

Investigation on Comparative Optical Absorption and Luminescent Property of Cerium Doped Potassium Halide Single Crystals

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ABSTRACT

The comparison of Optical absorption, Photoluminescence (PL), Thermoluminescence (TL) and other optical studies of X-ray irradiated Ce^{3+} doped KBr and KI single crystals were discussed. Photoluminescence of these crystals exhibits characteristic Ce^{3+} emission due to 5d-4f transition in both the studied material in addition to the host emission. Optical absorption and PL studies confirm the presence of Cerium ions in the trivalent state in both KBr and KI host. The characteristic emission due to Ce^{3+} ions in the spectral distribution under optically stimulated emission and TL emission confirms the participation of Cerium ions in the recombination process in both host material. Trap parameters for the TL process are calculated and compared.

Keywords : Ce^{3+} , Photoluminescence, Thermoluminescence, X-ray irradiation

I. INTRODUCTION

During the last few decades many luminescent studies have been reported on alkali halides doped with rare earth ions [1, 2]. The design of rare earth doped materials with potential application such as optical amplifiers (or) phosphors is an active area of research [3, 4]. Alkali halides have large band gap and simple structure. The lattice parameter of alkali halides are varying from 7.34 Å for RbI to 4.03 Å for LiF. This makes the easy incorporation of dopant ion of different size into them [5-8]. Substitution of impurities in a crystal lattice modifies the optical and other properties of the host. In most cases, the impurities enhance the performance of the host lattice. Potassium halides due their large ionic radius of K^+ are 1.33 Å permit the substitution of a large number of cations. Cerium is one of the major rare earth ion doped in different host lattice [9-12]. Potassium halides doped with Ce^{3+} ions have several technological applications. It forms a highly efficient blue phosphor for display application. Rare earth ions are known to give efficient luminescence and e.g. rare earth doped phosphors are applied in fluorescent lamps (or) in cathode ray tubes [13, 14]. The effect of radiation on the crystal phosphor is to create an electron hole pair followed by a trapping process, by already existing traps (or) induced defects by irradiation. Under an ideal condition, the trapped charge carriers

remains stable until an excitation (or) perturbation, usually stimulation by heat (or) light, releases the electron from the traps which in turn recombine with a hole centre to give rise to the emission of light. The trapping charge carrier properties and subsequent charge detrapping by heat (or) light stimulation are related to TL and OSL phenomena respectively [15]. Potassium halides doped with cerium ion subjected to X-ray irradiation and study the color centre phenomena in it which yielded valuable information regarding electronic processes occurring in crystals. Seitz and others summarized the important results in this field [16 -18]. Ce ion was found to become efficient emission centers in potassium halides, having relatively high transition probabilities originating from 4f – 5d electron configuration. It is shown that the Ce ion exhibits a blue emission with high color purity and stability for optical device applications [19]. Potassium halide doped rare earth ion crystals exhibits intense TL and OSL after X-ray and UV radiation and have a good potential as ionizing and UV radiation detectors, dosimeters and optical storage memory devices [20,21].

This paper presents and discusses the results obtained on the Optical absorption, Photoluminescence and TL of X-ray irradiated KBr and KI crystals doped with Ce^{3+} grown by Bridgeman Stockbarger method.

II. METHODS AND MATERIAL

Experimental Details

KI:Ce³⁺ and KBr:Ce³⁺ crystal were grown (1%,3%, and 5% Ce by weight) in the laboratory using the Bridgman Stockbarger technique. KI and KBr (99.99% Purity; Aldrich) and Cerium in the form of Cerium Fluoride (99.98% Purity; Aldrich) were used. Samples of size approximately 5x5x1 mm³ were used for all except the PSL and PL studies. For PSL and PL, 5x5x3 mm³ Samples were used. The result due to the three concentrations were similar expect for a high luminescence yield with higher concentration of Ce³⁺ ions. There was no qualitative change in the result, but there is a change in intensities of emission and absorption, due to different cerium ion concentrations. Hence the result pertaining to a Cerium 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 190-1100 nm. 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 glow were recorded using a PC-based TL analyzer (Hitachi make) at a heating rate of 120°C/min. The samples were irradiated with an X-ray source operating at 25 kV and 7mA . TL emission spectra were recorded in the region 200-900 nm, 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 400°C for 30mins. 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

Optical absorption spectra of trivalent cerium in the UV, Visible and near Infrared are due to transitions between 4f – 5d configuration of closely spaced mutiplets. The assignment of absorption bands has been done based on the energy level positions. Majority of the absorption bands originate due to the induced electric dipole contribution ($\Delta J \leq 6$) and a less number of transitions possess magnetic dipole contribution ($\Delta J=0,\pm 1$) [22].

