

Luminescence Properties and Optical Absorption of X-ray-Irradiated KBr: Ce³⁺, Tb³⁺ Crystals

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Abstract This paper reports that KBr doubly doped with Tb³⁺ and Ce³⁺ were prepared by Bridgman-Stockbarger method and characterized by Optical absorption, Photoluminescence (PL), Thermoluminescence (TL), Photo stimulated emission (PSL) and TL emission, after X-ray irradiation have been observed. The optical absorption measurement indicates that F and Z₃ centers are formed in the crystal during X-ray irradiation process. It was attempted to incorporate a broad band of Ce³⁺ sensitizer into the narrow band emission of Tb³⁺ in the KBr host without reduction of emission intensity. Co-doping of Ce³⁺ ions in KBr:Tb³⁺ crystal showed a broad band emission due to the d-f transition of Ce³⁺ and a reduction in the intensity of emission peaks due to ⁵ days → ⁷F₆ transition of Tb³⁺ when they were excited at 250 nm. These results supported that an effective energy transfer occurs from Ce³⁺ to Tb³⁺ in the KBr host. Co-doping Ce³⁺ ions greatly intensified the excitation peak at 260 nm for the emission at 390 nm of Tb³⁺ which means that more lattice defects, involved in the energy absorption and transfer to Tb³⁺, are formed by the Ce³⁺ co-doping. The integrated light intensity is two orders of magnitude higher as compared to the undoped samples for similar doses of irradiation and heating rate. Thermoluminescence process has been identified due to thermal mobilization of F-electrons and this causes peaks at 371 K and at 427 K, 457 K in KBr: Ce³⁺, Tb³⁺ crystals. The defects generated by irradiation were monitored by optical absorption and trap parameters for the TL process were calculated and presented.

Keywords KBr · Thermoluminescence · Photoluminescence · Tb³⁺ · Ce³⁺

Introduction

During the last few decades, energy transfer from Ce³⁺ to Tb³⁺ in luminescent materials has been studied extensively [1–4]. Rare earth doped materials have wide range of applications in lamp phosphors, image plate and neutron detection [5–7]. The luminescence from terbium doped phosphors was of great interest due to their strong green emission corresponding to the ⁵ days → ⁷F₅ [8]. We have recently studied the effect of introducing Ce³⁺ and Tb³⁺ in potassium iodide and some interesting results were obtained [4]. As a continuation of this work, we studied the effect of impurities Ce³⁺ and Tb³⁺ in potassium bromide. Co-doping of Ce³⁺ with Tb³⁺ doped luminescent materials is known to improve the luminescence efficiency [9–14]. Of several rare earth ions, Eu²⁺ and Ce³⁺ ions show a broad band emission in most host matrix [15–18]. The energy level of excited states of Ce³⁺ ions is strongly affected by the kind of host matrix and crystal field strength of crystalline surrounding them. In YAG host, Ce³⁺ ion yields a broad band emission between 480 and 680 nm [5, 19, 20].

In the recent past, our group carried out work on Ce³⁺, Tb³⁺ and Sm³⁺ doped potassium and rubidium halides respectively [21–23]. From this reported results, we observed the change in valence state of impurities on irradiation with X-rays (or) γ-rays. Of several rare earth ions cerium ion is known to act as sensitizer as well as activator. From our results of KBr doped Ce³⁺ and Tb³⁺ independently, cerium is known to be sensitizer for KBr doped terbium phosphor, we have tried to incorporate a broad band of Ce³⁺ activator into narrow band of terbium in KBr host without reduction of intensity. Also there are many papers reporting energy transfer from Ce³⁺ to Tb³⁺ in many

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hosts such as CaAl_2O_4 fiber, CaAl_4O_7 , GdOBr , $\text{Y}_3\text{Si}_2\text{O}_8\text{Cl}$ and so on [12, 13, 24–26].

In this work, KBr:CeTb crystals were prepared by Bridgmann-Stockbarger. Ce^{3+} ions were used as a co-activator to yield a band emission of KBr:Tb^{3+} phosphor without any loss of intensity. The results obtained on Thermo luminescence (TL), Photoluminescence (PL), Thermally stimulated luminescence (TSL), Photo stimulated luminescence (PSL) and optical absorption of KBr double doped with cerium and terbium irradiated with X-rays were discussed. The PL and TL properties of KBr:CeTb were systematically studied to see whether the brightness could be improved by cerium co-doping.

