}$:Tl^+(0.01 mol%) mixed crystal grown in vacuum shows an absorption band which is rather broad and flat at its peak around 4.7 eV in the A-band region and broad overlapping bands around 5.6 and 6.0 eV in the B and C-band region (Fig.2b, Curve a). It is interesting to note that the 5.6-eV band observed in air grown $KBr_{1-x}I_x$:Tl^+ (0.01 mol%) mixed crystals with x=0.10 appears in vacuum grown $KBr_{1-x}I_x$:Tl^+(0.01 mol%) mixed crystals with a lower iodine composition of x=0.05 itself. With a further increase in iodine composition x to 0.10 and 0.15, the absorption in the A-band region broadens further towards the low energy side indicating the presence of a new shoulder around 4.5 eV while a new absorption shoulder appears at about 5.35 eV in the B and C band region (Fig.2b, Curves b and c).

In the case of mixed crystals grown in vacuum, the escape of thallium and iodine from the melt during growth may be lesser to some extent when compared to that occurs during their growth in open-air atmosphere. This could have facilitated the incorporation of a relatively higher concentration of Tl^+ and I^- ions in the crystals grown in vacuum than those grown in open-air atmosphere. Thus, the observed differences between the absorption spectra of air grown and vacuum grown crystals discussed above are attributed to the different amounts of I^- and Tl^+ ions that have entered into these crystals.

Optical absorption spectra of $KBr_{1-x}I_x$:Tl^+ (0.05 mol%) mixed crystals grown in open-air atmosphere (Fig.2c), unlike those of air-grown $KBr_{1-x}I_x$:Tl^+ (0.01 mol%) mixed crystals (Fig.2a), show additional structures in the A-band region. However, the structural features of the A-band absorption are somewhat similar to those observed in vacuum-grown mixed crystals doped with 0.01 mol% TlI described earlier. For x=0.05, the flat portion of the peak of A-band extends from 4.6 to 4.76 eV; for x=0.10, it shifts and broadens inhomogeneoiusly towards low energy side while it appears to broaden towards both sides of the peak in the case of $x = 0.15$. The band around 5.5–5.6 eV band in the above air-grown mixed crystals shows a slight broadening towards the low energy side with increasing iodine composition. The observed differences between the spectra of air grown mixed crystals doped with 0.01 mol% and 0.05 mol% of TlI, is due to the different amounts of Tl^+ ions that have entered into these crystals. Perhaps, a small additional amount of iodine ions contributed by dopant TlI is also introduced into the mixed crystals in addition to that contributed by KI. This could also be a factor contributing to the differences in these spectra. Obviously, the suggested additional contribution of I^- ions from TlI would be higher in the case of 0.05 mol% of TlI doped crystals when compared to those doped with 0.01 mol% of TlI.

Optical absorption spectra of the KBr-KI mixed crystals grown in vacuum with the addition of 0.05 mol% of TlI in the melt (Fig.2d, Curves a, b and c) show composite A-bands which are slightly broader than those observed in 0.05 mol% of TlI doped mixed crystals grown in open air. In the case of mixed crystals with $x = 0.15$, the absorption in the A-band region appears to have broadened towards both low and high energy sides (Fig.2d, Curve c). Except for the presence of shoulders around 5.35–5.45 eV, the absorption in the B- and C-band region remains broad and featureless.

Optical absorption and luminescence studies (mainly at low temperatures) on $KBr_{1-x}I_x$:Tl^+ mixed crystals have been reported by a few authors[12–14]. Kleemann and Fischer[12] found that, at RT, the spectral peak position of the asymmetrical A-band absorption in $KBr_{1-x}I_x$:Tl^+ ($0<x<0.17$) mixed crystals grown from the melt in air shifted towards low energy side while its half width increased with iodine composition (x). From their figure indicating the variation of spectral peak position and half width of the A-band with iodine composition x at RT (figures of absorption spectra measured at RT were not shown in their report), it is verified that the behavior of the A-band in the air-grown $KBr_{1-x}I_x$:Tl^+ (0.01 mol%) mixed crystals of the present study is similar to that reported in their work.

