© 2016 IJSRST | Volume 2 | Issue 3 | Print ISSN: 2395-6011 | Online ISSN: 2395-602X
Themed Section: Science and Technology

Luminescence Spectroscopy of γ-ray irradiated KI, KCl doped with Terbium ion Crystals

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ABSTRACT

Terbium doped KI, KCl single crystals were prepared by Bridgman Stockbarger technique and characterization results such as optical absorption, Photoluminescence (PL), Thermoluminescence (TL), Thermostimulated emission (TSE) and Photostimulated emission (PSE) were investigated. The Optical absorption measurements indicate the formation of F and V-centre in the crystal after γ-ray irradiation process. Photoluminescence studies exhibit characteristics Tb^{3+} emission due to transitions from $^5D_3$ and $^5D_4$ levels to various levels ^7F_J (J=5,6) in both matrix. The deconvoluted glow peak reveals two clearly visible distinct peaks in both matrix and kinetic parameters calculated using Chen's peak shape method. The characteristic emission due to Tb^{3+} ions in the spectral distribution under PSE and TSE confirms the participation of the Tb^{3+} ions in the recombination process.

Keywords : Photoluminescence, Thermoluminescence, γ-ray irradiation

I. INTRODUCTION

The development of luminescent materials has been the subject of extensive research in the past few years and also particular interest has been focused on inorganic luminescent materials which have practical applications in almost all devices involving the artificial production of light. The luminescent materials are used in Cathode ray tubes (CRTS), Projection Television (PTVs), Fluorescent tubes, X-ray detectors and Field emission display (FED) etc., [1]. Rare earth doped alkali halides have been extensively applied as phosphors because of excellent luminescent properties [2]. The wide range of lattice parameter of alkali halides gives the possibility of incorporating impurity ions of different sizes in their lattice. The luminescence associated with terbium content in different host lattices has found applications related to its green light emission, which is important in the field of displays, sensors and lasers [3]. The past few decades have seen a lot of work reported on the use of Tb^{3+} as a dopant in the alkali halide phosphors as they have very good optical properties which make them part of many display devices[4]. Among all the rare earth ions, Tb^{3+} is most and also its use in commercial green phosphors. The ionic radii of Tb^{3+} are 1.04 Ǻ which is close K^+ having ionic radii of 1.38 Ǻ makes them easy to incorporate into it. Green emission is important component of white light which is generated by red/green/blue emission at a 3:6:1 ratio. Many intense green emitting Tb^{3+} containing phosphors such as YAG:Tb ; $Y_2 SiO_5$:Tb, Y_2O_2S:Tb, Gd_2O_2S:Tb, LaOBr:Tb, YBO_3:Tb and Sr_3AlO_4F:Tb have been thoroughly studied [5-10]. Of the known rare earth activators, Tb^{3+} has relatively simple energy level structure that consist of ^7F_j (J=6-0), $^5D_4$-$^5D_3$ states. The objective of the present investigation is to study the comparative optical absorption property of KCl : Tb^{3+} and KI: Tb^{3+} single crystals which is grown by Bridgman Stockbarger technique.

II. METHODS AND MATERIAL

Single crystals of KI: Tb^{3+} and KCl: Tb^{3+} were grown Bridgman Stockbarger technique. KI and KCl (99.99% Purity; Aldrich) and Terbium in the form of Terbium Fluoride (99.98% Purity; Aldrich) were used. The crystals were grown with three different concentrations of the impurity 1%, 2% and 3% by weight. Samples of size approximately 5x5x1 mm^3 were used for all expect the PSL and PL studies. For PSL and PL, 5x5x3 mm^3

samples were used. The result due to the three concentrations were similar expect for a high luminescence yield with higher concentration of Tb^{3+} ions. There was no qualitative change in the result, but there is a change in intensities of emission and absorption, due to different Terbium ion concentrations. Hence the result pertaining to a Terbium concentration of 3% by weight are presented and discussed. The absorption spectra were recorded using a Perkin Elmer Lambda 35 UV - Vis spectrophotometer in the region 190-1100nm. Photoluminescence spectra were recorded at room temperature, using a Perkin Elmer LS 55 luminescence spectrometer in the region 200-900nm, with spectral width of 5nm. TL glows were recorded using a PL-based TL analyzer (Hitachi) at a heating rate of 120ºC/min. The crystals were irradiated with a ^{60}Co γ-source at a dosage rate of 10.6 Gy/min. TL emission spectra were recorded in the region 200-900nm, using the Perkin Elmer LS 55 with the excitation slit being closed. Deconvolution of TL glow peaks were carried out using the software "Peak fit". Before every experiment, the crystals were annealed at 400ºC for 30 mins. and then quenched to room temperature to ensure homogeneous distribution of impurities and to remove any storage effect.