Experimental Details

Single crystals of pure KBr (99.99 % purity) and cerium terbium doped KBr (99.99 % purity) were grown using the Bridgman Stockbarger technique. Terbium and cerium were added in the form of terbium fluoride and cerium fluoride (Aldrich 99.99 % purity). The crystals were grown with three different concentrations of the impurity 1, 3 and 5 % by weight. Samples of size approximately $5 \times 5 \times 1 \text{ mm}^3$ were used for all except the PSL and PL studies. For PSL and PL, $5 \times 5 \times 3 \text{ mm}^3$ samples were used. The results arising from the three concentrations were similar and hence only the results pertaining to a cerium, terbium concentration of 3 % by weight are presented and discussed. The absorption spectra were recorded using Perkin Elmer Lambda 35UV-Vis spectrophotometer in the region 190–1100 nm photoluminescence spectra were recorded at room temperature using Perkin Elmer LS 55 Luminescence spectrometer in the region 200 to 900 nm with a spectral width of 5 nm. 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 7 mA. TL emission was recorded using Perkin Elmer LS 55 with the excitation slit being closed. Before every experiment, the crystals were annealed at 400 °C for half an hour and then quenched to room temperature to ensure homogeneous distribution of impurity and to remove any storage effect.

Optical Absorption

Figure 1 shows the optical absorption spectra of 3 % $\text{KBr:Ce}^{3+}, \text{Tb}^{3+}$ crystals, before and after X- irradiation for 30 min at room temperature. The unirradiated crystals exhibit a sharp absorption at 199, 200 nm and a broad shoulder at 255 nm as shown in [Fig.1a]. When the crystals were bleached with F-light for 2 min [Fig.1b], the F-band shows a broadening on lower wavelength side and the absorption around 255 nm

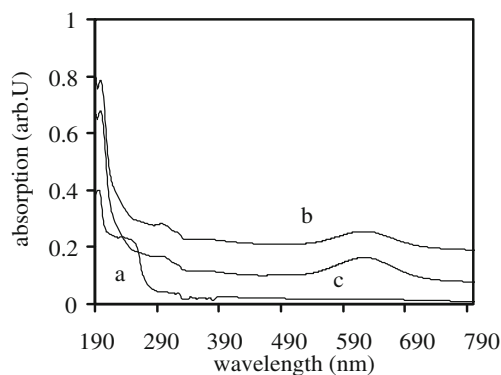


Fig. 1 Optical absorption of KBr:CeTb crystals (a) Unirradiated (b) F-bleached for 2 mins. c X-ray irradiated for 30 mins

disappears. This broadening is indicative of formation of new species. After 30 min of X-ray irradiation, crystals results in the formation of a characteristic F-band centered at 630 nm as shown in [Fig.1c]. In order to identify the species that has been formed, one has to look at the normalized absorption (taking the maximum of absorption as unity and rescaling of other areas under the curve). On normalizing the absorption bands in the F-band region before [Fig. 2 curve1] and after F-light bleaching [Fig. 2 curve2] and difference between the two is given in [Fig. 2 curve3]. It indicates formation of a new absorption around 546 nm which is on lower wavelength side of F-band. So this new absorption is attributed to Z_3 -centers. In our previous work [4], the new absorption band formed on longer wavelength side of F-band which is attributed to Z_1 -centers.

The well known perturbed F centers are the F_A and $F_Z(z)$ centers. F_A centers are formed when one of the six surrounding alkali ions is replaced by a different alkali ion of smaller size compared to the host cation [27]. Z centers are another type of perturbed F centers. Here the perturbation is due to a divalent cationic impurity and its associated cation vacancy (I-V) complex. After suitable optical and/or thermal treatment, as many as five types of (Z_1 to Z_5) perturbed centers are reported to be formed [28]. Considering the fact that the new absorption appears on F bleaching, it appears more appropriate to assign

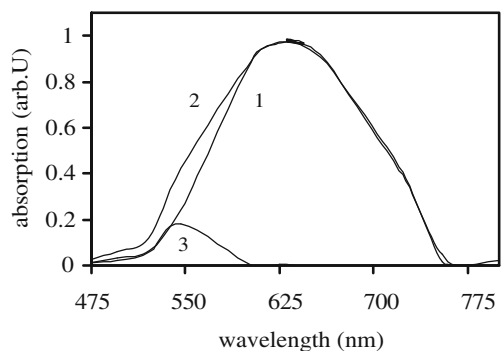


Fig. 2 Normalization to show the formation of the new band at 546 nm. 1) X-ray irradiated for 30mins 2) F-bleached for 2mins 3) Difference between the curves 1&2

the new absorption to an electron excess center. The divalent ion perturbed F-centers, namely the Z-center have been observed on the longer wave length side of the F-band.