The Ce³⁺ ion directly excited only possible with UV and/or visible radiation [14]. The optical absorption spectra of KI: Ce³⁺ and KBr: Ce³⁺ of as grown crystal are shown in Fig.1 (curve a) and Fig.1 (curve b) respectively.

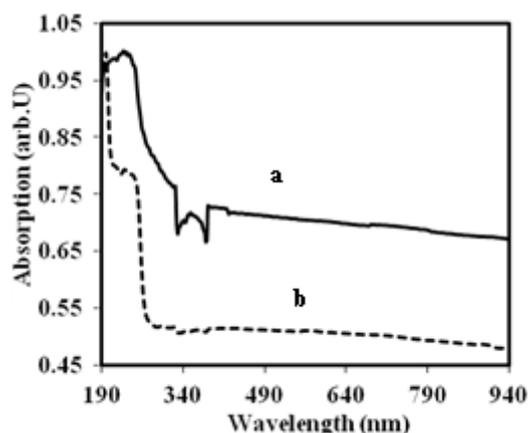


Fig. 1 Optical absorption of Ce³⁺ doped (a) KI , (b) KBr before X-ray irradiation

The unirradiated crystal of KI: Ce³⁺ shows a broad absorption around 250 nm and prominent shoulder around 270 nm (Fig 1 curve a). It also exhibits sharp band at 195 nm which attributed to the exciton absorption of the host matrix [23]. In glass ceramic sample, in which transitions from ground state to excited state are relatively sharper but it is difficult to observe well separated transition as the amount of glass is much more than crystalline [24]. From this discussion, we understood crystalline environment is easy to observe the transitions in a clear manner. Roth and Halperin [25], have reported the formation of intrinsic hole centers (V₄, V₂ and V₃) to absorb in the UV region at 318, 353, and 390 nm respectively. Of these, V₃ centers are more stable at room temperature [26]. The reduction in intensity of absorption between 310 nm to 390 nm can be attributed to the change in valence state of species. The band appearing due to V- centers are known to have large band width. This is in agreement with the earlier results on KBr and KBr: Cu reported by Murti et al [27]. The unirradiated crystals of KBr: Ce³⁺ exhibits a sharp band at 195 nm and broad absorption around 240 nm. The absorption below 290 nm is drastically reduced while a new broad absorption shows up 310 nm which is probably due to V - centers. On comparing both spectra of unirradiated crystal (Fig.1), the maximum intensity of absorption is same at 195 nm in both the matrix when it is doped with Ce³⁺. But the intensity of other absorption bands in KI matrix is high compared with the KBr.

The Optical absorption spectra of Ce^{3+} doped Potassium Iodide (curve a) and Potassium Bromide (curve b) after 30 mins. of X-ray irradiation are shown in Fig.2. Optical spectra of KCl, KBr and KI powders exposed to X-ray show the various band [28]. These were identified as the well known F and V-type centers [29]. The high energy excitation always excites the host lattice [14]. Fig.2 curve (a) and (b) exhibits sharp band at 195 nm which is noted before irradiation but with reduced intensity. After 30 mins. of X-ray irradiation, both curve results in the formation of the characteristic F-band centered at 690 nm in KI: Ce^{3+} and 630 nm in KBr: Ce^{3+} . The absorption below 290 nm is drastically reduced and V-centers are observed around 310 nm (curve a) in KI: Ce^{3+} . The band observed around 240 nm are due to hole type centers in KBr: Ce^{3+} and the prominent shoulder at 310 nm has also been observed. The slight variation in F-band wavelength is due to different crystalline environment of Ce ions.

