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Archives of Applied Science Research, 2011, 3 (2):143-154

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ISSN 0975-508X
CODEN (USA) AASRC9

Photoluminescence Behavior of $KBr_{1-X}I_X$: TlI Mixed Crystals

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ABSTRACT

Results on Photoluminescence (PL) studies of $KBr_{1-x}I_x$:TlI (0.01 mol%) mixed crystals grown in vacuum and open air atmosphere are presented in this paper. PL emission spectra of the mixed crystals excited in the A-absorption band of KBr:Tl^+ exhibited the characteristic emission bands of Tl^+ ions in KBr:Tl^+. When excited in the low energy tail of A-band absorption, a broad asymmetrical emission band around 3.64eV with long tail on the low energy side were observed. Comparing with earlier reports, excitation bands observed around 4.8, 4.6 and 4.4eV are attributed to complex thallium centres of the form $TlBr_{6-n}I_n$ (n = 0, 1, 2, 3).

Keywords: Photo luminescence; mixed crystals; Tl^+ doped KBr-KI Mixed crystals, A_X-A_T emission and complex centers.

INTRODUCTION

The luminescence in alkali halides doped with Tl^+-like impurities have been thoroughly investigated [1]. It mainly exhibit three absorption bands namely as A, B and C bands in the order of increasing energy. The absorption and emission spectra produces due to transition between $6s^2$ ground state and 6s6p first excited state are complex and depends on various factors such as Jahn-Teller effect, spin-orbit interaction, etc. [1]. However excitation in the A-band leads to the observation of two emission bands termed as A_T and A_X emission bands in the order of decreasing energy. Donahue and Teegarden [2] found that at very low temperatures (20K) the A_X emission is quenched while only A_T emission appeared at 3.94eV. With increasing temperature A_X emission appears and grows at the cost of A_T emission. Around 80K the two emission bands are well resolved. In contrast, the emission spectrum of KI (Tl^+) at 300K when excited in the A-band showed a broad band with peak at 3.02eV with a high energy tail which was fitted into a weak emission band around 3.47eV. The 3.02eV emission is the A_X emission of KI:Tl [2].

Kleemann and Fischer studied the optical absorption and luminescence of $KBr_{1-x}I_x$:Tl^+ mixed crystals at low temperatures (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 A_0 band in the mixed crystals was found to have the similar optical and luminescence characteristics to the A-band in KBr:Tl^+ single crystals. This band was attributed to the $TlBr_6$ centers (i.e, a Tl^+ ion surrounded by six Br^- ions as nearest neighbors) in the mixed crystals. The other additional A-absorption absorption bands at 4.66, 4.55 and 4.44eV (designated as $A_{1,}$ A_2 and A_3 bands respectively) which grew with x at the cost of A_0-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.

A number of alkali halide phosphors doped with impurities such as Eu^{2+}, Tl^+, Ga^{2+}, etc. have been investigated for their suitability as PSL X-ray storage phosphors employed in X-ray imaging plates [4-7]. Among them, CsBr:Eu^{2+} and RbBr:Tl^+ have already been commercialized [4,6]. Recently some Eu^{2+} ions and Tl^+ co-doped alkali halides have been found to have attractive PSL characteristics [8-11]. To our knowledge a thorough investigation of PL studies on thallium doped KBr-KI mixed crystals at RT is still lacking.

MATERIALS AND METHODS

The systems studied in the present work are KBr_{1-x} $I_{x:}$TlI (0.01mol%) mixed crystals grown in vacuum and open air atmosphere with x = 0.05, 0.10 and 0.15 by slow cooling from their melt. Analytical Reagent grade KBr and KI (99.9%) and the dopant in the form of TlI (99.99%) were taken in the required stoichiometric proportions as described in our earlier work[12]. The Photoluminescence (PL) measurements were carried out using a JOBIN YVON-Spex (Model FL3-11) spectrofluorometer. Spectral corrections were not made for the instrumental response.

RESULT AND DISCUSSION

PL emission of KBr:TlI under excitation at 258nm (4.80eV, A-band absorption in KBr:Tl^+) is known to produce two emission bands at 3.46eV and 3.94eV at room temperature (RT). The broad PL emission bands deconvoluted by Peak Fit software is shown in inset of Fig.1. At RT these bands are not completely resolved and the 3.46eV emission (known as A_X- emission) is slightly less intense than the 3.94eV emission (known as A_T emission) [13]. However, the shape and structure of the emission spectrum of KBr:Tl^+ does not change upon excitation at other wavelengths within the A-band as well as upon excitation in the B and C bands.

The normalized PL emission spectrum of $KBr_{0.95}I_{0.05}$:TlI (0.01mol%) grown in vacuum excited in the A_0-band at 258nm (4.80eV, A-band absorption in KBr:Tl^+) shows two emission bands resembling the A_T and A_X emission bands of KBr:Tl^+ single crystals (Fig.2.(A), curve a). However, unlike the case of KBr: Tl^+, where the intensity of A_{X}-emission is slightly lower than that of A_T emission, both the emission bands of $KBr_{0.95}I_{0.05}$: TlI crystals have nearly equal intensities. Excitation at 270nm (4.59eV) shows a broad asymmetrical emission band with peak at 3.64eV.