III. RESULTS AND DISCUSSION

A. Optical Absorption

The optical absorption spectra of Tb^{3+} doped KI (Curve a) and KCl (curve b) before irradiation were shown in Fig.1. The unirradiated crystals of both material exhibits a peak at 195nm is of high intensity which is due to the exciton absorption of the host matrix [11, 12]. The weak absorption band around 340nm has been observed in KI: Tb^{3+} which is attributed to V-centres. The absorption band at 340nm is attributed to terbium ions. This band is not observed in KCl: Tb^{3+} material. The absorption due to terbium ions were observed at 240nm in earlier reported work [13]. The optical absorption spectra of KI: Tb^{3+} (curve a) and KCl: Tb^{3+} (curve b) after irradiation were displayed in Fig.2. The band observed before irradiation were also noted after irradiation around 200nm. But the intensity of the absorption band at 195nm increased in KCl: Tb^{3+} crystal. On gamma ray irradiation, there is increased in absorption around 310nm. The same is attributable to the formation of hole centres which is observed at the wavelength of 290 - 390nm in both the material. KI: Tb^{3+} and KCl: Tb^{3+} crystals show the formation of F-band centred at 700nm and at 590nm respectively. It is known that the irradiation produces well known F band and V band in both the crystals. The optical absorption spectra of KI:Tb^{3+} (curve a) and KCl:Tb^{3+} (curve b) crystals after F-bleaching subsequent to γ-ray irradiation were exhibited in Fig.3.

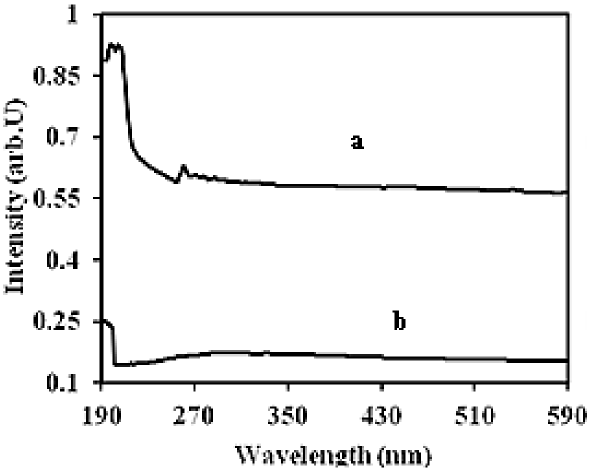

Figure 1. Optical absorption of Tb^{3+} doped Curve (a) KI , Curve (b) KCl single crystals before γ- ray irradiation.

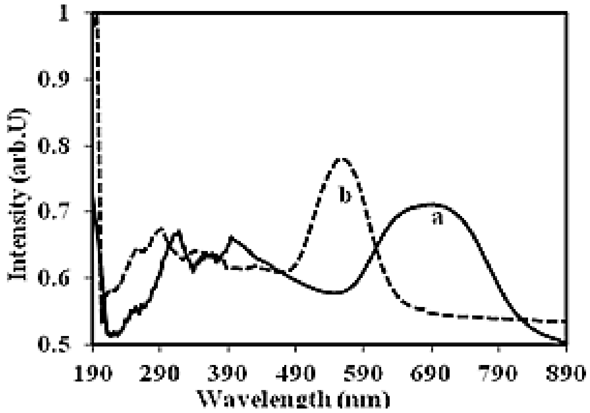

Figure 2. Optical absorption of Tb^{3+} doped Curve (a) KI, Curve (b) KCl single crystals after γ- ray irradiation.

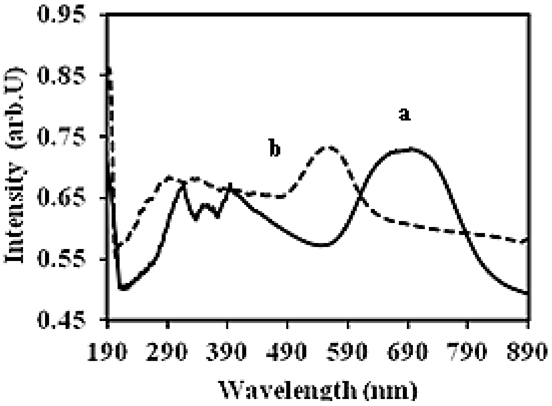

Figure 3. Optical absorption of Tb^{3+} doped Curve (a) KI, Curve (b) KCl after F bleach for 2 mins. subsequent to γ-ray irradiation.