The loss of prominence of the absorption at 255 nm can be viewed as a change in valence state of the species that absorbs in this region. This absorption is due to Tb^{3+} [23]. The reappearance of the absorption around 255 nm on F-light bleaching subsequent to irradiation indicates the Tb^{3+} acts as a hole trap, ie. it has lost an electron to become Tb^{4+} . Such results have been reported on Rubidium halides doped with Tb^{3+} by Manimozhi et.al. [4, 23, 27–34]. Considering the fact that the new absorption appears on F bleaching, it appears more appropriate to assign the new absorption to an electron excess center. This new absorption is on the lower wave length side of the F band which can be attributed to Z_3 centers [28, 34]. These centers were observed on the lower wavelength side of the F band. Considering this, it seems appropriate to assign the new absorption in KBr: CeTb to Z_3 bands [22, 23].

Photoluminescence

Figure 3 shows the PL emission spectra of KBr:Tb³⁺ and KBr:Ce³⁺Tb³⁺ crystals under excitation at 350 nm and at 260 nm respectively. The KBr: Tb crystals had one main peak due to the ⁵D₄→⁷F_j(j=6) transition between the wavelengths of 360 and 400 nm and a shoulder due to the ⁵D₃→⁷F_j(j=5) transition of Tb³⁺ between the wavelength of 410 and 450 nm [Fig. 3 curve1]. The KBr :CeTb crystals had a broad band at 390 nm characterizing the d-f transition of both Ce³⁺ and Tb³⁺ in the KBr host. It is notable that co-doping Ce³⁺ ions produce a strong emission at 390 nm [Fig. 3curve2], which is not found in KBr:Tb³⁺ crystals at the excitation wavelength of 350 nm. More details about this unusual luminous phenomenon are discussed as follows,

The emission spectra of KBr:Ce³⁺ and KBr: CeTb crystals under the excitation at 240 nm and 260 nm respectively were displayed in Fig. 4. The emission spectrum of KBr:Ce³⁺

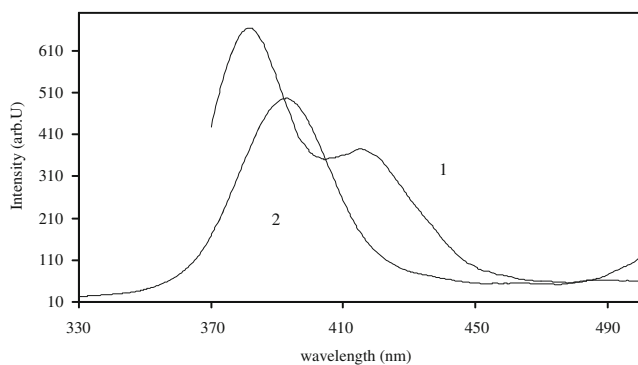


Fig. 3 (1) Emission spectra of KBr: Tb³⁺ excitation at 350 nm and (2) KBr: CeTb crystals, excitation at 260 nm

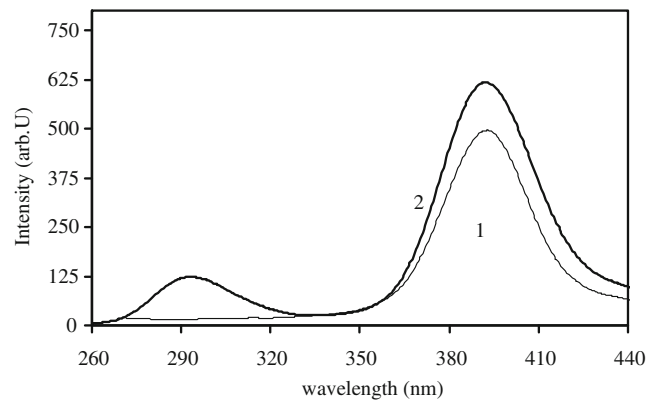


Fig. 4 (1) Emission spectrum of KBr: CeTb Excitation at 260 nm and (2) KBr: Ce³⁺ emission spectrum for excitation at 240 nm