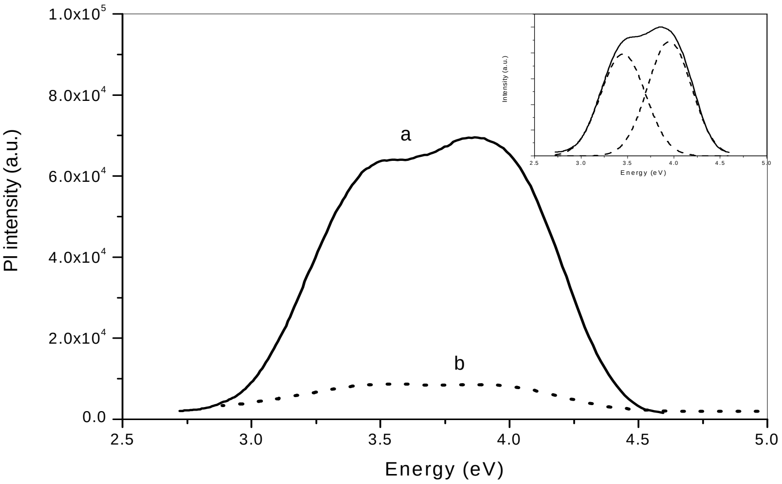

Fig. 1. PL emission spectra of KBr:TlI (0.01mol%) grown in vacuum for λ_{ex} = 258nm a) and λ_{ex} = 220nm b). Inset shows the deconvolution of a).

It has a long tail on the low energy side (Fig.2. (A) Curve b). The peak intensity is considerably higher than that of the emission under 4.8eV excitation. Exciting the crystal by radiation of wavelength 280nm (4.43eV) produces a broad emission with spectral peak position at 3.62eV (Fig.2. (A), curve c). The structure of the emission spectrum is similar to that observed with excitation at 270nm. But the peak intensity is slightly less than that for 270nm excitation (Fig.2. (A), curve b). Only weak emission observed when the crystal is excited in the B and C bands (5-6eV) show only weak emissions.

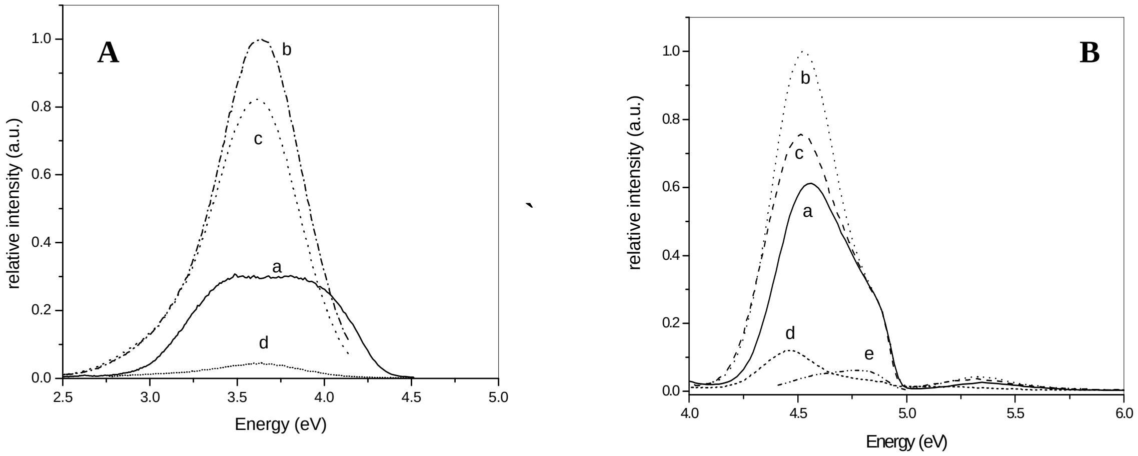

Fig.2. (A) PL Emission spectra of KBr$_{.95}$ I$_{.05}$:TlI (0.01mol%) mixed crystal grown in vacuum excited at different wavelengths λ_{ex} = 258 a), 270 b), 280 c) and 233nm d).
(B). PL excitation spectra of KBr$_{.95}$ I$_{.05}$: Tl^{+} (0.01mol %) mixed crystal grown in vacuum excited at different wavelengths λ_{em} = 320 a), 343 b), 360 c) 420 d) and 300nm e).

Excitations at 233nm (5.32eV) and 220nm (5.64eV) shows weak emission spectra whose structures and composition resemble that of the emission due to the excitation at 270nm. For brevity, only the PL emission for 233nm excitation is shown by curve d in Fig.2. (A). The excitation at 210nm exhibits an emission spectrum (consisting of two bands around 3.5-4.0eV) which is similar to the emission for 258nm excitation (Figure not shown). However, their intensities are very small.

The PL excitation spectra of $KBr_{0.95}I_{0.05}$:TlI (0.01mol%) crystals for wavelengths of emission at 320nm (around 3.94eV), 343nm (3.62eV), 360nm (3.4eV), and 420nm (2.95eV) (Fig.2.(B), curves a-e respectively) show main excitation peaks at 4.54. 4.52, 4.51 and 4.46eV respectively in the A-band absorption region (4-5eV).