However, at 20 K, 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 at 4.66, 4.55 and 4.44 eV appearing and growing (one after the other) at the cost of A_0 band at 4.8 eV 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^- ions respectively as nearest neighbors to the Tl^+ ions The existence of threshold compositions of iodine for the appearance of these additional A-bands was attributed to the non-uniform distribution of I^- ions in the mixed crystal lattice[12,13]. The additional bands observed at 5.74 and 5.4 eV on the low energy sides of B_0 and C_0 bands were designated as C_1 and B_1 bands respectively and they were attributed to $TlBr_5I$ centers. The B and C-bands of mixed centers with 2 and 3 I^- ion neighbours (i.e., B_2, C_2 and B_3, C_3 bands) are then expected to appear at still lower energies.

According to Kleemann and Fischer, the symmetry of the complex Tl^+ centre in the mixed configuration is reduced and this results in the splitting of the A-absorption band. In their model, the location of each component of the split band would be determined entirely by which anions overlapped the component of the p- function of the Tl^+ excited state that corresponds to the particular split component. The locations of the additional bands would then be independent of the nature of the residual anions in the centre.

However, from the theoretical calculations for the Tl^+ doped KBr-KI mixed crystal systems, Kristofel[14] attributed the A_0 and A_3 bands to the component phosphor bands (namely, A band of $KBr:Tl^+$ and $KI:Tl^+$ crystals respectively) and suggested that $TlBr_5I$ and $TlBrI_5$ are the only principal types of mixed centers formed in the mixed crystals giving rise to A_1 and A_2 bands respectively in between A_0 and A_3 bands. Tarasova and Shatseva[21] in their work on luminescence and excitation spectra of KCl-KBr mixed crystals doped with Tl^+ ions, observed that emission and excitation bands of their system did not behave in conformity with the above two models. They suggested that new bands in mixed crystals are due to the covalent interaction of the activator ion with nearby anions and the number of new bands corresponds to the number of mixed halide complexes formed by thallium in aqueous solution of the same alkali halide salts. Thus, in mixed alkali halide systems doped with thallous ions, the nature of the mixed centers giving rise to the additional absorption bands is not yet clear due to such controversies.

In the present study, the observed shift and broadening of the absorption bands in the A- band region towards the low energy side and the broadening and appearance of new bands on the low energy side of B and C bands in the mixed crystals of the present study could be attributed to the formation of such complex Tl^+ centers at the cost of $TlBr_6$ complexes.

Among the A, B and C bands of ns^2 ions in alkali halide single crystals, the C band is the strongest since it is associated with the symmetry- and spin-allowed transition $^1A_{1g}\rightarrow{}^1T_{1u}^*$[1,2]. 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[1]. Hence it is reasonable to expect that the intensity of C_n band of a particular $TlBr_{6-n}I_n$ (n=0, 1, 2, 3) complex center in $KBr_{1-x}I_x:Tl^+$ mixed crystals is relatively higher than the corresponding A_n band. This could be a reason for the relatively larger increase in the absorption on the low energy side of C_0 band (5.95 eV) with increasing iodine composition in the mixed crystals. The 5.74eV absorption band (Fig.2a, Curve b) is attributable to C_1 band[12].

The intensity of the 5.6 eV absorption band in $KBr_{0.9}I_{0.1}:Tl^+$ mixed crystals (Fig.2a, Curve c) is much higher than the B-band observed at 5.6 eV in $KBr:Tl^+$ single crystals (i.e., B_0-band in $KBr_{1-x}I_x:Tl^+$ mixed crystals). This may be related to the formation of some new complex centers in the mixed crystals at the cost of $TlBr_6$ centers rather than an enhancement of the B_0-band absorption since a decrease in the intensity of the A_0-band (4.8 eV) due to a reduction in the concentration of $TlBr_6$ centers will also cause a similar decrease in the corresponding B_0 and C_0 bands observed at 5.6 and 5.95 eV respectively. Therefore, the increase in intensity of absorption around 5.6 eV may be due to the appearance of an additional C-band of some of the complex Tl^+ centers with more than one iodine ions as nearest neighbour to the Tl^+ ion. By similar arguments it may be suggested that the band around 5.35−5.40 eV also has a contribution due to C-band of some thallium complex center ion the mixed configuration. The absorption bands around 5.6 and between 5.35−5.4 eV are tentatively assigned to C_2 and C_3 bands respectively. From the RT spectra of the present study, the position of the B_1, B_2 and B_3 absorption bands are not known clearly perhaps they are masked by the relatively stronger C bands.

