Luminescent Properties of Cerium Doped Potassium Iodide Single Crystals in Response to γ-irradiation

S. Bangaru · K. Saradha · G. Muralidharan

Abstract Potassium iodide doped with cerium ions were prepared by Bridgemann Stockbarger technique and investigated by optical absorption, Photoluminescence(PL), Thermoluminescence(TL), Photostimulated Luminescence(PSL) and TL emission. The optical absorption measurement indicates that F and V centers are formed in the crystals during the γ-ray irradiation process. Optical absorption and Photoluminescence studies confirm the presence of cerium ions in the trivalent state. Spectral distribution under the Thermoluminescence Emission(TLE) and Optically Stimulated Luminescence(OSL) support the idea that the defect annihilation process to be due to thermal release of F-electron in KI:Ce^{3+} crystals. Both Ce^{3+} and Ce^{2+} emissions were observed in the Thermoluminescence emission of the crystals. Thermoluminescence(TL) has been identified to be due to thermal release of electron produced during colouration process.

Keywords KI · Thermoluminescence · Photoluminescence · Ce^{3+}

Introduction

Phosphors doping with rare earth elements have attracted much attention because of their well defined transitions within 4f shell [1]. Rare earth elements have been considered as the most important and promising activators for phosphors due to

their emission characteristics in UV and Visible region . Among rare earth doped phosphors,Cerium activated ones are gaining much interest because of their spectroscopic properties and the ability of cerium to be incorporated into different host materials [2]. Substitution of impurities in a crystal lattice modifies the optical and other properties of the host. In most cases,the impurities enchance the performance of host lattice. Materials doped with cerium have attracted the interest of solid state researchers due to applications of these materials. Cerium enters into a specific site,their spectroscopic property is influenced by the co-ordination environment [3]. For example, the emission band of YAG:Ce^{3+} can be tuned from 520 to 580 nm by adding Ga^{3+},Lu^{3+} into lattice [4–6]. Cerium energy levels in crystals consist of two ground states 4f levels separated roughly by about 2000 cm^{-1}($^2F_{5/2}$,$^2F_{7/2}$) and upto five 5d split excited state energy levels. The emission of cerium is due to 5d-4f extent. Materials doped with cerium have attracted the interest of solid state researchers due to applications of these materials as phosphors, detectors for ionizing radiations, scintillators for elementary particles, UV emitters and activators for energy transfer [7–10]. Rare earth elements have been considered as the most important and promising activators for phosphors due to their emission characteristics in UV and visible region. Cerium has sharp emission of ultraviolet or blue colour with high intensity, so it is the most important blue emitting luminescence activators for several phosphors [11, 12]. Cerium doped alkali halide phosphors have been widely studied in last years [13, 14]. In the present work, Potassium iodide doped with cerium has been grown by Bridgeman Stockbarger technique. The grown crystal were characterized by optical absorption, photoluminescence(PL),Thermo luminescence(TL),Thermally stimulated Luminescence(TSL) and Photo stimulated luminescence(PSL). The purpose of this paper is to study the luminescent characters of cerium doped KI Single crystals. Therefore,in the present article, only work on luminescent

S. Bangaru (✉) · K. Saradha
Department of Physics, Arignar Anna Government Arts College,
Namakkal 637002, India
e-mail: ssbangaru@yahoo.co.in

G. Muralidharan
Department of Physics, Gandhigram Rural University,
Gandhigram 624 302, India

properties of KI:Ce^{3+} in response to γ-irradiation were presented and discussed.

Experimental Details

Single crystals of pure KI (99.99 % purity) and cerium doped KI (99.99 % purity) were grown using the Bridgman Stockbarger technique. Cerium was added in the form of 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 $5 \times 5 \times 1$ mm^3 were used for all except the PSL and PL studies. For PSL and PL, 5x5x3 mm^3 samples were used. The results due to the three concentrations were similar and hence only the results pertaining to a cerium 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 γ- 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°K for half an hour, and then they were quenched to room temperature to ensure homogeneous distribution of impurity and to remove any storage effect.