In all these cases, a prominent shoulder around 4.8eV is seen. The 4.8eV band is the A_0-band absorption reported by Kleeman and Fischer in their KBr-KI (Tl^+) mixed crystals at low temperatures [3]. In the region between 5-6eV (B and C-band absorption region), a broad and weak excitation band appears around 5.4eV for the 320nm emission and it shifts towards low energy side in the excitation spectra for longer wavelengths of emission. The intensity of the main excitation band for λ_{em} = 360nm (curve c) is higher than that for λ_{em} = 320nm (curve a) but it is slightly less intense than the 4.52eV excitation band for the 343nm (3.62eV) excitation (curve b). In these three cases, the 4.8eV shoulder has nearly the same intensity. This is due to the fact that the emission spectrum for 4.8eV excitation (Fig.2. (A), curve a) is nearly flat having nearly the same intensity between 3.4 and 3.9eV. The excitation bands for 420nm emission (curve d) are much weaker than those for the other wavelengths discussed above. The shift of peak positions of excitation bands for different emission wavelengths may be due to the overlap of different emission bands. The PL excitation spectra for λ_{em} = 300nm shows a weak band around 4.8eV which has a long tail on the low energy side (Fig.2. (B), curve e).

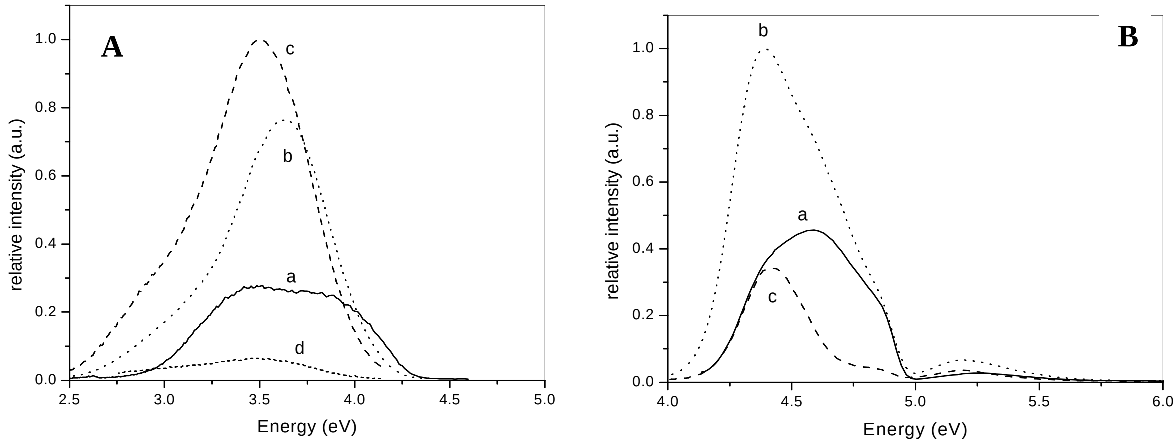

Fig.3.(A). PL Emission spectra of $KBr_{.9}$ $I_{.10}$:TlI (0.01mol%) mixed crystal grown in vacuum excited at different wavelengths λ_{ex} = 258 a), 270 b), 280 c) and 240nm d).
(B). PL excitation spectra of $KBr_{.9}$ $I_{.10}$: TlI (0.01mol %) mixed crystal grown in vacuum excited at different wavelengths λ_{em} = 320 a), 350 b) and 420nm c).

The PL emission peak positions are slightly shifted towards low energy side for $KBr_{0.90}I_{0.10}$:TlI (0.01mol%) crystals with λ_{ex} = 258, 270 and 280nm (Fig.3 (A), curves a, b and c respectively). In the PL emission for λ_{ex} = 258nm (A_0-band), the intensity of emission around the A_x emission of KBr:Tl (3.46eV) relative to that of its A_T emission (3.94eV) is slightly higher (Fig.1 curve a).

Unlike the case of $KBr_{0.95}$ $I_{0.05}$: TlI crystals, the emission for 280nm excitation has higher intensity than the emission for 270nm excitation in $KBr_{0.90}I_{0.10}$: TlI (0.01mol %) crystals. In addition, the peak position of emission shifts to a longer wavelength. Further, an additional shoulder around 2.9-3.0eV is observed in the emission for λ_{ex} = 280nm. The same shoulder, though not prominent, is also observed in the PL emission λ_{ex} = 270nm. These results suggest that some new thallium centers involving I^- ions whose absorption band is around 280nm (4.43eV) grow with iodide ion composition x in the KBr_{1-x} I_x: TlI mixed crystals.

The excitation at 240nm (5.17eV) also produces a weak emission spectrum (Fig.3 (A), curve d), which is similar in composition to the above emission spectrum for 280nm excitation. Hence the 280nm and 240nm excitation bands may be related to the same complex Tl^+ centers.

The excitation spectrum for emission at 320nm in vacuum grown $KBr_{0.90}$ $I_{0.10}$:TlI (0.01mol%) crystal shows a broad excitation band around 4.59eV with shoulders around 4.4 and 4.8eV in the A-band region while the weak excitation band in the B and C-band region is broad extending from 5.0-5.75eV (Fig.3 (B), curve a). The excitation spectrum for λ_{em} = 350nm (3.54eV) of the same crystal (Fig.3 (B), curve b) shows an excitation band around 4.45eV with unresolved shoulder around 4.6eV and 4.8eV in the A-band region.

