

Optical Studies on KBr:Tl and KCl-Br:Tl Mixed Crystals

P. ESWARAN*, A. ANBAGI and S. NAGARAJAN

*Department of Physics, SMK Fomra Institute of Technology,
Kelambakkam, Thaiyur, Chennai, Tamilnadu-603 103, India.

Department of Physics, Pondicherry Engineering College,
Puducherry-605 014, India.
eswaran_74@rediffmail.com

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Abstract: Optical absorption spectra of KBr:Tl⁺ (0.0125 mol%) single crystals shows A, B and C bands around 258, 220 and 210 nm respectively. In KCl_{0.1}Br_{0.9}:Tl⁺ (0.0125 mol%) mixed crystals exhibit slightly broadening of the A-band towards lower wavelength side. The broadening of the absorption spectra are suggested to be due to some complex Tl⁺ centers involving Br⁻ and Cl⁻ ions formed in the mixed crystals. When excited at A, B and C-bands of Tl⁺ ions, PL of KBr:Tl⁺ showed emission band around 320 with a prominent shoulder around 365 nm. In KCl_{0.1}Br_{0.9} mixed crystals the shoulder around 365 nm is not prominent due to the perturbing influence of Cl⁻ ions. Addition bands in the excitation spectra are attributed to the presence of Tl⁺ dimmers. PSL observed in X-ray irradiated crystals resembled their respective PL emissions indicating that PSL in them is due to Tl⁺ ions.

Keywords: Optical absorption, F-centers, KBr-Cl mixed crystals, A-band:Tl⁺ ions.

Introduction

The optical properties of alkali halide crystals containing heavy metal ions with S² configuration, so called KI:Tl⁺- type phosphors, have very widely been studied as a typical material doped with impurities¹. When one of these ions is substituted for an alkali ion, several absorption bands arise prominently at the low energy side of the intrinsic absorption edge of the host material. The bands named as A, B, C in the order of increasing energy and correspond to transitions from ¹S₀ ground state to ³P₁ excited state of the impurity ion. These structures depend strongly on the spin-orbit interaction of the excited states and Jahn-Teller effect². On the other hand, there have been few investigations for impurities in mixed crystals of alkali halides³⁻⁷. The absorption, excitation and luminescence bands in alkali halide crystals containing small amount of thallium are usually attributed to Tl⁺ ions that

replaces cations of the host materials. In mixed alkali halide 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^{8,9}.

In recent years, X-ray storage phosphors have gained interest in the fields of medical X-ray diagnostics, X-ray radiography *etc.* Important materials exhibiting such a behavior are the Eu^{2+} ions doped alkaline earth halides¹⁰⁻¹³ such as BaFBr:Eu^{2+} and RbBr:Tl^{+} and CsBr:Eu^{2+} CsBr-CsCl and Tl^{+} co-doped with Eu^{2+} mixed alkali halides¹⁴⁻¹⁷ proposed a new concept to explore the possibility of using mixed alkali halides as competitive image phosphors. In the present paper, Optical absorption (OA), Photoluminescence (PL) and Photoluminescence (PSL) studies of Tl^{+} doped KBr and $\text{KBr}_{0.9}\text{Cl}_{0.1}$ mixed crystals are reported.

Experimental

KBr: Tl^{+} and $\text{KCl}_{0.1}\text{Br}_{0.9}:\text{Tl}^{+}$ (0.0125 mol%) mixed crystals were grown in 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 work⁵. Optical absorption measurements were carried out using UV-Visible Shimadzu 3101PC spectrophotometer at room temperature. The Photoluminescence (PL) and Photostimulated Luminescence (PSL) measurements were carried out using a JOBIN YVON – Spex Spectro- fluorometer.

Results and Discussion

Optical absorption

Figure 1 (a) shows the optical absorption spectrum of a single crystal of KBr:Tl^{+} (0.0125%) exhibits an absorption band at 258 nm. On the shorter wavelength side of this band at least two overlapping bands around 220 and 210 nm are observed. Figure 1 (b) shows the optical absorption spectrum of $\text{KCl}_{0.1}\text{Br}_{0.9}:\text{Tl}^{+}$ (0.0125 mol%). It exhibits absorption broad bands at 256 nm and 210 nm with a shoulder around 220 nm. As the undoped alkali halides are usually transparent in these wavelength ranges these absorption bands are attributable to the doped impurity Tl^{+} ions.