crystals exhibited strong peak at 394 and 294 nm [4] as shown in [Fig. 4curve2]. In KBr: CeTb crystal, the emission spectrum at excitation of 250 nm showed a strong peak at 394 nm as shown in [Fig. 4 curve1]. But the peak exhibited at 294 nm in KBr:Ce³⁺ is not found in KBr: CeTb crystals due to co-doping of terbium impurities. On comparing emission spectra of KBr:Ce³⁺ and KBr: CeTb crystals, the peak at 394 nm in KBr:Ce³⁺ is similar to that of KBr: CeTb crystals.. Cerium ions emit efficient ultraviolet luminescence [14]. In our case, emission wavelength is at 394 nm, so ultraviolet emission were used to excite terbium ions. The excitation spectrum for KBr:Tb and KBr: CeTb crystals at emission of 390 nm were displayed in Fig. 5. The excitation spectrum of KBr:Tb for 390 nm exhibits two bands at 355 nm,268 nm and a prominent shoulder around 240 nm [35] as shown in [Fig. 5curve2]. In KBr: CeTb crystals, the excitation spectrum showed one strong excitation peak at 268 nm characterizing the f-d transition of each Terbium and Cerium ion [Fig. 5curve1]. But the excitation peak exhibited at 355 nm in KBr:Tb were suppressed due to co-doping of cerium ions. The excitation spectra of KBr:Ce³⁺ and KBr: CeTb were compared in Fig. 6. In KBr: Ce sample, there one distinct

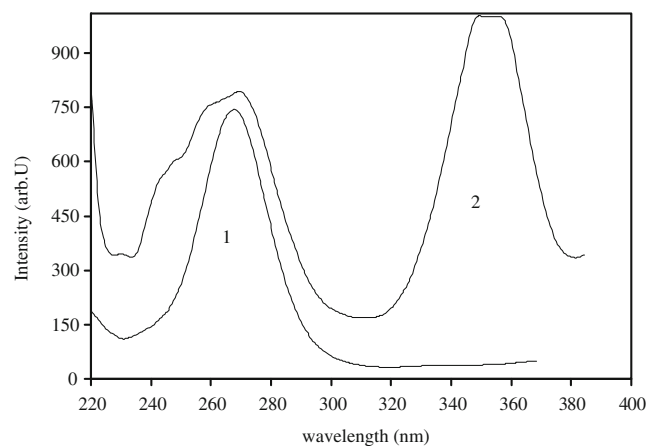


Fig. 5 (1) Excitation spectra of KBr: CeTb Emission at 390 nm and (2) KBr: Tb³⁺ Emission at 390 nm

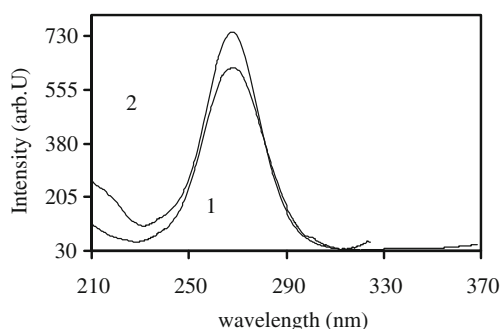


Fig. 6 (1) Excitation spectra of KBr: Ce for emission at 390 nm and (2) KBr: Ce Tb Emission at 390 nm

excitation peak ($\lambda_{em}=390$ nm) located at 272 nm [21] as shown in [Fig. 6 curve1]. In the excitation spectra of KBr: CeTb [Fig. 6curve2], bands corresponding to the ${}^2F_{5/2}(4f) \rightarrow {}^2T_{2g}(5d)$ transition were observed at 272 nm with enhanced intensity.

The exact energy level of a such a split state strongly depends on the strength of crystal field [36]. In our case the KBr: Ce $^{3+}$ sample showed strong excitation peak at 272 nm due to lattice defects. This means that most of the energies absorbed by the lattice defects of the KBr host disappear via radiationless pathway. The KBr:Tb $^{3+}$ crystals have two excitation peak at 355 and 268 nm for emission at 390 nm. The KBr: CeTb crystals, however do not have excitation bands at 355 nm. This result indicates that the emission pathway of Tb $^{3+}$ ion changes when they co-exist with Ce $^{3+}$ ions in the KBr host.

Energy transfer from a sensitizer to activator may takes place via radiative transfer, exchange interaction and electric multipole interaction. Exchange interaction needs a large overlapping between donor and acceptor orbitals leading to easy electronic change while both cerium and terbium ions, such an exchange require very high energy [37]. In LaOBr doped with Ce $^{3+}$ and various other activators like Tb $^{3+}$, Pr $^{3+}$, Eu $^{3+}$, Ho $^{3+}$ and Dy $^{3+}$ radiative energy transfer from Ce $^{3+}$ to these activators has been observed via radiative energy