The excitation spectrum for λ_{em} = 420nm in $KBr_{0.9}I_{0.10}$:TlI (0.01mol%) shows a prominent band around 4.42eV (Fig. Fig.3 (B), curve c). The excitation bands around 4.6 and 4.8eV that are seen prominently for λ_{em} = 350nm are suppressed. The excitation band around 4.42eV is the main excitation band for λ_{em} = 420nm (2.95eV) (Fig.3 (B), curve c). The intensity of the excitation band around 4.42eV for λ_{em} = 420nm is higher (almost double) in $KBr_{0.9}I_{0.10}$:TlI (0.01mol%) than that observed in $KBr_{0.95}I_{0.05}$:TlI (0.01mol%) mixed crystals grown in vacuum. This band is not seen prominently/ not resolved in the excitation spectra for 360 and 320nm emission wavelengths in $KBr_{0.95}I_{0.05}$:TlI (0.01mol%) crystal. Hence it is evident that the 4.4-4.5eV excitation band grows with increasing iodine composition. Comparing the excitation spectra for λ_{em} = 350nm and 420nm (Fig.3 (B), curves b and c respectively), it is obvious that the emission at these two wavelengths are excited by radiation of wavelengths around 280nm (4.43eV). Comparing with earlier reports by Kleemann and Fischer [3] and Hashimoto et al [14], the excitation band around 4.45eV closely resembles the A_3-absorption band due to complex $TlBr_{6-n}$ I_n centres with n = 3. Thus it may be concluded that when the KBr-KI (Tl^+) mixed crystals are excited at RT in the A_3 absorption band (4.43eV) two emission bands are observed around 350nm (3.54eV) and 420 nm (2.95eV) respectively.

The presence of a shoulder around 4.6eV in both the PL excitation spectra for λ_{em} = 320nm and 350nm (Fig.3 (B), curve a and b respectively) could be considered as an indication that the PL emission spectrum for λ_{ex} = 270nm also contains two emission bands around 320 and 350-360nm. The observed enhancement in the intensity of A_X emission (around 360nm) with x may be related to the increase in the concentration of complex $TlBr_{6-n}$ I_n centers responsible for those emission and excitation bands.

The PL emission spectra of $KBr_{0.85}I_{0.15}$:TlI (0.01mol%) mixed crystal excited at different wavelengths show bands which are similar to those observed in mixed crystals with x = 0.10 (Fig.4 (A)). However, there are some changes in relative intensities and peak positions which are slightly shifted towards low energy side. There is a further decrease (slight) with x in the relative intensity of the emission bands for λ_{ex} = 270nm (4.59eV) relative to those for λ_{ex} = 280nm (4.43eV). This change is observed upon comparing the emission spectra of mixed crystals with x = 0.15 with those having x = 0.05 and x = 0.10 for the abovementioned wavelengths of excitations (Figs. 2, 3 and 4 (A)). Also, the emission shoulder around 2.9-3.0eV in $KBr_{0.85}I_{0.15}$: TlI (0.01mol %) is relatively more prominent than the other two cases.

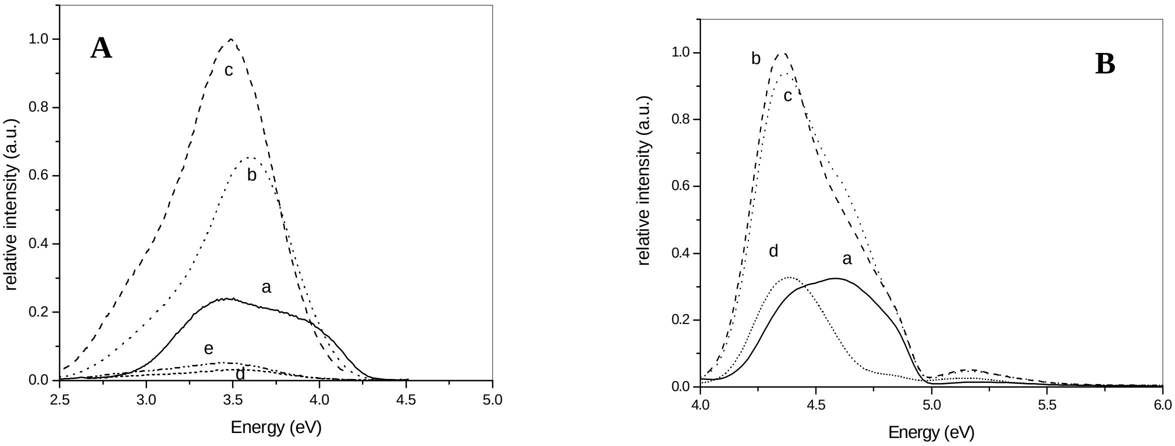

Fig.4. (A) PL Emission spectra of $KBr_{.85}$ $I_{.15}$: TlI (0.01mol %) mixed crystal grown in vacuum excited at different wavelengths λ_{ex} = 258 a), 270 b), 280 c) 233 d) and 240nm e).
(B). PL Excitation spectra of $KBr_{.85}$ $I_{.15}$: TlI (0.01mol %) mixed crystal grown in vacuum excited at different wavelengths λ_{em} = 320 a), 360 b), 350 c) and 420nm d).