Optical Absorption

UV-vis absorption by the crystals is one of the most direct methods of investigating the intrinsic optical properties related to the excitation of electron states in alkali halides. The optical absorption spectra of KI:Ce^{3+} crystals before and after γ-irradiation are shown in Fig. 1. The unirradiated crystals exhibit a broad absorption around 250 nm and prominent shoulder around 270 nm(Fig. 1 curve(a)). After 1 h of γ-irradiation results in the formation of a characteristic F-band centered at 690 nm(Fig. 1 Curve(b)). The bands observed at 318, 353 and 390 nm and broad shoulder at 260 nm are noted on irradiation, while the 205 and 215 nm bands are disappear. The absorption below 215 nm is drastically reduced while a new broad absorption shows up around 287 nm. The new band appearing around 287 nm is probably due to V-centers that are known to have large band width (FWHM). This is in agreement with the earlier results on KBr and KBr: Cu reported by Murthi et .al [15]. Roth and Halperin [16] have reported the formation of intrinsic V-centers (V$_4$, V$_2$ and V$_3$) to absorb at 318, 353 and 390 nm, respectively. Of these V$_3$ centers are the most stable at
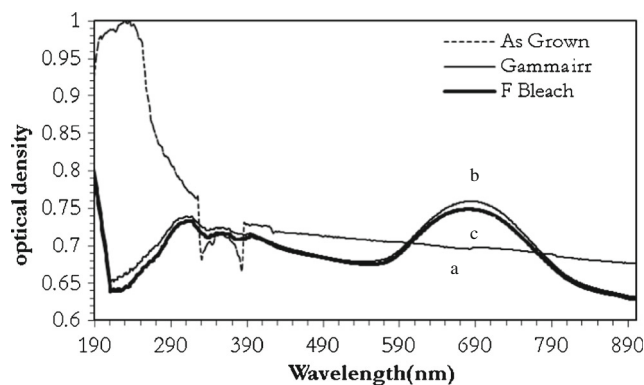

Fig. 1 Optical absorption of KI:Ce^{3+} (**a**) unirradiated (**b**) γ-irradiated for 1 h (**c**) F-bleached 2 min subsequent to γ-ray irradiation

room temperature [17]. The absorption in the UV-Region may include absorption due to V$_3$-centers that show a broad absorption due to V$_3$ centers that show a broad absorption with full width at half maximum around 1 eV.

The reduction in intensity of absorption below 287 nm can be seen as a change in the valence state of the species that absorbs in this region and F-light bleaching subsequent to γ-irradiation of cerium doped crystals indicates an increase in the absorption from 210 to 385 nm as shown in (Fig. 1 curve (c)) . On F-bleaching, absorption at the F-band shows a broadening on longer wavelength side [18]. The broadening is indicative of formation of new species. To identify the species that have been formed, the absorption in the F-band region was normalized, taking the maximum of absorption as unity and rescaling the other areas under the curve. On normalizing the absorption bands in the F-band region, before and after F-light bleaching, a new peak at 790 nm can be identified as shown in Fig. 2. 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. The divalent ion perturbed F-centers, namely the Z-centers have been observed on the longer wavelength side of the F-band.

But in the present work, the new absorption is on the longer wavelength side of the F-band. Vijayan and Murthi [19] in their work on Gd^{2+}-doped KCl, have reported the formation
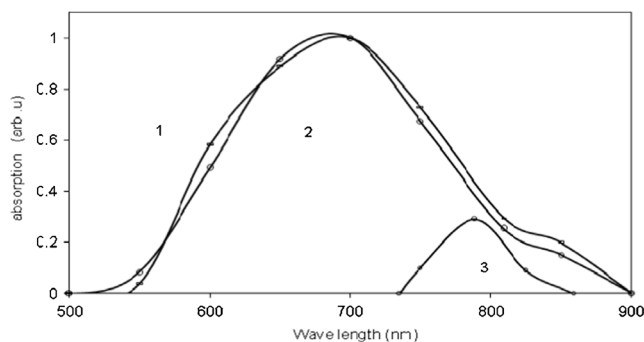
Fig. 2 Normalization to show the formation of the new band at 690 nm. *1*) γ− irradiated 1 h *2*) F-bleach 2 min *3*) Difference between the curves 1 & 2