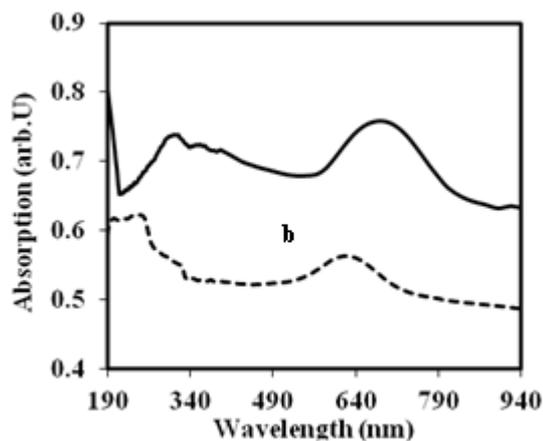


Fig. 2 Optical absorption of Ce^{3+} doped (a) KI, (b) KBr after X-ray irradiation

Fig.3 shows the spectra of F-light bleaching subsequent to X-ray irradiation of Cerium doped KI (curve a) and KBr (curve b) respectively. On F-bleaching, absorption at F-band shows a broadening on longer wavelength side [30] in both the matrix. The broadening is indicative of formation of new species. The intensity of the absorption band at 195 nm increased for KBr: Ce^{3+} . The intensity of KI: Ce^{3+} is high compared to KBr: Ce^{3+} above 290 nm. Vijayan and Murthi [31] in their work on Gd^{2+} doped KCl, have reported the formation of Z_1 centers. These centers were observed on the longer wavelength

side of F-band. The irradiated crystal contain interstitial defect clusters in different environment. Interstitial defects are known to have a tendency to cluster around I-V pairs in trivalent cation doped systems. After bleaching, more of I-V pairs get associated with F-centers, thus increasing the Z_1 center concentration. Thus F-light bleaching brings about a change in environment.

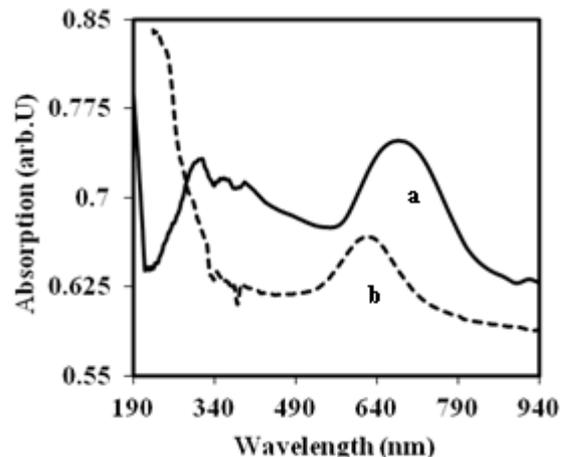


Fig.3 Optical absorption of Ce^{3+} (a) KI (b) KBr after F-bleach for 2 mins. Subsequent to X-ray irradiation

B. Photoluminescence (PL)

Fig.4 depicts the excitation spectra of Ce^{3+} doped KI (curve a) and KBr (curve b) for emission at 420 nm and at 390 nm respectively. For 420 nm emission, the excitation spectra of KI: Ce^{3+} consists of single broad band in the region of 230 nm – 290 nm which are ascribed to the transitions from the ground state to the excited state of Ce^{3+} . It is well known that the $4f^1$ ground state configuration of Ce^{3+} ions yield two levels $^2F_{5/2}$ and $^2F_{7/2}$ due to spin orbit coupling [32]. So the absorption band of KI: Ce^{3+} at 260 nm (curve a) are due to allowed transitions from the ground state to the crystal field splitting of 5d level. The excitation band altered by the surrounding crystallographic site. In KBr: Ce^{3+} , excitation spectrum shows a broad band with maximum at 270 nm (curve b). The presence of single broad peak in KI: Ce^{3+} and KBr: Ce^{3+} at 260 nm and at 270 nm respectively is probably due to the presence of Ce^{3+} at two different crystallographic sites. The slight variation in excitation wavelength of Ce^{3+} ions are due to different host lattice. The cerium emission bands remain unchanged upon varying the excitation wavelength and its emission

spectrum under ultraviolet excitation is similar to that under cathode ray excitation in the reported work [33]. The emission of Ce^{3+} usually includes two bands of the transitions of 5d excited state to $^2F_{5/2}$ and $^2F_{7/2}$ [34,35]. In $CaSO_4:Ce^{3+}$, Ce^{3+} ion give emission at 310 nm and 328 nm [35]. H.You et al [36] reported their work on luminescence studies on $Y_3Si_2O_8Cl:Ce^{3+} Tb^{3+}$ have two emission band at 358 nm and 376 nm for Cerium. Fig.5 gives the emission spectra of $KI:Ce^{3+}$ for excitation at 260 nm (curve a) and $KBr:Ce^{3+}$ for excitation at 270 nm (curve b) respectively. On excitation of $KI:Ce^{3+}$ at 260 nm, the emission spectrum exhibits a well defined two broad emission with maximum at 420 nm with high intensity and at 362 nm with low intensity. Similarly the emission spectrum of $KBr:Ce^{3+}$ excited by 270 nm (curve b) shows two bands at 390 nm and 290nm.

