Chapter - IV
4. Luminescence in KCl:Eu$^{2+}$, Tl$^+$. X-ray storage phosphors

4.1 Introduction

Luminescence in alkali halides doped with europium [1] and thallium ions [2] have been studied extensively in the past. KCl:Eu$^{2+}$, CsBr:Eu$^{2+}$, RbBr:Tl$^+$, etc. phosphors have shown characteristic features of photostimulable X-ray storage phosphors [3,4,5]. In Eu$^{2+}$ ions doped alkali halide crystals, the 4f$^7$ - 4f$^6$5d transition results in a bell-shaped absorption between 240-260 nm and a broad absorption between 330-390 nm with a staircase structure [1]. Generally, excitation at any of these bands results in a single emission around 420 nm.

Alkali halides doped with small amounts of thallous ions mainly exhibit three absorption bands designated as A, B and C bands in the order of increasing photon energy. The absorption and emission processes due to transitions between 6s$^2$ ground state and 6s6p first excited states are complex and depend on various factors such as Jahn-Teller effect, spin-orbit interactions, etc. [2]. However, emission spectra under A-band excitation have been studied extensively which generally exhibit two emission bands denoted as $A_T$ and $A_x$ emission bands in the order of decreasing energy. At RT, in KCl:Tl$^+$, excitation at the A-band...
absorption (247 nm) results in the observation of only $A_T$ emission at 301 nm [6]. It is interesting to learn that the A-band excitation as well as the A-band emission in KCl:Ti$^+$ crystals overlaps partially with the excitation spectrum of europium doped KCl crystals. In the present work, the effect of co-doping thallium ions on the Eu$^{2+}$ luminescence in KCl:Eu$^{2+}$ powder phosphors synthesized using graphite crucible under controlled flow of air (chapter2) is reported for the first time.

4.2 Results and Discussion

4.2.1 Photoluminescence (PL) Studies

Fig. 4.1 shows the PL emission spectra of KCl:Eu$^{2+}$ (0.1 mol %), Ti$^+$ (x mol%, $x = 0.0, 0.01, 0.03, 0.05, 0.075$) powder phosphors. The emission spectra ($\lambda_{ex} = 368$ nm) show a single emission band around 420 nm which is attributable to the characteristic emission band of Eu$^{2+}$ ions [1]. The intensity of the 420 nm PL emission band is found to change with the concentration of Ti$^+$. As the concentration of Ti$^+$ increases from 0.0 mol %, the intensity of 420 nm PL emission band also increases; it reaches a maximum for a Ti$^+$ concentration of 0.05 mol % and then it decreases for a further increase in ‘x’. The melting point of TlBr (460 °C) is considerably lower than that of KCl (771 °C). Hence it is likely that TlBr in the KCl:EuCl$_3$, TlBr mixture plays a role similar to that of a flux for KCl:Eu$^{2+}$ phosphors resulting in an increase of Eu$^{2+}$ concentration in the sintered
Fig. 4.1 Photoluminescence emission spectra ($\lambda_{ex} = 368$ nm) of KCl:Eu$^{2+}$ (0.1 mol %), Tl$^+$ (x mol %) phosphors: a) $x = 0.0$, (b) $x = 0.01$, (c) $x = 0.03$, (d) $x = 0.05$, (e) $x = 0.075$

phosphors. This could be a reason for the enhancement of the 420 nm emission for smaller concentrations of TlBr. The decrease in PL intensity for higher concentrations of TlBr may be due to concentration quenching of luminescence and/or formation of some complex centres involving impurity ions that inhibit the 420 nm luminescence.

Fig. 4.2 shows the dependence of PL intensity of KCl:Eu$^{2+}$, Tl$^+$ (0.05 mol %) powder phosphors on europium concentration. The emission spectra ($\lambda_{ex} = 368$ nm) KCl:Eu$^{2+}$ (y mol %, $y = 0.05$, 0.1 and 0.2), Tl$^+$ (0.05 mol %) powder phosphors
show that the PL emission band (420 nm) has maximum intensity for a concentration of \( y = 0.1 \) mol %. When the concentration of thallium ion is varied for each of these \( \text{Eu}^{2+} \) concentrations in the above doubly-doped phosphors, it is found that PL emission has a maximum intensity for a \( \text{TlBr} \) concentration of about 0.05 mol %. These results indicate that the optimum concentrations of \( \text{Eu}^{2+} \) and \( \text{Tl}^+ \)