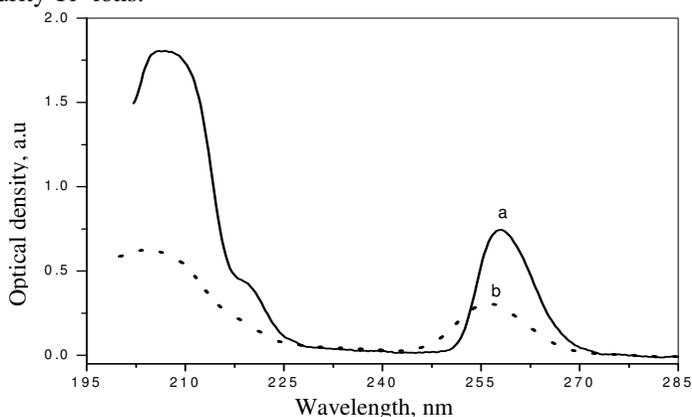


Figure 1. (a) Optical absorption spectrum of KBr:Tl^{+} (0.0125 mol%), (b) Optical absorption spectrum of $\text{KCl}_{0.1}\text{Br}_{0.9}:\text{Tl}^{+}$ (0.0125 mol%).

Tsuboi and Jacobs¹⁸ have observed the optical absorption bands due to Tl^+ ions in KBr at 258.2, 221.7 and 209.7 nm. 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 literature¹⁸, it is clear that these bands are due to A, B, C bands of the Tl^+ ions which have replaced substitutionally the host cations. Comparing Figures 1 (a) & (b) one finds that A- band of Tl^+ ions in the KCl-KBr mixed crystals is slightly shifted to the shorter wavelength side. It may be the formation of some complex centers, though in small numbers, cannot be ruled out.

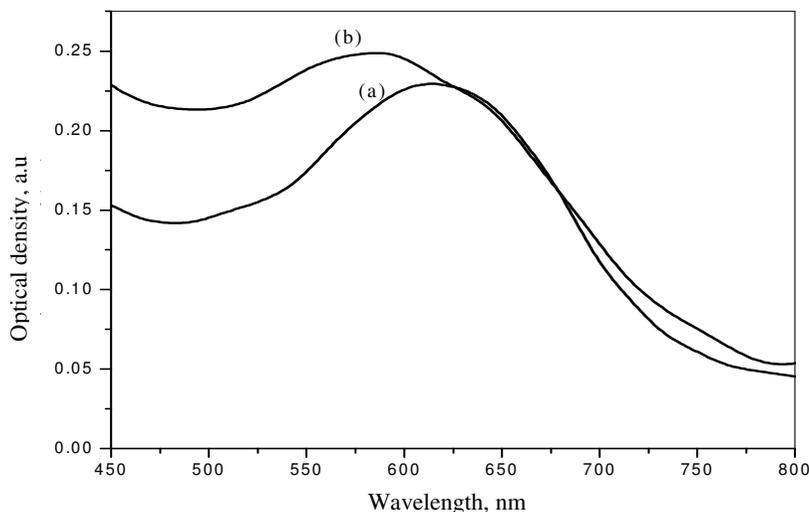


Figure 2. Normalized F -absorption bands (a) KBr: Tl^+ (0.0125 mol%), (b) $KCl_{0.1}Br_{0.9}:Tl^+$ (0.0125 mol%).

Weak absorption bands in the visible region at 632 nm in KBr: Tl^+ and around 600 nm in $KCl_{0.1}Br_{0.9}:Tl^+$ are observed after X-irradiation. These are due to F -centres formed in these crystals upon irradiation. Figure 2 (a) shows the F -absorption band observed in KBr: Tl^+ X-irradiated. While Figure 2 (b) shows the F -band of $KCl_{0.1}Br_{0.9}:Tl^+$ (0.0125 mol%) normalized to the peak value of F -band absorption in KBr: Tl^+ at 632 nm. It clearly indicates that there is an additional band on the short wavelength side of 632 nm.