The PL excitation spectra for different wavelengths within the emission bands (Fig.4 (B)) are also similar to those observed in $KBr_{.9}$ $I_{.10}$: TlI (0.01 mol %) mixed crystal. However, the excitation peaks are shifted slightly further towards low energy side. The main excitation band for λ_{em} = 420nm is observed at 4.38eV. Although the relative intensity does not increase appreciably, the excitation band at 4.38eV (Fig. 4(B), curve d) is considerably wider than the 4.42eV excitation band for mixed crystal with x = 0.05 and x = 0.10 (Figs. 2 and 3 (B), curves d and c respectively).

Similarly the PL emission and excitation spectra of KBr_{1-x} I_x:TlI (0.01 mol%) mixed crystal samples grown in open air (figures not shown) which are similar to those observed vacuum grown samples. However, for a given excitation, (especially for λ_{ex} = 270 and 280nm) spectral peak position of emission is slightly on the high energy side in the case of air grown crystals when compared to the corresponding mixed crystals grown in vacuum.

Kleemann and Fischer [3] studied PL spectra of Tl^+ doped KBr-KI crystals at 20K and 78K. The mixed crystals excited in the A_0-band (4.8eV absorption band) showed two emission bands at 3.46eV and 3.94eV which were closely related to the A-band emission (A_X and A_T emission bands respectively) in $KBr:Tl^+$ single crystals [2,13]. These authors found that these emission bands in the mixed crystals showed the same temperature behaviors as that of the A_X and A_T emission of $KBr:Tl^+$. Hence, the 4.8eV absorption band was attributed to the $TlBr_6$ complex centres (i.e, Tl^+ ions surrounded by six Br^- ions as nearest neighbor). They observed that excitation at A_1 and A_2 absorption bands resulted in an emission spectrum containing the same two bands which were shifted towards low energy side relative to the A_X and A_T emission bands excited in the A_0-band.

Kleemann and Fischer observed different sets of double emission bands upon excitation at A_1/A_2 and A_3 absorption bands. The temperature dependence of the intensities of the emission bands was similar to that of A_T and A_X emission bands observed when $KBr:Tl^+$ single crystals are excited in the A-band absorption (4.8eV). For simplicity, we denote the A_T and A_X emission bands due to excitation at A_0; A_1 or A_2 and A_3 absorption bands as $(A_T)_{0,}$ $(A_X)_{0, ;}$ $(A_T)_{1,2}$ $(A_X)_{1, 2}$ and $(A_T)_3$ and $(A_X)_3$ emissions respectively.

At 20K, for very low I^- compositions, excitation at various complex A-bands produced only their corresponding A_T emissions. Ax emissions appeared at higher iodine compositions only. While the A_T emission band due to A_0 and A_3 excitations (ie, $(A_T)_0$ and $(A_T)_3$ emissions) appeared around 4.0eV and 3.4eV respectively, the A_T emission due to A_1 /A_2 excitation (ie, $(A_T)_{1, 2}$ emission) appeared around 3.7eV. When the temperature was increased from 20K to 78K, A_X emission due to particular type of complex center was found to grow at the cost of its corresponding (A_T) emission. At 78K, in 6% KI doped KBr-KI (Tl^+) mixed crystals, $(A_X)_0$, $(A_X)_{1, 2}$ and $(A_X)_3$ bands appeared around 3.4, 3.00 and 2.85eV respectively. At 20K, these authors found that $(A_T)_0$ and $(A_T)_{1, 2}$ (as well as their corresponding A_X emission bands) shifted their peak positions slightly towards low energy side with increasing iodine compositions. On the other hand, the $(A_T)_3$ emission was reported to shift slightly towards high energy side. (A_X) emission band due to A_1 / A_2 excitation ($(A_X)_{1, 2}$ emission) which appeared at 20K for slightly higher I^- compositions also showed a similar behavior for further increase in iodine composition. Interestingly, the relative intensity between A_T and A_X emission bands of a given set is different from the other sets. At 78K, the intensities of $(A_T)_3$ and $(A_X)_3$ were nearly equal; intensity of $(A_T)_0$ emissions was slightly higher than $(A_X)_0$ emission. On the other hand, intensity of $(A_T)_{1, 2}$ emissions were found to be higher than $(A_X)_{1, 2}$ by an order of magnitude.

In the present work, excitation at 4.8eV (peak of A_0- absorption band) produces an emission spectrum comparable to that of the A-band emission in $KBr:Tl^+$ single crystal. Also, the emission spectra for this excitation shift to low energy side with increasing iodine composition in agreement with the earlier report [3]. The excitation spectra of $KBr_{1-x}I_x$:TlI mixed crystals (present study) clearly indicated the presence of 4.8eV excitation band as a shoulder to a relatively strong excitation band around 4.6eV. Thus the shoulder around 4.8eV is identified as the A_0-band due to $TlBr_6$ centers 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 (20K and 77K) in the $KBr_{1-x}I_x$:TlI mixed crystals which was found to be similar to that of the A-band emission in $KBr:Tl^+$ single crystals observed around these temperatures [3]. Thus comparing with the earlier report, the 4.8eV excitation band is attributed to the A_0 band.

As discussed earlier, the emission spectrum observed for 270nm (4.59eV) excitation (in vacuum grown crystals) shows an emission band whose peak position shifts from 3.64eV to 3.63eV with the composition of I^- ions. This emission covers a wide spectral range from 2.5 to 4.3eV. The mixed crystals doped with higher amount of KI and / or TlI show the presence of an additional broad emission around 2.9- 3.0eV which appears as a shoulder. The excitation at 280nm produces similar emission spectra which are slightly red shifted. The additional emission around

2.9- 3.0eV is relatively more prominent for the 280nm excitation than for 270nm excitation in mixed crystals with x = 0.10 and x= 0.15. The relative intensity of the main excitation band at 4.4eV for emission around 420nm (2.9eV) increases with iodine composition. Comparing this result with the earlier report, the 4.4eV excitation band is identified as the A_3 band [3].