of Z_1 centers. These centers were observed on the longer wavelength side of the F-band. Considering this, it seems appropriate to assign the new absorption in KI:Ce^{3+} to Z_1 bands.

Photoluminescence

Figure 3 presents the excitation spectra of Ce^{3+} doped KI phosphors for emission at 342 nm. The excitation spectrum contains single band at 260 nm with a shoulder at about 275 nm. These excitation bands formed are due to absorption of the incident radiation by cerium ions and results in the excitation of electrons from the 4f^1 ground state to the excited 5d^1 levels [20]. So the excitation spectrum of Ce^{3+} shows the direct splitting information of 5d orbital in the crystal field. It has been reported that the f-d transition of Ce^{3+} ion will exhibit subtle structure ion due to the influence of crystal field splitting and spin-orbit coupling [21–24]. The excitation spectrum of Ce^{3+} has been split into some degree. For this, the deconvolution of excitation peak has been done. The deconvolution of the luminescence curve is a usable method often employed to make the understanding on the spectra structure easier. So this method utilized in the present article and the result of the deconvolution of the excitation peak from 250 to 325 nm were exhibited in Fig. 4, in which a single fitted peak at 265 nm has 23.58 Full width half maxima, and its area 22.353 can be obtained. Figure 5 shows the luminescence pattern of Cerium doped KI excited with wavelength at 287 nm, the broad band located at about 340, 400 and 500 nm, which is due to allowed 4f^0 d^1→4f^{1}5d^0 transition of cerium ions. Obviously the emission are ascribed to the electron transitions from the lowest crystal splitting component of 5d level to the ground state of Cerium [25, 26]. The deconvolution of luminescence pattern of KI doped cerium were shown in Fig. 6. According to asymmetric peak shape and position, it can be deconvoluted into four peaks at
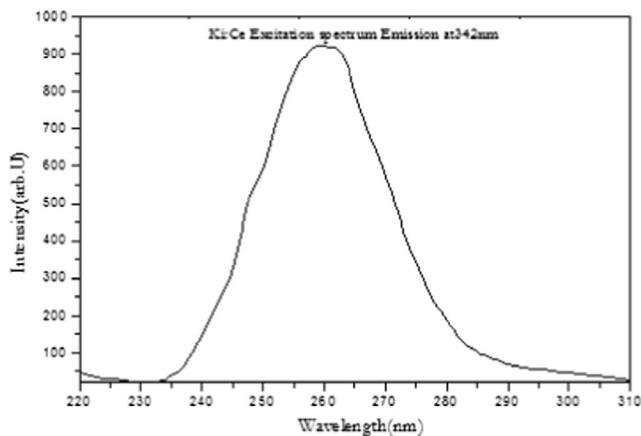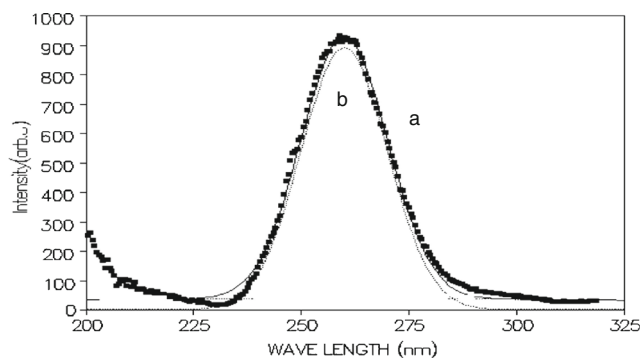

Fig. 4 Curve (**a**) PL excitation spectrum of KI doped Ce^{3+} single crystal in the region 225-300 nm with emission at 342 nm, curve(**b**)peak fit peak

338 nm(49 FWHM),395 nm(52 FWHM),500 nm(79 FWHM) and 627 nm(48 FWHM). Among these peaks, 338 and 395 nm peaks should be due to the emission of cerium and the peak at 500 and 627 nm may be attributed to host emission.