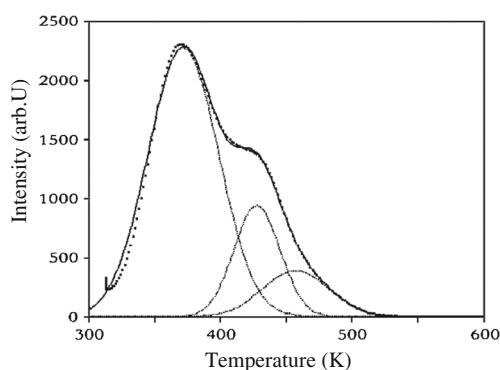


Fig. 7 Glow curve KBr: Ce Tb X-ray irradiated for 5 mins Deconvoluted

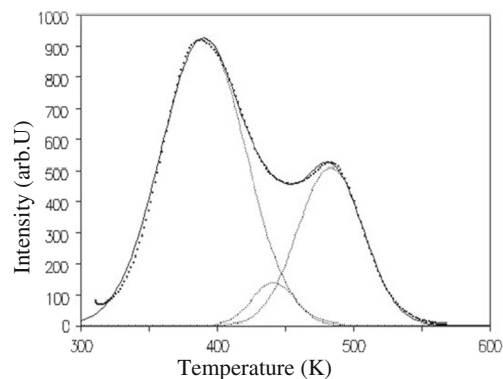


Fig. 8 Glow curve KBr: X-ray irradiated for 5 mins Deconvoluted

transfer [38]. This the case observed here. So the energy transfer in KBr takes place via radiative energy transfer.

If the energy transfer occurs from Ce $^{3+}$ to Tb $^{3+}$, emission band of Ce $^{3+}$ should overlap with absorption of Tb $^{3+}$ in KBr matrix. The Ce $^{3+}$ in the KBr host, however showed emission band around 290 nm. So there is an obvious overlap between the excitation of Tb $^{3+}$ and the emission of Ce $^{3+}$ between the wavelength of 260 nm-350 nm. Consequently an efficient energy transfer can occur and could be responsible for the band emission in the KBr host under the excitation at 240 nm. The emission spectrum of the KBr: CeTb crystals contain characteristic emission of terbium ions, indicating that Ce $^{3+}$ to Tb $^{3+}$ energy transfer is efficient. The emission band due to Ce $^{3+}$, which falls up between the narrow peak of the Tb $^{3+}$ activator was higher than that of the KBr:Ce crystals; one notable aspect was that the co-doping of Ce $^{3+}$ reduces the peak intensity at 394 nm, corresponding to the ${}^5D_4 \rightarrow {}^7F_3$ transition of Tb $^{3+}$. As shown in Fig. 4 KBr:Ce $^{3+}$ crystals can absorb this optical absorption efficiently, emission of Ce $^{3+}$ at 294 nm and 394 nm reemit the light via the PL. Thus we believed that some portion of the PL emission at 294 nm and 394 nm is reused to activate the terbium ions in the KBr: CeTb crystals.

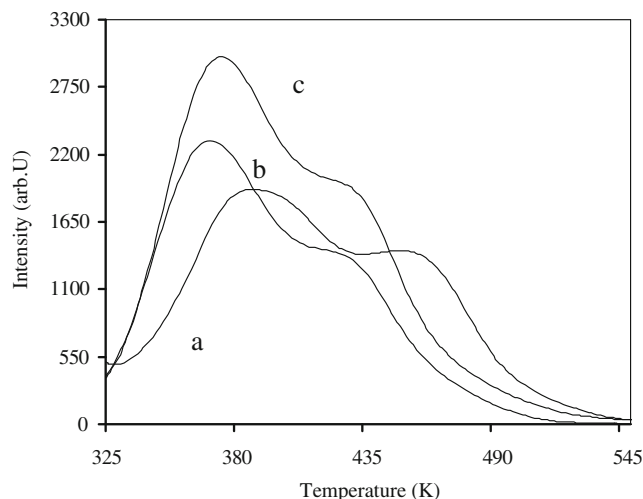


Fig. 9 Glow curves of X-ray irradiated KBr: CeTb3+ crystals a. 3 mins b. 5 mins c. 10 mins

Table 1 TL parameters of CeTb doped KBr X ray irradiated and with a heating rate of 120 °C/min

S.No	Peak Temperature in (K)	Peak intensity	Activation energy in (ev)	Frequency factor (s^{-1})	Order of kinetics
1	371	2276	0.40677	1.2439×10^7	I
2	427	941	0.8845	1.619×10^{10}	I
3	457	388	1.4211	1.406×10^{13}	I

Consequently, the KBr: CeTb crystals have an enhanced band emission compared with the KBr:Tb crystals. Besides the brightness, one important factor in selecting phosphor in color co-ordinates as was reported [21, 35]. Ce^{3+} known to be a sensitizer for Tb^{3+} in many hosts [9–14, 31]. The emission efficiency is the preferential factor for designing a new phosphor is then, we concluded that co-doping the Ce^{3+} ions is a helpful way to modify the emission band of the KBr:Tb phosphor and thereby brightness can be enhanced successfully.