As mentioned earlier, samples of the present study contain some OH^- ions. The reported peak position of the broad optical absorption band due to OH^- ions in KBr (5.79 eV)[22] is very close to the C_1 absorption band (around 5.74 eV) of the $KBr_{1-x}I_x:Tl^+$ mixed crystals of the present study. If OH^- ions present in the mixed crystals of the present study are assumed to give rise to an absorption band in the UV region similar to the ones observed in the single crystals of alkali halides, then the broad absorption bands of the mixed crystals of the present study in the B and C-band region may have some contribution from the absorption band due to OH^- ions also. Due to overlap with other bands in that region, it is not resolved.

In the Tl^+ doped KBr-KI mixed crystals of the present study, due to the considerable overlap of different A-bands of the thallium complex centres in the A-band region as well as the changes in their relative intensities with x, the absorption in the A-band region inhomogenously broadens towards low energy side. In these optical absorption spectra, the presence of the A_0 band (4.8 eV) is not obvious. However, it could be identified from the PL emission and excitation spectra of these mixed crystals (recorded using a Jobin Yvon–Spex (ModelFL3-11) spectro fluorometer)[17]. In all these mixed crystals, photo excitation at A_0 band produced two overlapping emission bands around 3.9 and 3.45 eV which resembled the characteristic A_T and A_X emission bands of $KBr:Tl^+$ single crystals[19]. The excitation spectra for the above PL emission bands (in mixed crystals of the present study) clearly indicated the presence of 4.8 eV excitation band as a shoulder to a relatively strong excitation band around 4.6 eV. Thus the shoulder around 4.8 eV is identified as the A_0-band due to $TlBr_6$ centres in the mixed crystals. This conclusion follows the results and interpretation of the temperature behaviour of the PL emission characteristics of A_0-band at low temperatures (20 K and 77 K) in the $KBr_{1-x}I_x:Tl^+$ mixed crystals which was found to be similar to that of the A-band emission in $KBr:Tl^+$ single crystals observed around these temperatures[12].

Photo-excitation at photon energies lower than 4.8 eV produced a very broad and asymmetrical emission band around 3.6 eV whose spectral peak position shifted to lower energies with *x*. In addition, an emission shoulder around 420 nm (2.9 eV), whose intensity increased with iodine composition *x*, was also observed. The PL excitation bands in the A-band region for λ_{em} = 320 and 420 nm in $KBr_{0.85}I_{0.15}:Tl^+$ (0.05 mol%) mixed crystals normalized to unity at their peak values are shown in Fig.3.

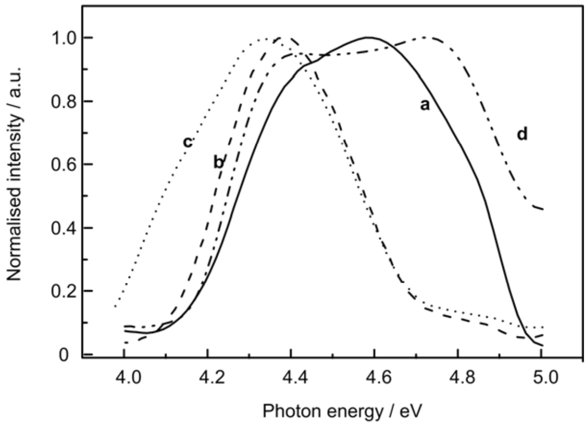

Fig.3 Comparison of A-band absorption of $KBr_{0.85}I_{0.15}:TlI$ (0.05 mol%) with PL excitation bands.