On F-bleaching, absorption at F-band shows a broadening on the longer wavelength side. In both materials the broadening is indicative of the formation of new centre which is due to optical release of F-electrons. They are formed by retrapping these electrons at other trapping sites. The reduction in intensity of absorption band has been observed after bleaching which is indicative of a valence change in Tb ions. After suitable optical and/or thermal treatment, as many as five types of z centres (z_1-z_5) were reported to be formed [14]. The colored alkali halide crystals give the well-known F-band absorption, whose peak is determined by the lattice constant of the material in which it is observed. The lattice constant of KCl:Tb^{3+} and KI:Tb^{3+} are different. So the F-band observed at various wavelengths. Potassium halide crystal contain trivalent impurity Tb^{3+}, the impurities may act either as additional electron traps (or) as a perturbing influence on F-electrons when potassium halide crystal containing impurities is colored by γ-ray irradiation and then bleached at room temperature, electrons are released from the F-centres and retrapped at different sites. In this process, new absorption band due to centres called Z-centres are observed[14]. The formation of Z_1 centres have been observed in both materials at longer wavelength side due to the accumulation of F- electrons.

B. Photoluminescence

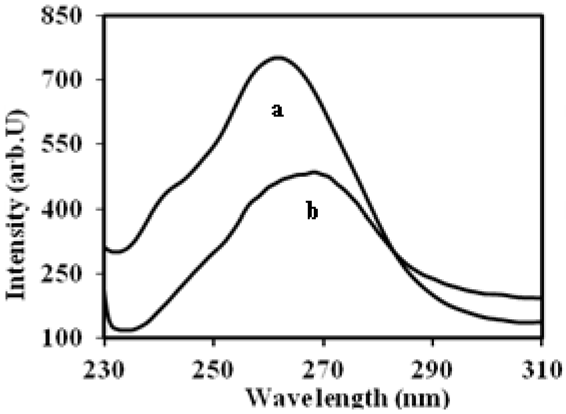

Figure 4. Excitation spectra of Tb^{3+} doped curve (a) KI with emission at 490nm, Curve (b) KCl with emission at 390nm

The photoluminescence studies gives light on different transition levels of a system. The PL excitation spectra are shown in Fig.4 for KI:Tb^{3+} (curve a) and KCl:Tb^{3+} (curve b) crystals at emission wavelength of 490nm and 390nm respectively. The excitation band monitored at 490nm for KI:Tb^{3+} consists of single band at 265nm, which are mainly ascribed to the allowed transition of Tb^{3+} from the 4f ground state to the 5d excited state and the shoulder at 240nm may partly contribute to the valence to conduction band of the KI host lattice according to discussion reported in earlier work [15]. The excitation spectra of KCl:Tb^{3+} exhibit a single broad band at 270nm which attributed to 4f-5d transition of terbium ions. This confirms that excitation is only due to terbium ions in both host material. The terbium ion found to enter the KI lattice in the trivalent state and the absorption band observed around 270nm in both the host has been attributed to the transition from the lowest ^7F_j level to one of the $^5D_3$ levels[16]. In the earlier reported work[16], the f-d transition spectra of Tb^{3+} appeared in the shorter wavelength region and f-f transition of Tb^{3+} ions in the longer wavelength side. The excitation spectrum of KCl:Tb^{3+} and KI:Tb^{3+} shows $4f^8 \rightarrow 4f^7 5d^1$ (f-d) transition of Tb^{3+} ions in the shorter wavelength region. The emission spectrum of the KI:Tb^{3+} (curve a) at excitation wavelength of 265nm and KCl:Tb^{3+} (curve b) at excitation wavelength of 270nm is shown in Fig.5. This spectrum gives emission due to transition from $^5D_3$