It is known that F -centres in KBr absorb at 632 nm while F -centre in KCl absorb¹⁹ at 564 nm. In KCl-KBr mixed crystal, it is likely that two types of F -centres are formed; one is due to the trapping of an electron by Br^- vacancy while the other is due to the trapping of an electron by Cl^- vacancy. Thus the broad absorption band observed around 600 nm may contain absorption bands due to both F -centres formed by capture of electron by Br^- vacancy (denoted as $F(Br^-)$) and F -centres formed by capture of electron by Cl^- vacancy (denoted as $F(Cl^-)$). Alternatively, it is suggested that the additional absorption on the short wavelength side of 632 nm in $KCl_{0.1}Br_{0.9}:Tl^+$ may be due to $F(Br^-)$ centers perturbed by Cl^- ions.

Photoluminescence

Photoluminescence (PL) emission spectrum of KBr: Tl^+ crystal excited at wavelength corresponding to the A-band maximum shows an emission band around 320 nm with a shoulder around 365 nm (Figure.3, (a)). Similar emission spectra are obtained when the

crystal is excited at wavelengths corresponding to the B and C absorption bands but with different relative intensities. Intensity of emission for excitation at A -band is the highest while that for excitation at C band is the least.

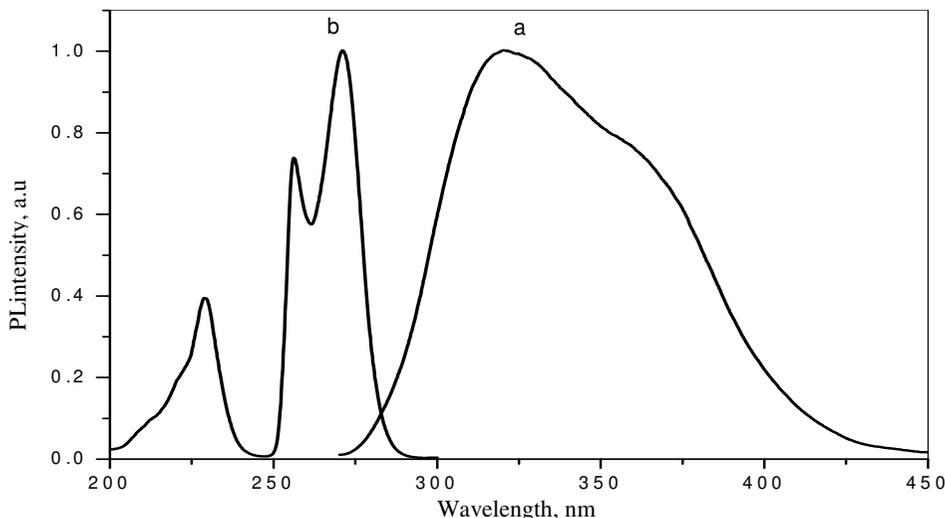


Figure 3. (a) PL emission spectrum of KBr:TI⁺(0.0125 mol%) for excitation at A-band (258 nm) and (b) PL excitation spectrum of KBr:TI⁺ (0.0125%) for emission at 320 nm.

Edgerton and Teegarden²⁰ have observed two emission bands (designed as A_T and A_X emissions) in KBr:TI⁺ around 310 and 363 nm upon excitation in any of the thallium absorption bands, A, B and C at room temperature. These bands are unresolved at room temperature but are resolved at lower temperatures. Roth and Halperin²¹ reported two PL emission bands at 310 and 365 nm due to monomer TI⁺ ions in KBr:TI⁺ at LNT. Thus the two PL emission bands observed in the present study are due to TI⁺ ions (monomer TI⁺ ions).

PL excitation spectra for both the emission bands at 320 and 365 nm show the same excitation bands at 271, 258 and 229 nm along with some weak shoulder around 220 and 210 nm. Figure 3 (b) shows the PL excitation spectrum for the emission at 320 nm.

Comparing with the absorption spectrum of KBr:TI⁺ (Figure 1 (a)), one infers that the excitation bands at 258, 221 and 210 nm corresponds to the A, B and C absorption bands respectively. However the presence of absorption bands corresponding to the 271 and 229 nm excitation bands is not obvious in the optical absorption spectrum of KBr:TI⁺ (Figure 1 (a)). The excitation at 271 and 229 nm resulted in the same PL emission and no additional emission band has been observed.