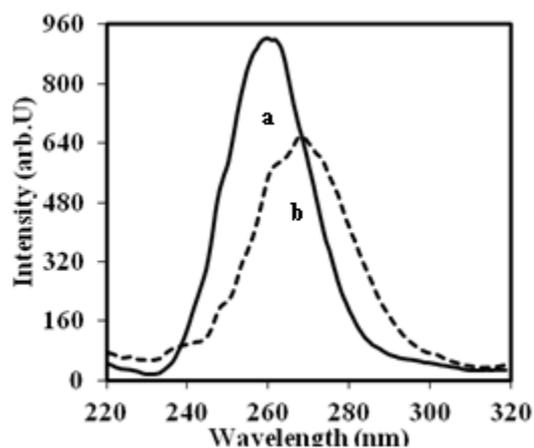


Fig.4 Excitation spectra of (a) $KI: Ce^{3+}$ emission at 420 nm (b) $KBr: Ce^{3+}$ emission at 390 nm

The change in emission wavelength is probably due to the excitation 5d level which is not screened from the crystalline[37]. The emission peak of Ce^{3+} is at 420 nm in KI host and at 390 nm in KBr host confirms the Ce^{3+} emission which is attributed to the transition from 5d excited state to $^2F_{5/2}$ and $^2F_{7/2}$ ground state level. But the intensity of Ce^{3+} emission peak is greater when it is in the KBr host compared to the KI. The 5d¹ band of Ce^{3+} is split into five separate bands by the crystal field. The exact energy level of such split state strongly depends on the strength of the crystal field. The crystal field of KBr and KI is different because of the presence of different halide ions. Because of

this, the emission wavelength and its intensity varied in both host when it is doped with cerium ions. But $KI: Ce^{3+}$ and $KBr: Ce^{3+}$ emits blue light which is very useful for optical device applications.

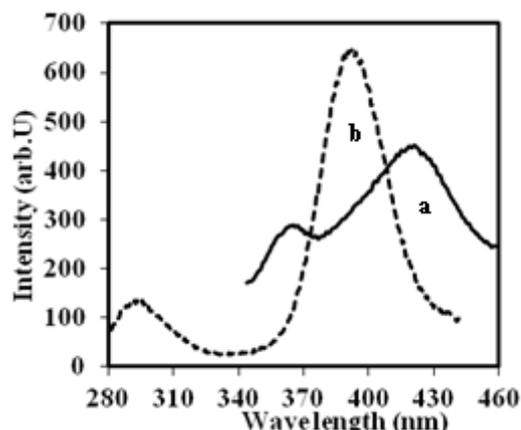


Fig.5 Emission spectra of (a) $KI:Ce^{3+}$ excitation at 260 nm (b) $KBr:Ce^{3+}$ excitation at 270 nm

C. Thermoluminescence (TL)

The TL glow curve shows the nature of traps present in the material and also gives us information about the energy absorbed by the material during irradiation. The deconvoluted TL glow curve of X-ray irradiated $KBr:Ce^{3+}$ and $KI:Ce^{3+}$ were shown in Fig.6 and Fig.7 respectively. The normal TL glow curve X-ray irradiated $KI: Ce^{3+}$ (curve a) and $KBr: Ce^{3+}$ (curve b) were shown in Fig.8. The TL glow peaks indicate the existence of shallow as well as deep traps for this phosphor material which are responsible for the trapping charge carriers produced by the irradiation process. The TL glow curve can be deconvoluted by means of using “peak fit software”. The trapping mechanism as well as the recombination process may be modified by addition of doping impurities process. A very important method, the computerized glow curve deconvolution has been used in recent years for calculating the trapping parameters of localized energy levels within the crystal and defects in the phosphor [38-41]. This method is very useful for analyzing composite glow peaks. The glow curve of $KBr: Ce^{3+}$ reveals two clear and well distinguished peaks at 378 K and 423 K. The glow curve of $KI: Ce^{3+}$ exhibits two peaks at 408 K and 438 K. The TL kinetic parameter of $KBr: Ce^{3+}$ and $KI: Ce^{3+}$ are calculated by peak shape method. A study of kinetic parameter such as the activation energy(E) and frequency factor(s) provide information about the defect