Thermoluminescence

TL glow of x-irradiated doubly doped KBr: Ce^{3+} Tb^{3+} (Fig. 7) crystals for 5 mins exhibit a peak at 371 K and a shoulder around 420 K. When pure KBr crystals were irradiated for the same duration, a peak at 380 K and a shoulder around 480 K could be observed in Fig. 8. The deconvolution of pure crystals reveal three peaks at 383 K, 434 K and 486 K. The Ce, Tb doped KBr crystals shows three peaks at 371 K, 427 K and 457 K on deconvolution. TL glow for different durations of exposure of Ce^{3+} , Tb^{3+} doped KBr are shown in the Fig 9.

The intensities of the glow peaks in KBr: Ce, Tb crystals are found to be higher by an order of magnitude than those of pure KBr clearly indicating the participation of Ce, Tb ions in the TL process. The growth of the low temperature peak on bleaching with F-light suggests that the electrons are released from a trap of larger trap depth and are retrapped at sites with low trapped depth. This process of transferring charge from a higher trap depth (high temperature peak) to lower trap depth (low temperature peak) is commonly referred to as photo transfer. TL recorded so is known as photo transfer TL. Such photo transfer is done for materials showing anomalous fading of their TL glow. We have used glow curves of pure KBr and demonstrated that the weak shoulder that occurs at 500 K at the high temperature side of the main peak 400 K can be integrated over a wide range 120 °C/min using the principle “Peak Fit”. It can be used in many cases for integrating TL signals relevant to TL dosimetry/TL dating. In our recent paper, the analysis of the major TL peaks of KBr: Tb has been reported by us [35]. The values of the trapping parameters (activation energy ‘E’, frequency factor ‘S’ and order of kinetics ‘I’) are also presented in Table 1. Glow curves of Ce^{3+} , Tb^{3+} doped KBr samples excited with a heating rate

120 °C/min are shown in Fig. 7. In all the cases three clear TL peaks were seen. However, when subjected to 4th derivative plot using “peak Fit” the presence of three glow peaks is clearly revealed in Fig. 9. The deconvoluted peak as obtained by “peak Fit” of one such case (120 °C/min) are shown in Figs. 7 and 8. Following the same process, all the glow curves are deconvoluted and the signals are integrated. The dose response curves of the main peak (350 K) along with the one that occurs in the high temperature side 450 K are shown in Fig. 7. Thus, by using “peak Fit”, one can integrate any stable signal for dosimetry, for similar doses of irradiation and heating rate as seen in Figs. 7 and 8. As the time of irradiation is increased from 3 min., 5 min., and 10 min., a new shoulder starts growing around 450 K, there by making the 371 K peak sharper and dominant. It is quite possible that new peaks can appear or a redistribution of charges takes place, when an irradiated crystal is illuminated with F-light. When this bleaching is done at F-band, new-type centers can be formed. On F-light bleaching only the peak observed around 370 K is retained while the high temperature peaks disappear as shown in Fig. 10. From the results obtained on the optical absorption of KBr: Ce, Tb and the TL glow of crystals bleached with F-light subsequent to irradiation, it can be concluded that the 371 K glow peak observed in the present study is due to Z_3 -centres [22, 23]. The TL glow gives only the trapping parameters like E, S and I. For better understanding of the TL process, studies like TL emission (Spectral distribution), optical absorption, photo stimulated emission and few complementary measurements are necessary. TL emission gives a better understanding of the recombination processes. Stepwise annealing of color centers can be monitored through

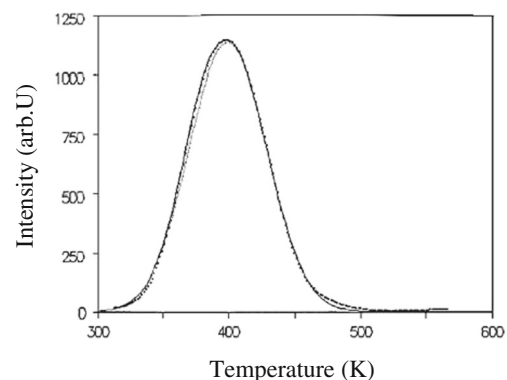


Fig. 10 Glow curve KBr: Ce Tb crystals F light bleached 1 min subsequent to X-ray irradiation for 5 mins