and $^5D_4$ excited levels to ^7F_j (J=5, 6) ground state levels. In KI: Tb^{3+}, emission bands observed at 490nm and also at 520nm as a doublet which is attributed to the transition of $^5D_4 \rightarrow {}^7F_6$ and $^5D_4 \rightarrow {}^7F_5$ respectively. The emission peaks at 390nm, 410nm and 550nm in KCl:Tb^{3+} were assigned to the transitions of $^5D_3 \rightarrow {}^7F_6$, $^5D_3 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_6$ and $^5D_4 \rightarrow {}^7F_5$ respectively. The results has been comparable with the earlier reported work[17,18]. The intensity of transitions from $^5D_3 \rightarrow {}^7F_5$, $^7F_6$ is high in KCl:Tb^{3+} crystal compared to the transition from $^5D_4 \rightarrow {}^7F_5, {}^7F_6$ in KCl:Tb^{3+} crystal. However in KI: Tb^{3+}, intensity of transition is vice-versa. So the visible light observed in KCl:Tb^{3+} crystal is at lower wavelength side and in KI:Tb^{3+} is at longer wavelength side. The change in intensity of transition and shift in wavelength are due to surrounding crystalline environment. However the emission intensity is high for KCl:Tb^{3+} compared to the KI:Tb^{3+} crystals. This confirms that the PL of these crystals exhibit characteristics Tb^{3+} emission due to transitions from $^5D_3$ and $^5D_4$ levels to various levels ^7F_J (J=5,6). The partially electric dipole transitions and partially magnetic dipole transition have high intensity[17]. So the maximum intensity emission band are due to partially electric dipole and magnetic dipole transitions.

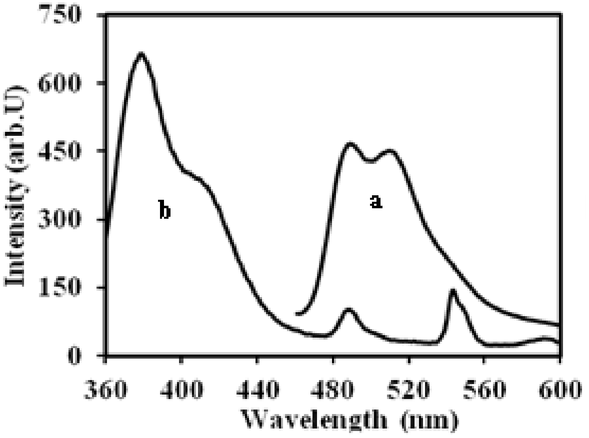

Figure 5. Emission spectra of Tb^{3+} doped curve (a) KI with excitation at 210nm, Curve (b) KCl with excitation at 265nm

C. Thermoluminescence

TL glow curve of gamma ray irradiated KI: Tb^{3+} and KCl: Tb^{3+} crystal is shown in Fig. 6 and Fig.7. respectively. Before taking the TL, the sample is annealed at 400°C and then irradiated at a gamma ray dose of 10.6 Gy/min. To avoid the possibility of error, TL measurements are carried out soon after irradiation of the sample. The TL is observed up to 600°K at a heating rate 120°C/m. The glow curve of the sample KI: Tb^{3+} and KCl : Tb^{3+} irradiated with gamma rays has been deconvoluted in order to obtain the value of trap parameters characterizing the different glow peaks. The peaks were deconvoluted using the software "Peak fit", making a Lorentzian fit for the individual peaks and the trap parameters were calculated for each deconvoluted peak by Chen's method [19]. The deconvolution of the TL glow peaks explains the TL glow to be a twostep annihilation process. The process of deconvolution was carried out with the entire TL glow and it was completed only when the best fit was obtained. The best fit allows a complete deconvolution of the composite glow curve. From these deconvoluted peaks, the half width and full maxima were measured.

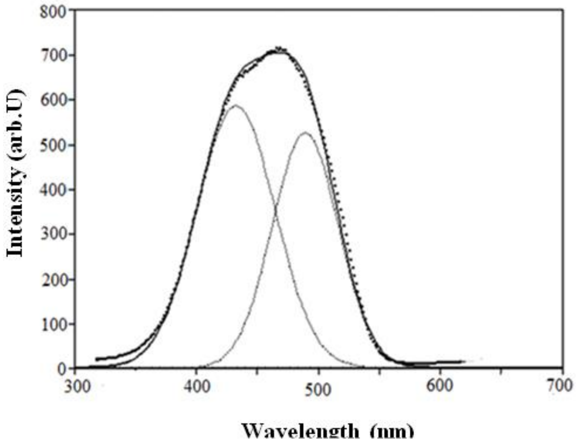

Figure 6. Deconvoluted TL Glow curve of Tb^{3+}: KI after γ – ray irradiation for 1 hour