centers responsible for TL in the material [42,43]. Trap parameters were calculated by means of using Chen's method [44]. As shown in the table.1, T_m is the peak temperature; T_1 and T_2 are the temperature at half intensity on either side of the peak. τ , δ and ω are the half width on low temperature side, half width on high temperature side and full width at half maximum respectively.

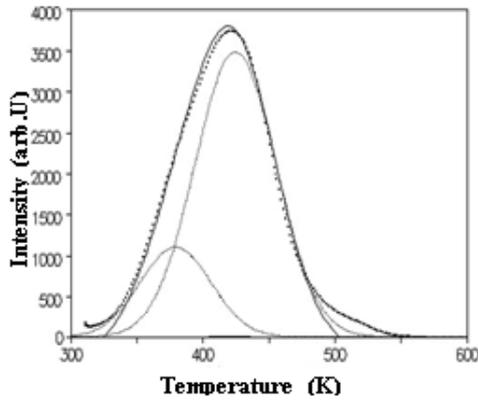


Fig.6 Deconvoluted TL glow curve of a KBr:Ce³⁺ X-ray irradiated for 5 mins.

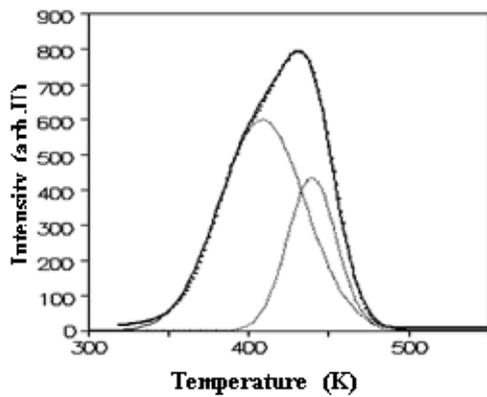


Fig. 7 Deconvoluted TL glow curve of KI: Ce³⁺ X-ray irradiated for 1 hour

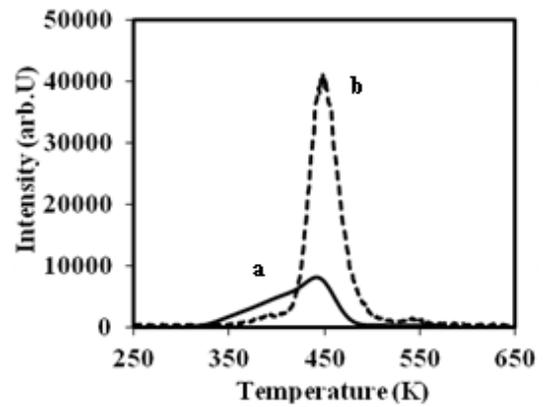


Fig.8 TL glow curve of X-ray irradiated Curve (a) KI: Ce³⁺ for 1 hour, Curve (b) KBr: Ce³⁺ for 5 mins.

They are the temperature difference between T_m-T_1 , T_2-T_m and T_2-T_1 . The Peak shape method is generally used to calculate the order of kinetics and is obtained from the geometric factor. The geometric factor can be calculated as

$$\mu_g = \frac{\delta}{\omega} \text{-----(1)}$$

The order of kinetics depends on the shape of the peak. The value of μ_g for first and second order kinetics is 0.42 and 0.52 respectively.