![Graph showing variation of PL intensity with concentration](image)

**Fig. 4.2** Variation of PL intensity of \( \text{KCl:Eu}^{2+}(y \text{ mol }\%\), \( \text{Tl}^+(0.05 \text{ mol }\%\) powder phosphors with concentration of \( \text{Eu}^{2+} \) ions: a) \( y = 0.05 \), b) \( y = 0.1 \) and c) \( y = 0.2 \)

ions in \( \text{KCl:Eu}^{2+}, \text{Tl}^+ \) phosphors for maximum PL intensity is around 0.1 and 0.05 mol % respectively. So the results of \( \text{KCl:Eu}^{2+}, \text{Tl}^+ \) (x mol %) phosphors for the optimum europium concentration (0.1 mol %) is discussed in the following section.
The excitation spectrum corresponding to the 420 nm emission in KCl:Eu$^{2+}$ (0.1 mol %) phosphors shows a weak band around 250 nm and a broad staircase structure between 320 - 400 nm (Fig. 4.3, curve ‘a’). KCl:Eu$^{2+}$ (0.1 mol %) phosphors co-doped with different concentration of TlBr also show similar excitation spectra (Fig. 4.3, curves ‘b-e’). Even though it is not well resolved, the possibility for the presence of more than one band in short wavelength range around 250 nm in these excitation spectra cannot be ruled out. This is due to the fact that the short wavelength excitation band of KCl:Eu$^{2+}$ (around 250 nm) and the A-band excitation of thallium doped KCl crystals (around 247 nm) fall under the
In KCl single crystals doped with higher concentrations of thallium ions (> 0.01 mol %), new absorption bands on the long wavelength side of the A-band [as well as B and C bands] due to dimers of Tl⁺ ions have been reported [7]. Two types of Tl⁺ dimers are formed in alkali halides with different symmetries (D₂h or D₄h). The A-band absorption /excitation bands of D₂h and D₄h dimers of Tl⁺ ions in KCl appear around 254 and 252.5 nm respectively and photo-excitation at these dimer bands is known to result in an additional emission at 475 nm at low temperatures. With increasing temperature towards RT, the additional emission band reduces drastically in intensity [8, 9].

![Photoluminescence emission spectra](image)

**Fig. 4.4 Photoluminescence emission spectra of KCl:Eu²⁺,Tl⁺ (x mol %) powder phosphors:** (a) x = 0.0, (b) x = 0.01, (c) x = 0.03, (d) x = 0.05, (e) x = 0.075 for 258 nm excitation
In order to study the effect of Tl$^+$ ions on the luminescence of Eu$^{2+}$ ions in KCl, PL emission spectra of KCl:Eu$^{2+}$, Tl$^+$ for excitation at 252 and 258 nm are also recorded. The resulting emission spectra for $\lambda_{\text{ex}} = 258$ nm (Fig. 4.4) as well as those for $\lambda_{\text{ex}} = 252$ nm (Fig. 4.5) contain an additional emission band around 300 nm and a weak shoulder around 380 nm in addition to the characteristic Eu$^{2+}$ emission at 420 nm. The dimer emission around 475 nm is not present. The 300 and 380 nm emission bands are relatively weaker than the 420 nm band and are not observed in KCl:Eu$^{2+}$ phosphors.

PL excitation spectra for the 300 nm emission in KCl:Eu$^{2+}$, Tl$^+$ powder phosphors are shown in Fig. 4.6 (A). For the sake of comparison, PL emission
Fig. 4.6 Photoluminescence (PL) spectra of KCl:Eu$^{2+}$(0.1 mol %), Tl$^+$($x$ mol %) powder phosphors: a) $x = 0.0$, (b) $x = 0.01$, (c) $x = 0.03$, (d) $x = 0.05$, (e) $x = 0.075$ and (f) PL excitation spectrum of KCl:Eu$^{2+}$ (0.1 mol %), Tl$^+$ (0.05 mol %) for 420 nm emission spectra of these phosphors for $\lambda_{ex} = 258$ nm (shown in Fig 4.4) are reproduced in Fig. 4.6 as Fig 4.6 (B). The PL excitation spectrum of KCl:Eu$^{2+}$ for 300 nm emission wavelength does not show any excitation band (Fig. 4.6, curve ‘a’). In the case of KCl:Eu$^{2+}$, Tl$^+$ ($x$ mol %) phosphors, a broad excitation band around 249 nm is observed for $x = 0.01$ mol% (curve b) which broadens and shifts slightly (to 251 nm) towards the long wavelength side for higher values of ‘$x$’ (Fig. 4.6 (A), curves...
This indicates clearly that these excitation bands correspond to the emission due to Tl$^+$ impurity ion centres. The curve 'd' in Fig. 4.3 is reproduced as curve 'f' in Fig. 4.6 (A) to show the extent of overlap of the excitation spectrum of Eu$^{2+}$ ions on the excitation and emission spectra of Tl$^+$ ions in the powder phosphors of the present study.