Thermo Luminescence Glow Curve

Figure 6 shows the TL glow curve of KI:Ce^{3+} obtained after 1 h of γ-irradiation. The TL glow peak of KI:Ce^{3+} crystals could be deconvoluted into two glow peaks,with peaks at 393 and 445 K. The glow curve of pure KI after γ-irradiation of 1-h were shown in Fig. 7. The 445 K peak in pure KI is due to thermal release of electrons from F-centres and their recombination with V-type centres. As reported earlier, 190 °C peak is nominally pure KCl is due to thermal release of electrons from F-centres and their recombination with counterparts (i.e.,) V-type centres [27].

Bleaching with F-band light often helps in identifying the nature of charge centres associated with a particular glow peak in a TL curve. The low temperature glow peak loses its prominence when cerium doped samples are exposed to F-light, subsequent to γ-irradiation. On prolonged F-light exposure, low temperature peak disappears. This is a usual observation

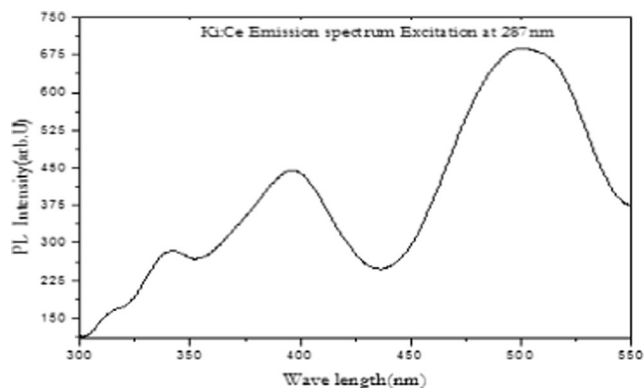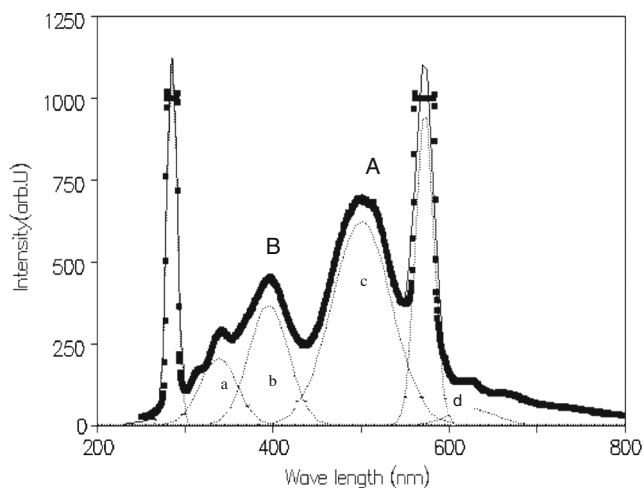**Fig. 3** Excitation Spectrum of KI:Ce^{3+} with emission at 342 nm nm

**Fig. 5** Emission Spectra KI:Ce^{3+} with excitation at 287 nm

Fig. 6 Curve(**a**)& Curve(**b**) are emission spectra of KI:Ce3+ with excitation at 287 nm, Curves a,b,c and d are the peak fitted peaks

in the sense that high temperature glow peak shows a higher trap depth value. All the observed glow peaks except the peaks at 445 K have been attributed to F-centres,since the intensity of other glow peaks decreases on F-bleaching as observed in the pure KI (400 and 500 K) as shown in Fig. 8.