The excitation spectra for different wavelengths of emission in these samples show broad excitation bands which are not resolved completely. When the wavelength of excitation is increased, the corresponding emission spectra also show a similar behaviour. Generally, the PL emission and excitation spectra of Tl^+ doped alkali halides are broad at RT. Hence it is likely that excitation at a wavelength within a given excitation band produces emission bands due to other excitation bands that ly adjacent to it on either side

In our opinion, the so called "A_X emission" bands observed by Kleemann and Fischer at 20K in their work $KBr_{1-x}I_x$:Tl^+ mixed crystals for higher KI content [3], may not be the A_X-band of the particular complex A-band. Instead, it may be the weak A_T-emission due to partial excitation in the A_1/ A_2/ A_3 -complex A-bands that lies adjacent to it. This suggestion follows the facts that (i) even at 20K, the absorption bands due to complex Tl^+ centers (i.e, A_1, A_2, and A_3-absorption bands) show a considerable overlap [3] and (ii) only the A_T-emission band is excited at very low temperatures in many alkali halides doped with Tl^+ ion [15]. However, this suggestion requires further confirmation.

The shifting of the peak position of emission for excitation at a particular wavelength with iodine compositions may be attributed to the change in the relative intensity of these excitation bands with iodine composition. Earlier report on low temperature luminescence of KBr_{1-x} I_x: Tl^+ mixed crystals suggested that the various emission bands ((A_T) $_0$, (A_T) $_{1, 2}$ etc) shift their position in a complicated way depending on the iodine composition. In the absence of studies related to temperature variation of emission in these mixed crystals between 78K and RT, it is difficult to fix the number of emission bands, their spectral positions, half width, relative intensities etc at RT [3]. If this kind of shifting of peak position of each emission component with iodine compositions reported at low temperature is assumed to be present even at RT, then it can also be considered as a factor contributing to the observed shifting of the emission spectra at RT with I^- ion composition. In our opinion, the shifting of the peak position of the emission bands with iodine composition may be a result of the overlap of the excitation bands.

Excitation at 270nm and 280nm produce broad emission with maximum around 3.64 and 3.60eV respectively in $KBr_{0.95}$ $I_{0.05}$: TlI (0.01mol %) grown in vacuum. Though the presence of emission around 420nm is not evident, there is a slight increase in the intensity of emission around this position (Fig.2 (A), curve b and c). However, the excitation spectrum for λ_{ex} = 420nm in this crystals, shows a band around 4.46eV as the main component. Thus, A_3 band is observed even for x = 0.05 and it is found to grow with increasing I^- ion composition. The emission around 400-420nm could be the A_X component of the A_3 emission.

We speculate that, the broad emission in the region between 2.5 - 3.2eV consists of both (A_X) $_3$ and (A_X) $_{1, 2}$ emission bands with the (A_X) $_3$ emission lying on the low energy side around 2.9eV. The peak position of the (A_T) $_3$ emission band may be close to 3.4-3.5eV. This is the peak position of emission observed for 280nm excitation in $KBr_{0.85}$ $I_{0.15}$: Tl^+ (0.01mol %) crystals grown in vacuum. Similarly the $(A_T)_{1,2}$ emission may have its positions some where around 3.6-3.7eV. These positions are assumed tentatively by considering the overlap of A- band emission due to other centers[3]. Perhaps, at high temperature (RT), (A_x) bands of complex Tl^+ centers with one or more I^- neighbor are less intense than their corresponding A_T emission bands.

The approximate peak positions of $(A_T)_3$ and $(A_T)_{1,2}$ emission bands at 20K for small I^- concentrations as found from the PL emission spectra at 20K of the earlier report were around 3.4 and 3.7eV respectively [3]. Considering this fact together with the observed PL in the present study, the tentative peak positions of these emission bands at RT appears to be reasonable. However, the study of variation of PL emission and excitation spectra in the temperature range between 77K to RT would reveal a clear picture.

Kleemann and Fischer in their KBr-KI (Tl^+) mixed crystals at low temperatures did not discuss the presence of B and C excitation bands in their PL studies. Comparing with earlier results [3,16], the absorption bands at 5.6, 5.4, 5.95, 5.74 and in the region 5.35-5.4eV have been identified tentatively as the B_0, B_1, C_0, C_1 and C_2, C_3 absorption bands respectively. Since, the PL excitation bands in the B and C-bands region are weak and overlapped, they could not be identified clearly. However, the weak excitation bands in the B and C bands region are found to shifts towards low energy side with x as observed in the optical absorption spectra .C-bands are absent in the excitation spectra for different emission wavelengths. This seems peculiar in the sense that C-bands are the most prominent in the absorption spectra [16]. Perhaps the C-band emission is quenched in the mixed crystals as observed in the case of KI:Tl^+ where one of the three C-bands (C_1- band) was found to be quenched at RT [15, 17].