It is well known that A band (247 nm) excitation in KCl: Tl$^+$ produces 301 nm emission band at RT. Hence the 300 nm emission and its corresponding excitation around 249 nm in the present study are attributed to the Tl$^+$ ions which have replaced the alkali cations substitutionally. It is interesting to note that for a given 'x' value ( > 0), the excitation band is unusually more intense (nearly twice) than the corresponding 300 nm emission (Fig. 4.6). This leads us to conclude that the 300 nm emission of Tl$^+$ centres is partially absorbed by some other luminescent centres. The broadening and/or shifting of the 249 nm excitation band with Tl$^+$ concentration (Fig. 4.6) may be due to the appearance of a new excitation band on the long wavelength side of A-band of KCl:Tl$^+$ attributable to the formation of some complex Tl$^+$ centres. These bands are not resolved at RT due to overlap.

The D$_{4h}$ dimer centres of Tl$^+$ ions have been identified to give rise to an additional emission band around 380 nm in heavily doped KCl: Tl$^+$ crystals [7]. In an earlier report on KCl:Tl$^+$, Cd$^+$ crystals, a similar emission band at 380 nm was
suggested to be due to complex centres involving Ti\(^+\) and Cd\(^+\) ions [10]. Comparing with these reports, the 380 nm emission observed in the present study could be attributed to some complex centres (such as Ti\(^+\) dimers or centres involving Ti\(^+\) and Eu\(^{2+}\) ions). The saturation of the 300 nm Ti\(^+\) monomer emission for 'x' between 0.03 and 0.05 could be attributed to the formation of such complex centres. The decrease of PL intensity of 420 nm emission band for larger values of 'x' (TlBr concentration) is attributed to a concentration quenching as discussed earlier. The 300 nm emission intensity is comparatively higher for 252 nm excitation than that for 258 nm excitation. This is due to the fact that 252 nm wavelength lies closer to thallium monomer as well as dimer bands than the 258 nm excitation wavelength.

The increase in the intensity of the 420 nm emission with 'x' observed under excitation at 252, 258 and 368 nm appears to be similar. But the 368 nm excitation produces only the 420 nm emission (Fig. 4.1) while excitation at the other two wavelengths produces both 300 and 420 nm bands along with 380 nm shoulder (Fig. 4.4 and Fig. 4.5). The thallium emission bands at 300 and 380 nm in KCl:Eu\(^{2+}\),Tl\(^+\) phosphor overlap partially with the excitation spectrum for the 420 nm emission of Eu\(^{2+}\) centres (Fig. 4.6 (A), curve ‘f’ and 4.6 (B), curves ‘b-e’). Hence, reabsorption of a part of the thallium emission by some Eu\(^{2+}\) ions in their ground state (i.e. energy transfer from Ti\(^+\) → Eu\(^{2+}\) ions) is more probable and this
could cause an enhancement of the Eu\textsuperscript{2+} emission. This enhancement is expected on account of the overlap of the 250 nm excitation band of the Eu\textsuperscript{2+} emission with the 250 - 260 nm excitation bands of the thallium emission bands. However, one may argue, following the discussion on Fig. 4.1 that the increase of the 420 nm emission under 250 - 260 nm excitation (present study) is mainly due to the incorporation of a higher concentration of Eu\textsuperscript{2+} ions in these phosphors rather than an energy transfer between Tl\textsuperscript{+} and Eu\textsuperscript{2+} ions.