Tsuboi and Jacobs¹⁸ have reported that KI and KBr crystals having more than 0.01 mole percentage of TI⁺ ions exhibited weak additional absorption bands (hidden under the TI⁺ monomer bands) due to the formation of TI⁺ dimers -aggregate of pair of TI⁺ ions. These hidden bands have been reported to be found mainly from the excitation spectra. They also reported that, at low temperatures, excitation at the dimer bands resulted in an additional emission at 443 nm. In the present study the additional excitation bands at 271 and 229 nm have their peak position very close to the reported A₁ and B₁ side bands respectively. The higher intensity of the A₁ side band suggests that a quite a good number of dimers have been formed in these crystals. However, the excitation at 271 and 229 nm did not result in any additional emission band.

PL emission spectrum of $\text{KCl}_{0.1}\text{Br}_{0.9}:\text{Tl}^+$ (0.0125%) excited at A-band shows an emission band at 320 nm in the region between 275-450 nm (Figure.4 (a)). Similar emission spectra are obtained when the crystal is excited at B and C bands but with different relative intensities (figure not shown). Emission band observed at 365 nm in $\text{KBr}:\text{Tl}^+$ (Figure 3(a)) is not prominently seen in $\text{KCl}_{0.1}\text{Br}_{0.9}:\text{Tl}^+$. This may be due to the perturbing influence of the Cl^- ions present in this crystal.

PL excitation spectrum for the 320 nm emission exhibits broad excitation bands around 259, 220 and 210 nm (Figure 4 (b)) which are close to the peak positions of A, B, C absorption bands of $\text{KBr}:\text{Tl}^+$. The excitation at 220 and 210 nm resulted in the same emission and no additional emission bands have been observed. The excitation band showed a broader A-band (half width= 0.33 eV) when compared to that of the A- absorption band whose half width is about 0.202 eV only. This broadening of A- excitation band may be an indication that, A-side bands are hidden under the A-excitation band.

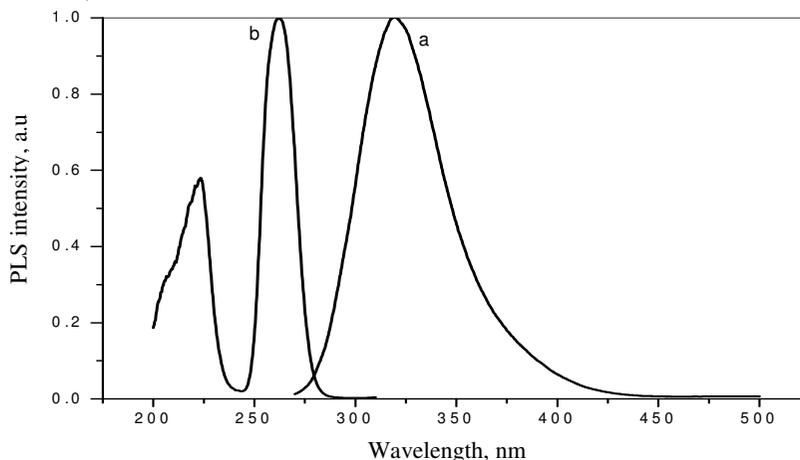


Figure 4. (a) PL emission spectrum of $\text{KCl}_{0.1}\text{Br}_{0.9}:\text{Tl}^+$ (0.0125%) for excitation at A-band, (b) PL excitation spectrum of $\text{KCl}_{0.1}\text{Br}_{0.9}:\text{Tl}^+$ (0.0125%) for emission at 320 nm.