The variation in spectral peak positions of excitation bands for various emission bands in $KBr_{1-x}I_x$:TlI (0.01 mol%) mixed crystals grown in vacuum and open air atmosphere is shown in Fig. 5.

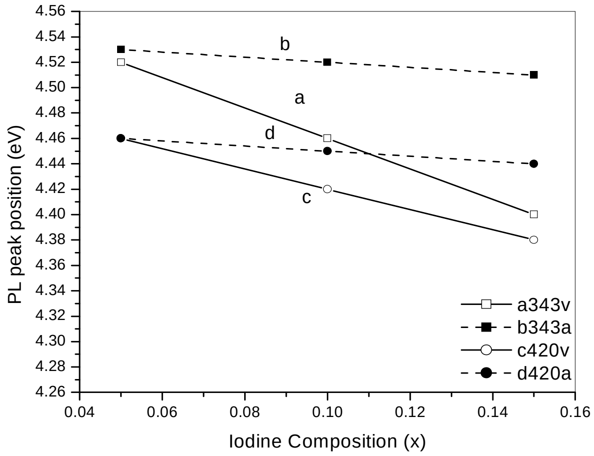

Fig.5. Spectral peak positions of PL excitation bands of $KBr_{1-x}I_x$:TlI (0.01mol%) grown in vacuum (solid line) and air (dashed line) for λ_{em} = 343nm a) and b)and for λ_{em} = 420nm c) and d).

The observed differences could be attributed to the different amounts of I^- and Tl^+ ion that have entered into the crystals grown in open air atmosphere when compared to those crystals grown in vacuum. Since thallium is volatile at the melting point of most of the alkali halides hosts, some of the thallium may be lost by evaporation [18]. In a similar manner some amount of iodine may also be lost by evaporation. In the case of mixed crystals grown in open air atmosphere, the amount of thallium and iodine ion lost by evaporation from the melt during growth may be relatively more than that grown in vacuum.

As a consequence, the concentrations of different complex Tl^+ centres formed in air grown crystals are expected to be less than that formed in vacuum grown crystals. The observed difference between the optical absorption spectra of samples grown in open air and vacuum are also attributed to such concentration difference of impurity ions[16]**.** However, in the case of $KBr_{1-x}I_x$:TlI (0.01mol%) mixed crystals grown in open air atmosphere (Figure not shown), the intensity of the 2.9-3.0eV additional emission shoulder and the intensity of its corresponding excitation band around 4.4eV are relatively higher than those observed in $KBr_{1-x}I_x$:TlI (0.01mol%) mixed crystals grown in vacuum. It may be due to some kind of preferential association/aggregation of the impurity ions to form predominantly the centres responsible for the emission and excitation bands under the conditions of growth. In heavily doped $KBr:Tl^+$ crystals, Gindina et al [19] and Tsubai [20] observed a new emission band around 400nm (3.1eV) which was excited in the excitation /absorption band at 267nm (4.64eV). They have attributed these emissions and excitation bands to Tl^+-trimers- an aggregate of three Tl^+ ions. Although this PL emission of Tl^+-trimer is close to the 2.9eV emission band of the present study, the peak positions of the excitation bands are different. Thus, the reason for this peculiar behaviour in the present study is not known clearly at present.

The variation in the spectral peak position of PL emission for λ_{ex} = 270 and 280nm with I^- ion composition x in the $KBr_{1-x}I_x$:TlI mixed crystals grown in vacuum and air are shown in Fig. 6.

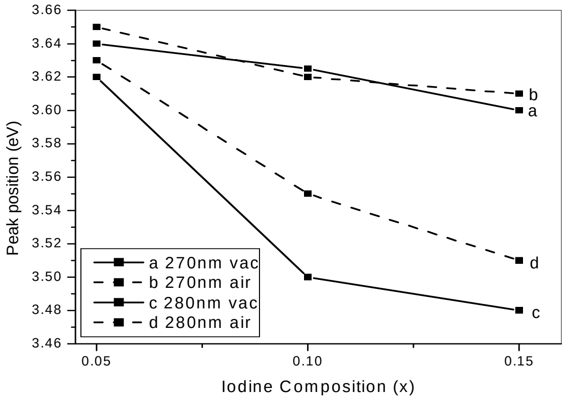

Fig.6. Spectral peak positions of PL emission bands of $KBr_{1-x}I_x$:TlI (0.01mol%) grown in vacuum (solid line) and air (dashed line) for λ_{ex} = 270nm (a), (b) and (c),(d) for 280nm.

The shifts in peak positions with x may be attributed to the appearance of new overlapping bands on the low energy side. The change in the structure of the emission and excitation bands may be due to the combined effect of Br^- and I^- ions on the Tl^+ ions and their energy levels.

Fig.7. (A) shows the PL emission spectra of the $KBr_{1-x}I_x$:TlI (0.01 mol%) mixed crystals grown in vacuum for λ_{ex} = 258nm normalized to unity at the dominant emission band. It shows that the

emission spectrum shifts with x to low energy side (curves a-d of Fig.7 (A)). Also, the relative intensity of A_T emission (around 3.94eV) which is the highest in KBr:Tl^+ (Fig.7 (A) curve a), decreases with increasing iodine composition in the $KBr_{1-x}I_x$:TlI (0.01mol%) mixed crystals (curves b-d). This may be due to the appearance and growth of an additional emission band with iodine composition whose peak position is close to the A_X emission (3.46eV). This additional emission band may be due to some complex Tl^+ centre involving I^- ions.