For comparison, normalized excitation spectrum for λ_{em}=420 nm in $KBr_{0.85}I_{0.15}:Tl^+$ (0.01 mol%) mixed crystals and the normalized A-band absorption in $KBr_{0.85}I_{0.15}:Tl^+$ (0.05 mol%) mixed crystals are also shown in the same figure. The excitation spectrum for λ_{em}=320 nm (Fig.3, curve a) clearly indicates the presence of overlapping excitation bands around 4.4, 4.6 and 4.8 eV respectively. By comparing with the earlier report[12], the 4.4 eV band could be identified as the A_3 band and the 4.6 eV excitation band to A_1 and/or A_2 bands. Perhaps the A_1 and A_2 bands are not resolved at RT. However, the shift of the 4.6 eV PL excitation band towards low energy side with x may be related to the change in their relative intensities. In the absorption spectra of the present study the 4.6 eV band is not resolved due to overlap with other A-bands.

In mixed crystals doped with 0.05 mol% of TlI, the 4.4 eV excitation band of the 420nm emission observed in crystals doped with 0.01 mol% of thallium iodide (Fig.3, Curve b) shifts its peak position slightly and also it broadens inhomogeneously towards long wavelength side indicating the presence of a shoulder around 4.15 eV on its low energy side (Fig.3, curve c). This new band falls in the low energy tail region of the A-band absorption where no structure of any absorption band could be identified. This type of behaviour observed at RT in heavily doped KBr:Tl^+ has been related to the Tl^+ dimer aggregate centers [3,20]. The weak absorption bands due to these dimer centers on the long wavelength tail of much stronger A, B and C bands were observed only at low temperatures, and at high temperatures their presence is identified from the broadening of A, B and C absorption bands towards low energy side. However, their structure is better expressed in the excitation spectra for their emission bands, which contain an additional emission band (mainly at low temperatures) on the long wavelength side of the monomer like emission bands[3]. In heavily doped KI:Tl^+ crystals, the excitation peaks of some of the A- emission bands were found to be located on the low energy side edge of the A-absorption band and they were attributed to aggregates of thallium with some impurity[23]. Higher aggregates of Tl^+ ions such as, trimers, tetramers etc have also been reported to be formed in heavily and very heavily doped KBr:Tl^+ crystals[24,25] which were identified from additional absorption and emission bands on the low energy side of the monomer A-band absorption and emission respectively. In the present study, the appearance of the 4.15 eV excitation band is tentatively related to the formation of aggregates of some complex Tl^+ centers in the mixed configuration. Hashimoto *et al.*, have assigned the 4.35 eV absorption band observed at 4 K in their $KBr_{1-x}I_x$:Tl^+ thin films samples to the aggregates of centers responsible for the A_2 absorption band[13]. Thus, the broadening of the 4.4 eV excitation band without a corresponding structure in the optical absorption spectra of the present study (except for a broadening in its low energy tail region) may be attributed to some unidentified aggregates of complex Tl^+ centers formed in the mixed crystals of the present study . The abovementioned aggregation process (present study) is speculated to be induced by the presence of relatively larger iodine content since I^- ions are selectively collected around the Tl^+ activator ions in the mixed alkali halide crystals. When the concentration of Tl^+ ions is also higher, the formation of such aggregates by a similar preferential and selective association will be more probable. Optical absorption and other studies such as polarized luminescence and luminescence decay at low temperatures are required to confirm this view.

Optical absorption spectra of γ-irradiated $KBr_{1-x}I_x$:Tl^+ mixed crystals (gamma dose= 500 Gy) are reported in the present work. The spectra show the presence of F-band whose peak position shifts towards low energy side with iodine composition as shown in Fig.4, for γ-irradiated $KBr_{1-x}I_x$:Tl^+ (0.01 mol%) mixed crystals grown in vacuum with x = 0.0, 0.05, 0.10, 0.15 and 1.0. In mixed crystals, the F-band peak position does not follow the Mollwo-Ivey relation[26]. F-absorption bands in gamma irradiated KBr:Tl^+ and KI:Tl^+ appear around 1.98 and 1.80 eV respectively (Fig.4, Curves a and e). In the case of vacuum grown $KBr_{1-x}I_x$:Tl^+ (0.01 mol%) mixed crystals with x = 0.05, 0.10, 0.15 (Fig. 4, Curves c, d and e), F-band appears around 1.97, 1.95 and 1.925 eV, respectively. Earlier Reitz *et al*[27] studied F-band absorption in additively colored undoped KBr–KI mixed crystals. For similar compositions, the F-band peak positions of the present study are comparable but slightly on the low energy side of the earlier reported values. In addition to the spectral shift of the F-band towards low energy side, a slight increase in the half width of F-band with x was also observed. Smakula *et al*[28] suggested that distortion of the crystalline electric field is the cause of spectral shift and broadening of the F-band in mixed alkali halides.