The activation energy E and frequency factor S, for any order of kinetics can be calculated as.

$$E = C_\alpha \left(\frac{KT_m^2}{\alpha} \right) - b_\alpha (2 K T_m) \text{-----(2)}$$

And

$$S = \frac{\beta E}{T_m K} \left(\frac{1}{1+(b-1)\left(\frac{2KT_m}{E}\right)} \right) \exp \left(\frac{E}{E T_m} \right) \text{---(3)}$$

Where α stands for τ , δ and ω respectively, β is the heating rate, k is Boltzmann constant and b is order of kinetic, which can be determined from equ.1. The constants in equ.2 obtained using the expressions.

$$\begin{aligned} C_\tau &= 1.51 + 3.0(\mu_g - 0.42), & b_\tau &= 1.58 + 4.2(\mu_g - 0.42) \\ C_\delta &= 0.976 + 7.3(\mu_g - 0.42), & b_\delta &= 0 \\ C_\omega &= 2.52 + 10.2(\mu_g - 0.42), & b_\omega &= 1 \end{aligned}$$

Table.1. Calculated Peak shape parameters for TL deconvoluted peaks

S.No	Material	Peak Temperature T_m (K)	Half width on low temperature side (τ)	Half width on high temperature side (δ)	Full width at half maximum intensity (ω)	Geometric Factor (μ_g)
1	KI:Ce ³⁺	408	375	438	63	0.48
		438	420	458	38	0.53
2	KBr:Ce ³⁺	378	347	412	65	0.52
		423	385	460	75	0.50

Table.2. Calculated trap depth E (eV) and Frequency factor S (s⁻¹) values for TL deconvoluted peaks.

S.No	Material	Peak Temperature T_m (K)	Intensity (arb.U)	Trap depth E (eV)	Frequency factor S (s ⁻¹)	Order of kinetics
1	KI:Ce ³⁺	408	600	0.74107	0.04245 x 10 ⁶	I
		438	430	1.50339	18302.6 x 10 ⁶	II
2	KBr:Ce ³⁺	378	1110	0.6066	4.9172x 10 ⁶	II
		423	3500	0.6541	2.691x 10 ⁶	I

The parameter τ , δ and ω were initially determined for temperature T_1 , T_m and T_2 . These values are used to calculate the geometric factor μ_g from equ.1, which determines the order of kinetics. The values of E and S were then calculated from equ.2 and equ.3 and are given in table.2. The dosimetric properties of the TL material mainly depend on the kinetic parameters of their glow peak and kinetic parameters give valuable information about the technique responsible for the TL emission in the material. From table.2, high temperature glow peak have high trap depth value. This is in good agreement with earlier reported work [46]. The activation energy and frequency factor difference between two peaks in KI: Ce³⁺ is large compared to KBr: Ce³⁺ material. From data in table 1, the high temperature glow peak in KI: Ce³⁺ and low temperature glow peak in KBr: Ce³⁺ follows the second order kinetics. Hence there is chance of retrapping in these glow peaks. The activation energy of various traps are different. Therefore it is clear that there is formation of some deep and shallow trap. The high temperature peak corresponds to deep trap and low temperature peak correspond to shallow trap. Furthermore, the frequency values are also different. This may be because competition among various traps might be giving various escaping and

retrapping probabilities, which might have resulted in different frequency factors. The traps could be either electron traps (or) hole traps (or) both.

D. Thermo stimulated Emission (TSE) and Photo stimulated Emission (PSE)

To understand the mechanism of the recombination process TSE and PSE were studied. Fig.9 shows the TL emission spectra under glow curve 438 K and 423 K for KI: Ce³⁺ (curve a) and KBr: Ce³⁺(curve b) respectively. There are two aspects about the thermally mobilized species and recombination sites. In one it is said that the electrons are thermally released and their recombination results in the TSE [47]. The other aspects talks about the thermal mobilization of hole centers [48]. The emission spectra exhibit band at 430 nm for KI:Ce³⁺ (Fig.9 curve a) and at 450 nm for KBr: Ce³⁺ (Fig.9 curve b). The band formed at 430nm and 450nm in TL emission spectrum (Fig.9) confirm the participation of Ce ions in TL process. The presence of these emissions indicate the capture of an electron by Ce⁴⁺ ions possibly formed during irradiation process.