Fig. 4.7 Relative intensity of 420 nm emission in KCl:Eu\textsuperscript{2+}, Tl\textsuperscript{+} phosphors
In order to clarify this point, the intensity of 420 nm emission in KCl:Eu$^{2+}$ (0.1 mol %), Tl$^+$ (x mol%, x = 0. 0, 0. 01, 0. 03, 0. 05, 0. 075) phosphors relative to that in KCl:Eu$^{2+}$ phosphors (i.e. without TlBr co-doping (x = 0)) for a given excitation wavelength is calculated for all the three excitation wavelengths separately ($\lambda_{ex} = 252, 258$ and 368 nm). The result of the calculation is shown as a plot of the relative intensity as a function of TlBr concentration x for each excitation wavelength (Fig. 4.7, curves ‘a-c’).

Interestingly, the increase of this relative intensity for lower to middle values of ‘x’ is significantly higher for 252 and 258 nm excitations than that for 368 nm excitation. This result suggests that the relative enhancement of the 420 nm emission is higher when excited at 252/258 nm than that produced by excitation at 368 nm. This is a clear indication that the enhancement of the Eu$^{2+}$ emission (for $\lambda_{ex} = 250 - 260$ nm) is not only due to an increase in the concentration of Eu$^{2+}$ ions in the Tl$^+$ co-doped phosphors but also due to an energy transfer from Tl$^+$ to Eu$^{2+}$ ions.

4.2.2 Photostimulated luminescence (PSL) studies

PSL spectra of $\gamma$-irradiated samples of KCl:Eu$^{2+}$,Tl$^+$ phosphors ($\gamma$ - dose = 14 Gy) are shown in Fig. 4. 8 and Fig. 4. 9. PSL emission spectra of KCl:Eu$^{2+}$
samples show the 420 nm emission due to Eu$^{2+}$ ions and the thallium co-doped KCl:Eu$^{2+}$ samples show a weak emission band at 300 nm (A-band emission of Tl$^+$ ions in KCl from PL spectra) in addition to the main 420 nm emission band (Fig. 4.8). PSL stimulation spectra for the 420 nm emission show a broad stimulation band around 550 nm, which is correlated to the F-band absorption in irradiated KCl (560 nm) [11]. The PSL intensity is found to decrease initially with the increase of Tl$^+$ concentration in KCl:Eu$^{2+}$, Tl$^+$ phosphors (Fig. 4.9, curves ‘a-c’). However, when the Tl$^+$ concentration is increased above 0.01 mol%, the PSL intensity increases and it shows a maximum for a concentration of $x = 0.05$ mol%.

Fig. 4.8 Photostimulated luminescence emission spectra of KCl:Eu$^{2+}$, Tl$^+$ (x mol %) powder phosphors: (a) $x = 0$, (b) $x = 0.01$, (c) $x = 0.03$, (d) $x = 0.05$ and (e) $x = 0.075$ under F-band stimulation.
Similar variation in PSL intensity with thallium concentration is observed in KCl:Eu\(^{2+}\), Tl\(^{+}\) (x mol %) powder phosphors containing different amounts of Eu\(^{2+}\) ions (Figure not shown).

![Diagram](image)

**Fig. 4. 9** Photostimulated luminescence stimulation spectra of KCl:Eu\(^{2+}\),Tl\(^{+}\) (x mol %) powder phosphors: (a) x = 0.0, (b) x = 0.01, (c) x = 0.03, (d) x = 0.05 and (e) x = 0.075 for 420 nm emission

It is well known from earlier reports that in alkali halides doped with Eu\(^{2+}\) ions, during irradiation, Eu\(^{2+}\) ions act as hole trap centres while in alkali halides doped with Tl\(^{+}\) ions, the Tl\(^{+}\) ions simultaneously can act as both electron and hole trap centres (i.e. Tl\(^{2+}\) and Tl\(^{0}\) centres are formed simultaneously upon irradiation)
Butterworth et al. have found that in KCl containing small concentrations of TI$^+$ ions, TI$^0$ centres are formed in large numbers upon irradiation. On the other hand, in KCl crystals doped with large amounts of TI$^+$ ions, hole trapped thallium centres are found to be formed predominantly [12]. The presence of 420 and 300 nm emission in the PSL spectra of the KCl:Eu$^{2+}$, TI$^+$ phosphors (present study) suggests the formation of Eu$^{3+}$ ions from Eu$^{2+}$ and TI$^{2+}$ from TI$^+$ on $\gamma$-irradiation.