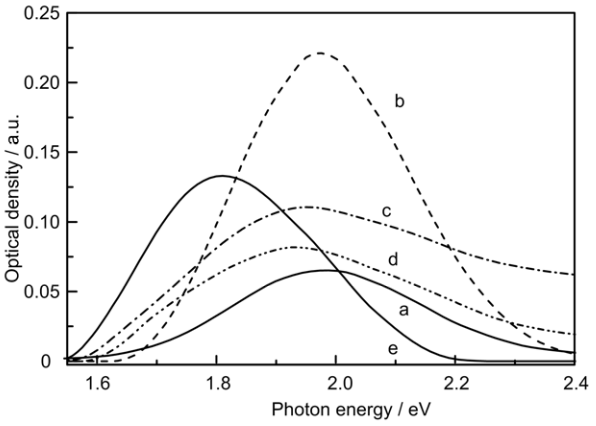

Fig.4 F-band in gamma irradiated KBr$_{1-x}$I$_x$:TlI (0.01 mol%) mixed crystals grown in vacuum, (a) x=0.0, (b) x=0.05, (c) x=0.10, (d) x=0.15 and (e) x=1.0.

Apart from the appearance of F-band, upon γ-irradiation, the intensity of absorption in the A, B and C-bands regions due to the complex Tl$^+$ centers generally decreases slightly in most of the mixed crystals with different amounts of TlI and KI. However, some of them had a slight increase of absorption in the A-band region and the valley around 5 eV, but a decrease of absorption in the B and C-band region. As a typical example, absorption spectra of unirradiated and γ-irradiated KBr$_{0.95}$I$_{.05}$:Tl$^+$ mixed crystals grown in open air are shown in Fig.5.

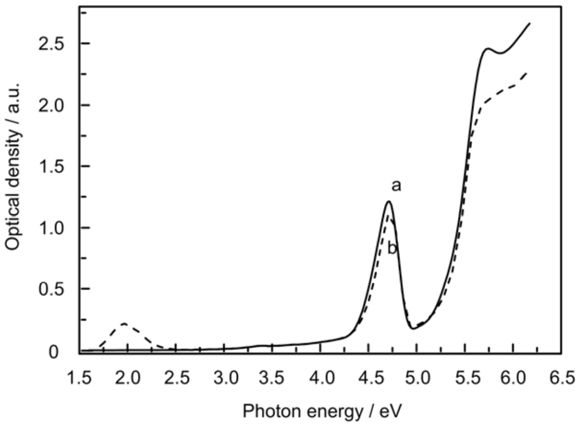

Fig.5 Optical absorption spectra of KBr$_{0.95}$I$_{0.05}$:TlI (0.01 mol%) mixed crystals, (a) unirradiated and (b) gamma-irradiated (dose=500 Gy).

The reduction in intensity of A, B and C absorption bands can be correlated to the formation of F-centers by assuming a change in the valence state of Tl$^+$ ions to Tl^{2+} upon irradiation[29]. The observed increase in the intensity of the absorption in the A-band region of some of the mixed crystals after irradiation may be due to the formation of V type centers in them during irradiation. In undoped KBr, X-ray irradiation at RT is reported to produce V$_2$-absorption band around 4.7 eV[30] and V$_3$-band around 4.85 eV in the optical absorption spectra[31]. If V$_2$ and V$_3$ centers are formed on irradiation in the mixed crystals of the present study, then the appearance of these V-bands will increase the absorption around the A-band region of the spectra while the change in the valence state of some of the Tl$^+$ ions to Tl^{2+} will reduce it. Depending on the relative magnitudes of these changes, the intensity of absorption in the A-band region will decrease or increase upon irradiation.