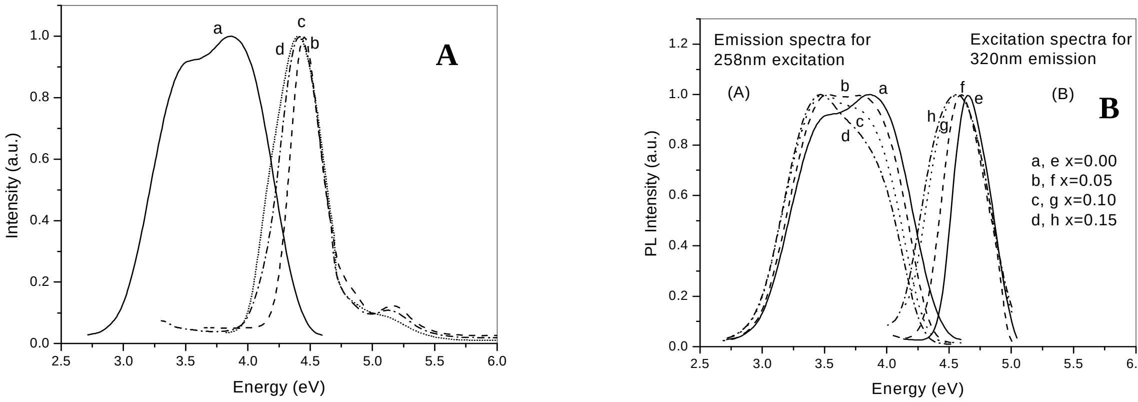

Fig.7. (A) Normalized PL spectra of $KBr_{1-x}I_x$: TlI (0.01mol %) grown in vacuum a-d emission for 4.8eV (258nm) excitation e-h excitation for 3.94eV (320nm) emission.
Fig.7. (B).PL emission for A-band excitation (λ_{ex} = 258nm) in KBr:Tl^+ (curve a) and PL excitation spectra of $KBr_{1-x}I_x$: TlI (0.01mol %) grown in vacuum for (λ_{em} = 420nm) x = 0.05 b), 0.10 c) and 0.15d).

In Figs. 7 (A)), normalized excitation spectra for the 320nm emission in $KBr_{1-x}I_x$:TlI (0.01 mol%) crystals with different iodine composition are also shown in curves e-h respectively. The excitation spectra for the 320nm show a slight shift in peak position (around 4.6eV) with x but they show an appreciable inhomogeneous broadening towards low energy side which may be attributed to the growth of an additional excitation band on the low energy side of the 4.6eV excitation band. Interestingly, the excitation band for λ_{em} = 320nm for higher iodine compositions, overlaps partially with the A_T emission of the KBr:Tl^+ single crystals. The progressive shift of the emission spectra for λ_{ex} = 258nm with I^- ion composition in the $KBr_{1-x}I_x$: TlI mixed crystals may be attributed to the reabsorption of a part of the A_T emission by the complex Tl^+ centers responsible for this low energy excitation band around 4.4eV. The extent of overlap of the emission spectrum for λ_{ex} = 258nm with the excitation spectra for λ_{em} = 420nm is even larger.

The excitation spectra for λ_{em} = 420nm in the $KBr_{1-x}I_x$: TlI mixed crystals (Figs. 7. (B)) show a weak band around 4.8eV (A_0) on the high energy side of the intense main excitation band around 4.4eV. The low energy tail of the main excitation band at 4.4eV (curves b-d in Figs. 7. (B)) overlaps the high energy side of the A_T emission band of KBr:Tl^+ (curves a in Fig. 7. (B)). Hence, a part of the A_T-emission energy may be reabsorbed by the A_3-centres responsible for the 4.4eV excitation band. This may result in emission excited in the A_3-band at 4.4eV. This could be the reason for the appearance of the 258nm excitation band along with the 4.4eV excitation band for λ_{em} = 420nm. The decrease in the relative intensity of the 4.8eV excitation band with x could be due to the decrease in the concentration of the A_0-centres (i.e, $TlBr_6$ centers responsible for the A_0-excitation band at 4.8eV in the KBr-KI:TlI mixed crystals) with x as the $A_{1,}$ $A_{2,}$ A_3-centers (i.e, $TlBr_{6-n}$ I_n centers responsible for the $A_{1,}$ $A_{2,}$ A_3-excitation / absorption bands[3,14] increase in concentration at the cost of A_0-centres with x in the KBr_{1-x}-KI_x:TlI mixed crystals.

CONCLUSION

In the present study, the change in the composition of emission bands, width and / or spectral peak position of the emission bands in the $KBr_{1-x}I_x$:TlI mixed crystals could be accounted for by the superposition of two or more emission bands which correspond to the complex Tl^+ centers of the form $TlBr_{6-n}$ I_n centers with n = 0, 1, 2, 3. The poor structure of the excitation spectra of KBr-KI (Tl^+) is partially due to the presence of overlapping bands closely located to each other and not resolved.

Acknowledgments
One of the authors would like to acknowledge Dr. M. T. Jose, Dr. Meenakshisundaram and Dr. A. R. Lakshmanan, Radiological Safety Division (RSD), IGCAR, Kalpakkam, India for extending their experimental facilities for the completion of this research work.

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