Upon photo stimulation in the F-band, some of the electrons released from F-centres may recombine with Eu$^{3+}$ and TI$^{2+}$ ions converting them into Eu$^{2+}$ and TI$^+$ ions in their respective excited states. When these ions relax to their ground states they give rise to their characteristic emission bands at 420 nm (Eu$^{2+}$ emission) and 300 nm (TI$^+$ emission) respectively. The TI$^0$ centres, if any, present in the irradiated samples have no direct role to play in the PSL processes. This follows from the fact that photostimulation at F-band will have no effect on the TI$^0$ centres since the absorption band of TI$^0$ centres lies in the IR region (1225 nm), far away from the F-band [13]. But their formation in large numbers certainly reduces the concentration of F-centres formed on irradiation [14, 15] as TI$^+$ ions compete with F-centre traps (anion vacancies) for the trapping of electrons during irradiation. Considering the above discussion based on the earlier reports, the decrease of PSL intensity of 420 nm emission for smaller concentrations of TI$^+$
in KCl:Eu\(^{2+}\), Ti\(^{+}\) phosphors is tentatively attributed to the efficient formation of Ti\(^{6+}\) centres upon irradiation and the consequent reduction in concentration of F-centres produced.

The enhancement in the PSL emission of \(\gamma\)-irradiated KCl:Eu\(^{2+}\), Ti\(^{+}\) phosphors doped with higher concentrations of thallium impurity may be attributed to the formation of hole trapped thallium centres in large numbers. Obviously, an enhancement in the trapping of holes by the impurity ions during irradiation would increase the concentration of F-centres formed, too [15]. Hence, more F-centre electrons would be released upon F-band stimulation resulting in the enhancement of 420 nm PSL emission due to the recombination of free electrons with Eu\(^{3+}\) centres formed on irradiation. Some of the electrons released upon F-band photostimulation would recombine with Ti\(^{+}\) ions in the thallium centres resulting in the characteristic Ti\(^{3+}\) emissions (300 nm and 380 nm). As observed in the PL emission, an energy transfer from Ti\(^{+}\) → Eu\(^{2+}\) ions would enhance the PSL emission in the irradiated samples. Thus the PSL emission in KCl:Eu\(^{2+}\) phosphors can be enhanced by co-doping them with appropriate amounts of Ti\(^{+}\) ions. However, further experimental studies are required to confirm the nature of defect centres produced and their role in the energy transfer from Ti\(^{+}\) to Eu\(^{2+}\) ions in PL and PSL.

As energy transfer from Ti\(^{+}\) → Eu\(^{2+}\) ions is observed in the KCl:Eu\(^{2+}\), Ti\(^{+}\)
phosphors, an increase in the decay time of PL and PSL is expected in them. Luminescence decay and lifetime of emission of these doubly doped phosphors have not been studied. However, the change in intensity of PSL signal (normalized to unity at its maximum) with time under continuous stimulation at the peak of the PSL stimulation band (550 nm) of γ-irradiated KCl:Eu$^{2+}$ (0.1 mol %) and KCl:Eu$^{2+}$ (0.1 mol %), Tl$^+$ (0.05 mol %) phosphors is shown in Fig. 4.10. The PSL intensity of Tl$^+$ co-doped KCl:Eu$^{2+}$ powder phosphors decreases slowly with time when compared to KCl:Eu$^{2+}$ powder phosphors. This indicates that PSL emission

![Diagram](image_url)

**Fig. 4.10 Variation in peak intensity of PSL of γ-irradiated phosphors a) KCl:Eu$^{2+}$, b) KCl:Eu$^{2+}$,Tl$^+$ with time on continuous exposure to F-light (550 nm).**

Source of F-light: Xenon lamp of the spectrofluorometer, slit width = 1 nm
Influence of Tl⁺ activators on the luminescence properties of KCl:Eu²⁺ powder phosphors were investigated. An enhancement in PL and PSL efficiency is observed in Tl⁺ co-doped KCl:Eu²⁺ phosphors. It shows a maximum for a Tl⁺ concentration of 0.05 mol %. This enhancement is attributed to the increase in the concentration of Eu²⁺ ions in the phosphors as well as energy transfer from Tl⁺ → Eu²⁺ ions. In PSL studies, the observed changes in the intensity of PSL emission with concentration of Tl⁺ in KCl:Eu²⁺, Tl⁺ phosphors are attributed to a combination of various competing effects such as change in relative concentrations of various defect centres present in the samples, the ability of different thallium centres to trap electrons or holes efficiently on irradiation etc. From the results, it can be concluded that PL and PSL emission in KCl:Eu²⁺ phosphors can be enhanced by co-doping them with appropriate amounts of Tl⁺ ions.
References