It has been reported that in ns^2 ions doped mixed alkali halide crystals such as Tl^+ doped KCl-KI and KBr-KI , iodine anions are collected preferentially around the impurity cations as their nearest neighbours⁸. The polarisability of I^- is larger than that of Br^- ions and also the polarization effect of Tl^+ ions is more pronounced than that of K^+ ions. Hence the preferred position of I^- in the surrounding of the activator ion could be explained by the larger polarization energy of the ion pair Tl^+-I^- than that of K^+-Br^- and K^+-I^- . Similar arguments have been put forward for the formation of $[\text{SnCl}_{6-x} + \text{Cation Vacancy}]$ complex centers in the KCl-KI (Sn^{2+}) mixed crystals²². In Tl^+ doped KCl-KI and KBr-KI mixed crystals, it has been suggested that complex Tl^+ centers of the type $\text{TlX}_{6-n}\text{I}_n$ ($X = \text{Cl}$ or Br depending on the host, $n = 0, 1, 2, \dots, 6$) are formed⁹. Kleemann and Fischer have suggested that TlBr_6 , TlBr_5I , TlBr_4I_2 and TlBr_3I_3 complex centers (*i.e.*, $\text{TlX}_{6-n}\text{I}_n$ centers with $n = 0, 1, 2, 3$) are formed predominantly in KBr-KI mixed crystals doped with Tl^+ ions. The broad A-band absorption due to these complex centers ($\text{TlX}_{6-n}\text{I}_n$) with number of nearest neighbor iodine anions, $n = 0, 1, 2, 3$ observed. The absorption bands observed at 4.8, 4.66, 4.55 and 4.44 eV at 20 K in KBr-KI mixed crystals were designated as A_0 , A_1 , A_2 and A_3 bands respectively. The broadening of the A-band absorption/ excitation (as well as B and C bands) in $\text{KCl}_{0.1}\text{Br}_{0.9}:\text{Tl}^+$ (0.0125%) (Present study) is also similar to that observed in KBr-KI mixed

crystals⁹. Hence the broadening of the mixed crystal of the present study is attributed to the appearance of new bands due to the complex Tl^+ centres in the mixed configuration with both Cl^- and Br^- ions as nearest neighbours to the Tl^+ ions. Similar effects have been observed in the case of B and C-bands of these complex Tl^+ centers in the mixed crystals. As 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.

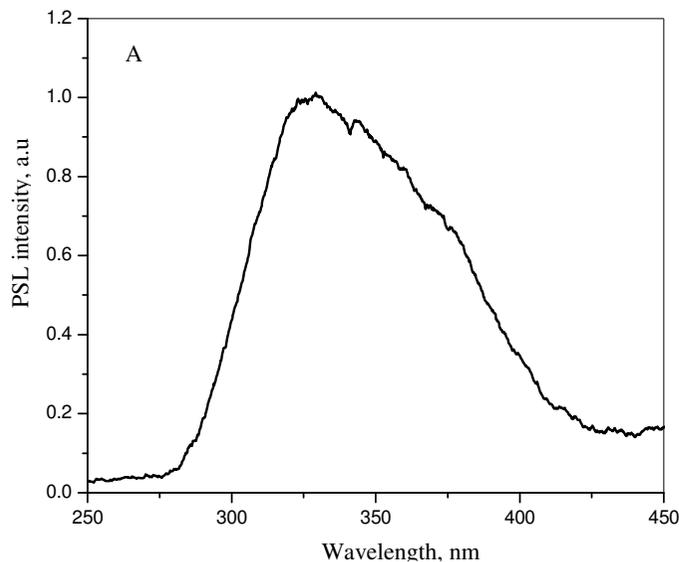
Photostimulated luminescence

Figure 5 (A). Shows the PSL emission spectrum of X- irradiated $KBr:Tl^+$ crystal stimulated at F-band. $KBr:Tl^+$ crystal shows a PSL emission band around 320 nm with a shoulder around 365 nm. These emission bands are similar to the PL emission bands excited at the wavelength corresponding to the A-band maximum and hence it may be concluded that PSL emission in X-irradiated $KBr:Tl^+$ crystals is due to Tl^+ ions.

PSL stimulation spectra for the emission at 320 nm showed maximum around 633 nm, which is close to the peak wavelength of F- band absorption in $KCl_{0.1}Br_{0.9}:Tl^+$ shown in Figure (Figure.5. (B), curve b).