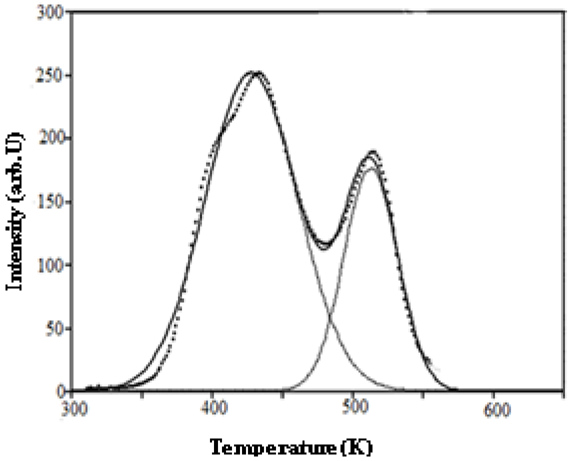

Figure7. Deconvoluted TL glow curve of Tb^{3+}: KCl after γ– ray irradiation for 1 hour

The calculation of trap parameters consists of the measurements of the total half width (ω), low temperature half width (τ) and high temperature half width (δ) of the deconvoluted glow peaks. The equation deduced by Chen is

$$E_\alpha = (C_\alpha \ \ KT_g^2/\alpha)-[b_\alpha(2KT_g)]$$

which is the first order kinetics equation, where E_α is the activation energy and α can be either $\omega = T_2$-T_1, $\tau = T_2$-T_g (where T_g is the glow peak maximum Temperature (or) $\delta = T_2$-T_g and K is the Boltzman's constant. The values of c and b are constants and are given by Chen [19].

The frequency factor is calculated using the equation:

$$S = S_0 T_g$$

Where,

$$S_0 = [(E/\ KT_g^2)+a/T_g]\ X\ b/[\exp(-E/\ KT_g) - 1/T_g]$$

Where E is the activation energy,
T_g is maximum glow peak temperature,
K is the Boltzmann's constant and a and b are constants whose values are given by Chen.

The trap parameters are presented in Table.1. The nature of the centres responsible for the observed TL glow peaks in both the crystals could be studied by observing the TL glow after thermal cleaning of these centres. The high value of trap parameters is indicative of a larger thermal stability for the trapped charges. The TL glow peaks indicate the existence of shallow as well as deep traps for this phosphor material which are responsible for the trapping of charge carriers produced by irradiation process Table.1 summarizes the numerical values of E ranging from 0.69 to 1.08 eV for low temperature and high temperature glow peak of KI:Tb^{3+}. Similarly in KCl:Tb^{3+}, E values ranging from 1.33 to 3.37 eV for low temperature and high temperature glow peak. The calculated parameters of each trap for both the material are different which is due to surrounding crystalline environment of Terbium ions as well as the defects in the form of aggregates and dislocations including those defects created by irradiation effects.

Table 1. Trap depth, E(eV) and Frequency factor S(s^{-1}) values for deconvoluted peaks

S. No	Material	Peak Temp. T_m(K)	Intensity (arb.U)	Trap depth (eV)	Frequency factor (ω)	Geometric Factor (μ_g)	Order of kinetics
1	KI:Tb^{3+}	430	580	0.6788	3.471×10^6	0.53	I
		487	526	1.0799	619.53×10^6	0.52	I
2	KCl:Tb^{3+}	425	250	1.3362	137.65×10^6	0.52	I
		513	172	3.3775	1.0984×10^{16}	0.50	I

In the present work, we observed two glow peaks at 430K and 487K for KI: Tb^{3+} and two glow peaks at 425K and 513K for KCl: Tb^{3+} crystals. From table.1, trap depths and frequency factor are different. This indicates that there are different electron trap with different perturbations due to environmental disturbances. Tb^{3+} donates an electron on irradiation and becomes Tb^{4+}. One of the two peaks in both materials is ascribed to be due to recombination of an F- electron with neighbouring Tb^{4+} ions as was reported in earlier work [20]. The calculated parameters indicated in table 1. (i.e.) Activation energy and frequency factor increases with increase in temperature. This shows that the trapped e^- in shallow trap were detrapped with less energy whereas in deep trap with more energy. The escape factor value also increased with temperature which proves that e^- trap emptied at high temperature (i.e.) electron completely escaped out from the trap. The appearance of various such peaks in the glow curve of phosphor suggests that there are perhaps more than two types of trapping levels, one of which shallower leading to the peak at lower temperature and others which are deeper contributing to the high temperature peaks [21]. The high temperature peak is due to high energy traps and it is very useful for TLD phosphor characteristics [22].