The intensity of F-band is higher in KBr$_{0.95}$I$_{05}$:Tl$^+$ mixed crystals when compared to that of KBr:Tl$^+$ single crystals (Fig.4). However, with further increase in iodine composition, the F-band intensity decreases. Same trend has been observed in each series of the mixed crystals. These changes in intensity of F-band could be related to various factors such as the actual concentration of Tl$^+$ ions and I$^-$ ions in the samples, the number of Tl$^+$ ions that have changed their valence state to Tl^{2+} on irradiation, concentration of V-centers produced etc. Generally, in most of the mixed alkali halides, the intensity of F-band is less than that observed in any of the two base materials for the same dose of irradiation[26,28]. This reduction in the F-band intensity with increasing impurity anion composition has been attributed to the lattice distortion in the mixed crystal lattice that decreases the trapping of electrons by anion vacancies during irradiation. However, in the case of 3-MeV electron irradiated (−190℃) undoped KCl-KBr mixed crystals, Smakula *et al*[28] observed a variation in the intensity of F-band which was similar to that observed in the present study. These authors suggested that such a complicated intensity change in KCl-KBr mixed crystals is an indication that the solid solution might not be completely random at all compositions. As discussed earlier, in the mixed crystals of the present study also the impurity anions (I$^-$ ions) are not randomly distributed but are preferentially collected around the

Tl^+ activator ions. Although the suggested mechanism of F-centre formation in the Tl^+ ions doped KBr-KI mixed crystals of the present study is different from that in undoped mixed alkali halides[26], the similarity between the experimental observations on these two systems lead us to conclude that the intensity variation of F-band in the present study could be due to the preferential association of I^- ions with Tl^+ ions in the KBr-KI mixed crystals.

The peak position of F-band observed in irradiated mixed crystals plotted as a function of the iodine composition x is shown in Fig.6.

Generally, the spectral peak position of the F-band shifts towards low energy side with x[26]. In mixed crystals grown in air, the variation in peak position with x is relatively small in the 0.01 mol% TlI-doped crystals, compared to that in 0.05mol% TlI-doped crystals. Similarly the peak position of F-band in a mixed crystal grown in air is at higher photon energy than that grown in vacuum with the same x and the same amount of TlI. The difference in the rates at which F-band peak position shifts with x in the $KBr_{1-x}I_x:Tl^+$ mixed crystals is attributed to the different amounts of iodine anions present in the mixed crystals.

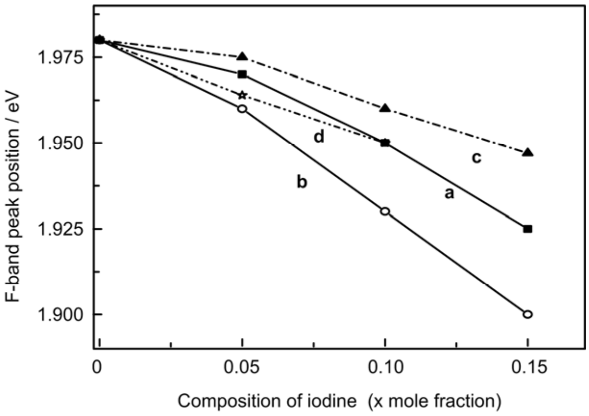

Fig.6 F-band Peak position in $KBr_{1-x}I_x$:TlI doped mixed crystals grown in vacuum, (a) 0.01 mol%, (b) 0.05 mol% of TlI in the melt and in open air, (c) 0.01 mol% and (d) 0.05 mol% of TlI in the melt

4 Conclusion

The changes in the half width of the absorption spectra and the spectral peak position by doping with KI may be accounted for by the superposition of two or more absorption bands corresponding to the complex Tl^+ centers with Tl^+ ions surrounded by different numbers of I^- ions. The broadening and poor structure of A and B absorption bands of the KBr-KI:TlI is probably due to the appearance of new absorption bands on the low energy side of these bands closely located to each other and not resolved. The appearance of new bands is caused by the coexistence of these complex centers

By comparing with earlier reports, these additional bands are attributed to Tl^+ ions of the complex centers of the type $TlBr_{6-n}I_n$ (n=1,2…5). These centers are formed, perhaps, in more numbers than the actual composition of Iodine ions, which is attributable to the preferential enrichment of I^- ions around the Tl^+ ions even for a lower composition of I^- ions.

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