Table 2 TL parameter of Ce Tb doped KBr X ray irradiated 5 min and F-light bleached for 1 min after recorded with a heating rate of 120 °C/min

S.No	Peak Temperature in (K)	Peak intensity	Activation energy in (ev)	Frequency factor(s ⁻¹)	Order of kinetics
1	399	1139	0.42833	8.66×10 ⁹	I

optical absorption, Photo Stimulated Luminescence and Thermal Stimulated Luminescence lead to a better understanding about the centers that are mobilized during warming of the crystals.

The glow peaks were deconvoluted using the software peak fit. The results on TL parameters were tabulated [4, 23] in Tables 1, 2 and 3. It shows the relevant TL parameters for KBr: CeTb before and after F-bleaching and pure KBr having trap depths. 0.37, 1.05 and 0.79 eV respectively. This is usual observation in the sense that a high temperature glow peak shows a higher trap depth value. This behavior is similar to that observed in the RbCl:Eu²⁺ system [39] overlapping glow peaks (main peak) can lead to the broadening of the glow peak and consequently appear, to lower the value of trap depth and lower the value of the frequency factor [39].

The trap parameters have been calculated using Chen’s method [40]. Modifying the method proposed by Halperin and Braner [41], Chen proposed an easy and non-iterative way to calculate the trap parameters like activation energy and frequency factor [40]. The method consists of the measurements of the total half-width [W], low temperature-side half-width (ξ) and high temperature-side half-width (δ) of the glow peaks. The equation deduced by Chen is $E_{\alpha}=(C_{\alpha}KT^2g/\alpha) - (b\alpha(2KTg))$, where E_{α} activation energy and α can be either $W=T_2-T_1$ (where T_1-T_2 are low and high maximum intensity temperature). $\xi=T_2-T_g$ (where T_g is the glow peak maximum temperature) or $\delta=T_2-T_g$, K is Boltzmann’s constant. The values of C and b are constant given by Chen. The glow peaks are deconvoluted using the software “Peak fit” from which the values of T_1 , T_2 and T_g are determined and the trap parameters are calculated and tabulated in Table 1. The values of the trap parameters are comparable with the reports given by [40, 42, 43]. The kinetic order indicated that the peaks can be categorized as first order or second order by a shape factor μ_g i.e. $\mu_g=\delta/\omega$, where δ is the high temperature half-width, ω is the total half-width of glow peak. The glow shape factor is $\mu=0.42$ for the first order and $\mu=0.52$ for the second order glow peaks. The glow peaks have been deconvoluted using the

software “peak it” and results of TL parameters have been tabulated in the Tables. 1, 2 and 3.

Photo Stimulated Luminescence and Thermo Luminescence Emission Spectra

Figure 11 shows the TL emission spectra of pure KBr at about 383 K(curve a) and 434 K(curve b). In the pure KBr spectra, there are two recombination centers exist and that they give two bands at 450 nm and 390 nm. Thus broad emission bands are the electron hole recombination luminescence. The TL emission spectrum of KBr:CeTb at 371 K(curve c) and 427 K(curve d) consists of narrow bands as shown in Fig. 11. The band located at about 450 nm originated from the electron hole recombination luminescence. The emission under the 371 K glow peak contains three emission bands. One band at 390 nm and two more around 450 nm and 540 nm. In the PL of these samples, it was noticed that Tb³⁺ emission were observed at 390 nm. From these results it is seen that the doped impurities take part in the TL process.

The difference between TL and PSL is that the heating of the crystals can ionize not only the electrons from F centers (or) other electron trap centers but also the holes from the V₂ centre (or) relevant hole centres. In general, the diffusing holes in the KBr:CeTb crystal is the specific situation. Some CeTb²⁺ ions, which act as electron trap defects, can recombine with the diffusing holes. This recombination results in the oxidation of CeTb²⁺ to CeTb³⁺ in an excited state, which in turn gives rise to a characteristic emission of CeTb. We observed this CeTb³⁺ emission in the glow peaks of V₂ centers as shown in Fig. 11. Another peculiarity of the TL spectra of CeTb doped crystals is that it shows emission of CeTb²⁺ in the glow peak at 389 K.It is known that this glow peak originates from a electron trap centre. According to our proposed model of TL, this emission should arise from the recombination of electrons with CeTb³⁺ ions, but there raises the question of why this kind of electrons does not appear in the PSL (or) in