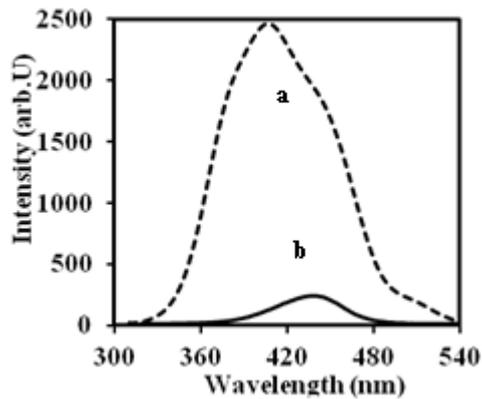


Fig. 9 TL emission Ce^{3+} doped (a). KI (b). KBr under glow curve 438 K and 423 K respectively

This capture leaves a Ce^{3+} ion in an excited state, which on relaxation yields the 430 nm and 450 nm emission in KI: Ce^{3+} and KBr: Ce^{3+} respectively. This indicates that on high energy irradiation Ce ions also act as hole traps (electron donors) and there by becoming Ce^{4+} ions and which thermally deexcite as Ce^{3+} emissions. Hence we could observe Cerium emission in TSE spectra. In Ca doped KCl [49], the emission bands are reported at 415 nm and 455 nm. Comparing these with the present study in KI: Ce^{3+} and KBr: Ce^{3+} , we find that the host emission are missing. This may be due to suppression of recombination processes which lead to these emissions. To understand TL mechanism better, one can record the emission spectrum under selective mobilization of charges using optical methods. This is named as Photo stimulated emission (PSE). In this process, the irradiated sample was illuminated with light in F-band. This is expected to optically release the F-electrons and their subsequent recombination yield a spectrum. This is different from PL in the sense that the emission in PSE can be on lower wavelength side of the stimulating radiation. The Photostimulation under F-band of KI: Ce^{3+} (curve a) and KBr: Ce^{3+} (curve b) material are shown in Fig.10. This gives emission spectrum with dominant peak at 320 nm in KI: Ce^{3+} and at 415 nm in KBr: Ce^{3+} . The same emission was also present in TL emission of the crystal.

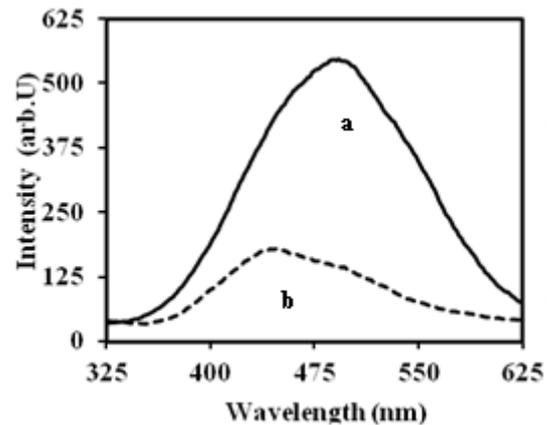


Fig.10 Photo stimulation under F-band of Ce^{3+} doped Curve (a) KI, Curve (b) KBr

On comparing these emission with the TL emission, it seems that the TL process is due to thermal release of F-electrons and their subsequent recombination with hole centers. The TSE emission at 420 nm in KI: Ce^{3+} and 450 nm in KBr: Ce^{3+} and PSE emission at 320 nm in KI: Ce^{3+} and 415 nm in KBr: Ce^{3+} indicate that the cerium ions take part in the recombination process. The small shift in wavelength is due to overlapping of the neighboring emission bands. The presence of Cerium emission in TSE and PSE are indicative of change of valence state of Ce^{3+} ions during the irradiation process. The presence of Ce^{3+} emission in the recombination with F-electrons is suggestive of the formation of Ce^{4+} during irradiation process. Photo stimulation done at room temperature whereas TSE recorded at an elevated temperature. So the shift in emission peaks can be due to association of more phonons at high temperature.

IV. CONCLUSION

Ce^{3+} ions act as both electron and hole traps on exposure to high energy radiation. It was found that the PL emission at 420 nm in KI: Ce^{3+} and 390 nm in KBr: Ce^{3+} under 260 nm and 270 nm excitation wavelength respectively, due to $5d - 4f$ transition of Ce^{3+} ion. KBr and KI doped with Ce^{3+} shows fair TL characteristics with two deconvoluted glow peaks. Calculation of kinetic parameters for each individual peak using Chen's peak shape method shows that it follows both first order and second order kinetics. Hence there is chance of retrapping in the second order glow peak. Cerium enters the KBr and KI lattice in its trivalent state.

The TL emission under high temperature glow peak contains the characteristic blue emission of the Ce^{3+} ions. Photostimulation with F-light and the subsequent recombination emission yield bands similar to those observed in TSE, strongly implying that the TL process is due to thermal release of F-electrons and their recombination with V- centers and Ce^{3+} ions.

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