D. Photo stimulated Emission and Thermo stimulated Emission

To gain deeper insight into the TL process, the spectral distribution under the TL glow peaks was studied. In KI: Tb^{3+}, TL emission under the 430K glow peak (Fig.8a) exhibit emission bands at 426nm and weak shoulder at 474nm. In KCl: Tb^{3+}, TL emission at 425K glow peak (Fig.8b) shows broad emission band at 470nm obtained are due to the thermal release of F electrons recombined with hole centers, which is similar to the reports by

Nagarajan [23]. The spectral distribution under the TL glow peaks was studied to obtain a clear picture of the TL process. The peaks obtained in both materials are similar which is in the visible range of 420nm- 475nm in KCl: Tb^{3+} are attributed to the recombination of thermally released F electrons with Tb ions. The intensity of the emission band in KI: Tb^{3+} is higher compared to band obtained in KCl: Tb^{3+} which is due to different central metal ion are the terbium ions. The photo stimulation at the F- band (fig.9) gives emission spectra similar to the TL emission bands, showing strong emission bands at 464nm in KI: Tb^{3+} and 429nm in KCl: Tb^{3+}. This is in the visible region of the spectrum. From the result of TSE and PSE, the TSE band at 426nm in KI: Tb^{3+} and 474nm in KCl: Tb^{3+} are attributed to the recombination of thermally released F-electrons with Tb^{3+} ions and the TL process is due to thermal release of F- electrons. Comparing PSE and TSE band of KI: Tb^{3+} and KCl: Tb^{3+}, the band obtained in KI: Tb^{3+} is of high density compare to the KCl: Tb^{3+} material which is due to the different crystalline environment of the terbium ions. But emission wavelength of both materials is in the visible region, which is very useful for LED applications.

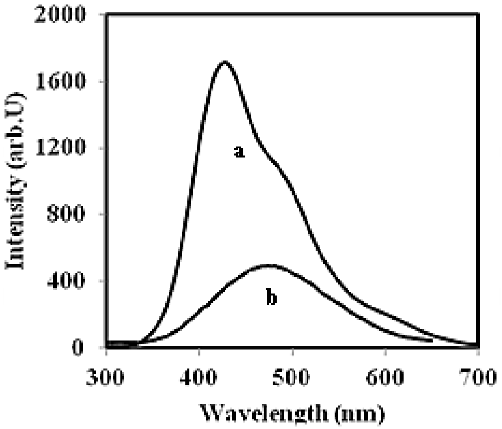

Figure 8. TL emission Tb^{3+} doped (a) KI, (b)KCl single crystals

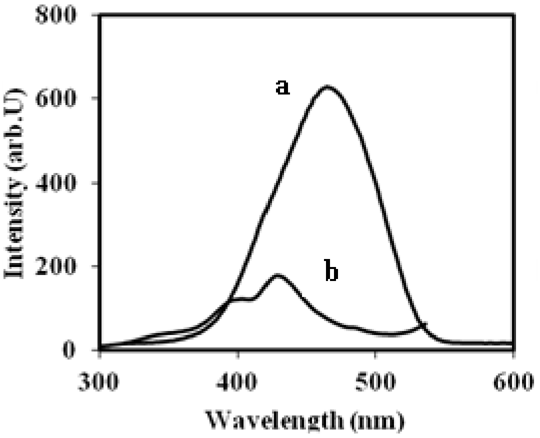

Figure 9. Photo stimulation under F band of Tb^{3+} doped (a)KI, (b) KCl single crystals

IV. CONCLUSION

The photoluminescence studies confirm the presence of Tb^{3+} ions in the trivalent state. The photoluminescence of these crystals exhibit characteristics Tb^{3+} emission due to transitions from $^5D_3$ and $^5D_4$ levels to various levels ^7F_j (J=5,6). TL properties of the grown crystal investigated and TL parameters were calculated. From this concluded that the high temperature peak are due to high energy traps and its very useful for TLD phosphor characteristics. TL emissions under glow peak of both materials contain the characteristic emission of terbium ions. Photostimulation with F- light in Tb^{3+} doped KCl and KI strongly supports the possibility that the TL process is due to the thermal release of F electrons. The photostimulation and thermal stimulation contain the characteristic Tb^{3+} emissions.

V. ACKNOWLEDGEMENTS

One of the author (S.B) great fully acknowledges the radiation – safety division, IGCAR for Atomic Research, Kalpakkam, India for providing experimental support.

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