Table 3 TL parameter of pure KBr X ray irradiated 5 min and with a heating rate of 120 °C/min

S.No	Peak Temperature in (K)	Peak intensity	Activation energy in (ev)	Frequency factor (s ⁻¹)	Order of kinetics
1	389	923	0.379562	2.62×10 ⁸	I
2	441	138	1.05646	7.71×10 ¹¹	I
3	483	507	0.79855	8.97×10 ¹²	I

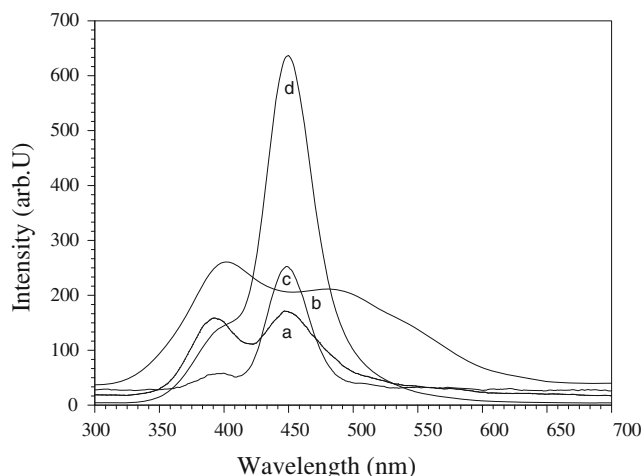


Fig. 11 Emission spectra of (a) pure KBr, under 383K glow peak (b) pure KBr under 434 K glow peak (c) KBr:Ce,Tb, under 371K glow peak (d) KBr:Ce,Tb, under 427K glow peak

the glow peaks of TL at temperature above 421 K. PL emission associated with Stokes shift. PSE refers to photo stimulated emission which is a release of trapped species. PSE gives information on the various recombination processes. The emitted light can be on the lower wavelength side for the stimulating wavelength also. To identify the thermally mobilized species, Photo stimulated emission spectra was studied. The photo stimulation under F-Band (Fig. 12) gives emission spectra similar to the TL emission bands, suggesting the recombination processes in the TSE and PSE to be similar. PSL emission showed a sharp band at 420 nm and a broad emission at 450 nm as shown in Fig. 12 [4, 43] which can be attributed to CeTb ions. The PSL and TSL contain the characteristic CeTb³⁺ emission. The bandwidth and the position indicate that the 420 nm emission spurious (a sub multiple of the excitation wavelength 630 nm). The use of an appropriate optical filter could have removed the spurious nature of 420 nm emission. So, in the given work such a filter was not used. The photo stimulation under the F-band(630 nm) suggests that CeTb ionized in the irradiation process leading to

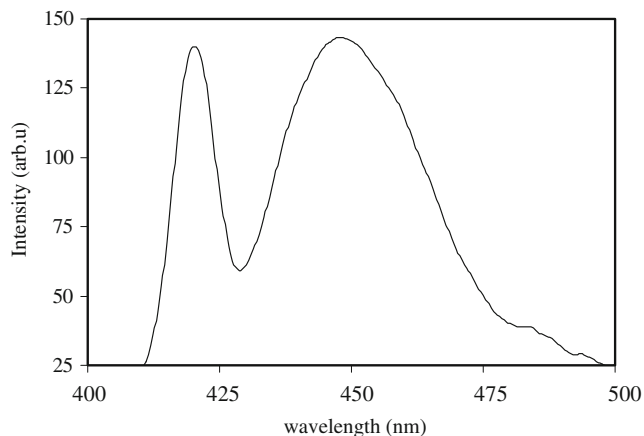


Fig. 12 Emission spectra excitation at F band 630 nm

the formation of Ce⁴⁺, Tb⁴⁺ and recombination of F-electrons with these centers produce the Ce³⁺, Tb³⁺ emission in the TSE and PSE. From these studies, it can be concluded that TL process is due to thermal mobilization of F-electrons.

Conclusions

The luminescence properties of Ce³⁺, Tb³⁺ ions were studied in the KBr host. The emission spectrum of the KBr:CeTb crystals contain characteristic emission of terbium ions, indicating that Ce³⁺ to Tb³⁺ energy transfer is efficient. Co-doping KBr crystals show better TL glow. On bleaching the X-ray irradiated crystal with F-light, Z₃ centers are formed. The low temperature peak can be attributed to Z₃ centers. TL emission spectrum suggests that the impurities take part in the recombination process related to both peaks. TL process has been identified to be due to thermal mobilization of electrons

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