The PSL emission spectrum of X-irradiated $KCl_{0.1}Br_{0.9}:Tl^+$ crystal stimulated at 633 nm shows PSL emission around 325 nm with a weak shoulder around 370 nm crystal (Figure.5. (B), curve a). This PSL emission spectrum is more or less similar to the PL emission spectrum of $KCl_{0.1}Br_{0.9}:Tl^+$. The corresponding stimulation spectrum showed a band with maximum around 630 nm indication that F (Br^-) centers play a major role in the PSL emission of $KCl_{0.1}Br_{0.9}:Tl^+$ crystals

Von Seggern *et al.*¹¹, studied the PSL emission and stimulation spectra of $RbBr:Tl$ at 206 K and at ROOM TEMPERATURE. Stimulation spectrum was observed at 695 nm. This wavelength agrees well with the published data for F-absorption band maximum of $RbBr$. Due to quantitative agreement between the stimulation spectrum and the F-centre absorption band the nature of the electron trap was attributed to the F- centres in $RbBr:Tl$.



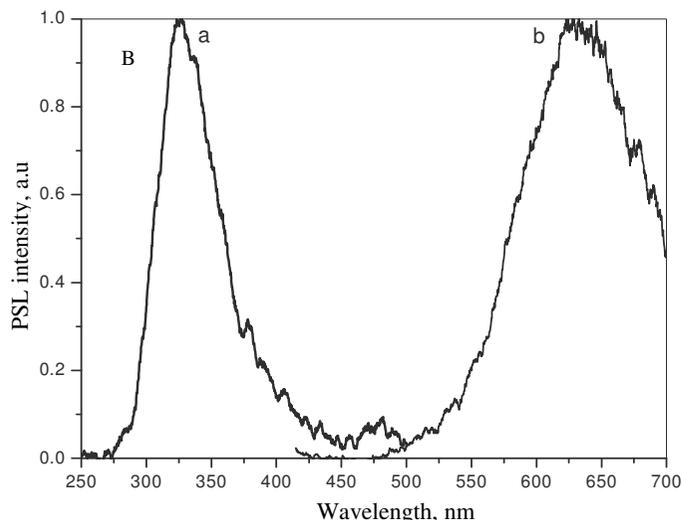


Figure 5. (A). PSL emission spectrum of KBr :Tl⁺(0.0125 mol%), (Figure (B), curve a) PSL emission spectrum of KCl_{0.1}Br_{0.9}:Tl⁺ (0.0125%) for stimulation in the *F*-band and (Figure (B), curve b) PSL stimulation spectrum of KCl_{0.1}Br_{0.9}:Tl⁺ (0.0125%) for 320 nm emission.

From the above results it may be suggested that during X- irradiation, Tl⁺ ions trap holes becoming Tl²⁺ ions while the corresponding electrons are trapped at anion vacancies forming *F*- centres. Trapping of some holes by Tl⁺ dimers or Tl⁺ ion complexes may also happen²¹. During PSL, stimulation at *F*-band may result in the release of *F*-centre electrons into the conduction band, which are mobile. When these mobile electrons recombine with Tl²⁺ ions, they are converted into Tl⁺ ions in the excited state (³P₁). When they relax to the ground state (¹S₀) they emit the characteristic Tl⁺ emission. Recombination of electrons with hole trapped Tl⁺ aggregates may also result in monomer like emission as observed in PL.

A similar mechanism was proposed by Von Seggern *et al*¹¹., in RbBr:Tl⁺. However they observed in a later study that the temperature dependence of PSL was solely determined by lifetime of Tl⁺ ions in the range 50-500 K and that there was no decrease in PSL below 80K where release of electrons into conduction band becomes less probable¹¹. This observation prompted them to propose a tunneling mechanism.

Conclusion

In the present study, optical absorption spectra of KBr:Tl⁺ single crystal exhibited the characteristics A, B and C bands of Tl⁺ ions. In mixed crystal slight changes in the half width of the absorption and excitation spectra doping with KBr due to influence of Cl⁻ ions. It may be the formation of some complex centers, though in small numbers, cannot be ruled out. PSL emission bands observed in KBr:Tl⁺ emission band very closely resemble with PL emission bands. PSL studies of the KCl_{0.1}Br_{0.9}:Tl⁺ mixed crystal suggested that *F* and Tl²⁺ centers play the role of electron trapped centers and the hole trapped centers, respectively, in the PSL process.

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