In KI:Ce sample,445 K peak is possibly due to thermal release of electrons from F-centres at high temperature. This view finds support from the fact that 445 K peak decrease in intensity,if the sample is F-bleached/stimulated prior to TL run. Even a short exposure to F-light prior to TL run diminishes 445 K peak completely,presumably because the charge centres responsible for this peak are in their initial stage of formation. In this case,oppositely charged counter parts are located nearby and available in plenty. The glow peaks at 393 K,however,are not as easily bleachable as the one mentioned earlier. Even 48 h of F-bleaching could not erases the TL curve at this temperature,although F-centres are completely absent after light exposures. This indicates the
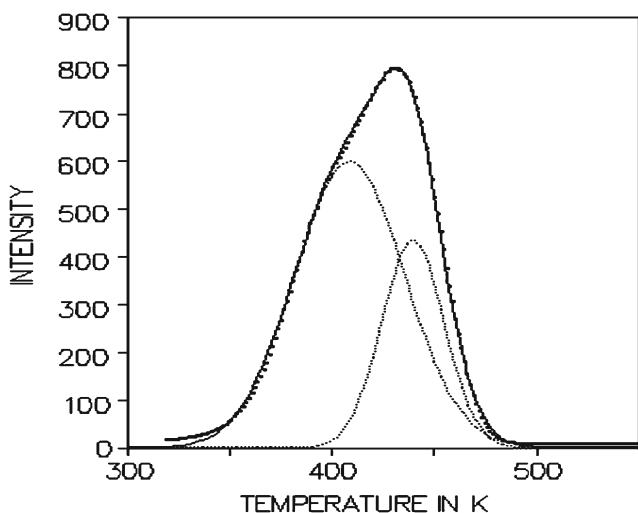
Fig. 7 TL glow curve of KI: Ce^{3+} γ-irradiated for 1 h
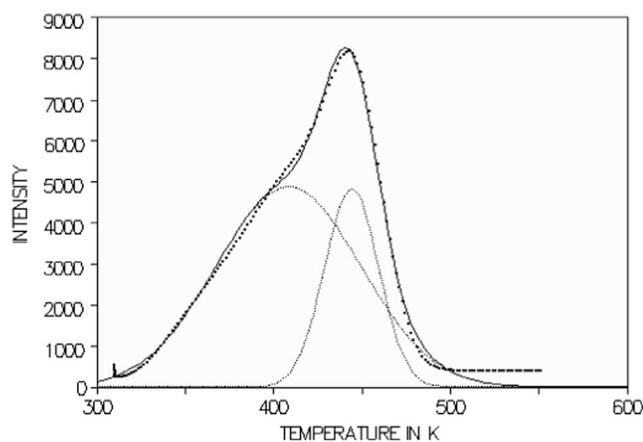
Fig. 8 TL glow curve for pure KI γ -ray irradiation 1 h deconvoluted

low temperature glow peak at 393 K are in some way related to impurity centres such as Ce centres in different charge states. Short duration optical bleaching of the irradiated crystal in the F-band due to cerium atom at cation sites,drastically reduced the 393 K peak but enchances the 445 K peak. With further F-bleaching, 445 K peak decreases after passing through a maximum for 3 min bleaching to values less than those of the as irradiated crystal. After 20 min of F-bleaching at 393 K the peak starts developing again as a small peak together with the reduced 445 K peak.

It is shown that TL glow curves and TL spectral data can be used to identify recombination processes while the relative strengths of these processes can be used to posses the concentration of the different valence states and their stabilization under various treatment. The glow curve and TL spectral data of the present investigation helped to identify that cerium centres are mainly responsible for 393 K peak giving predominant emission. F-centres are mainly responsible for 445 K peak as the dominant recombination. Cerium centres are thermoluminescent. So we can infer from the TL results that on F-light bleaching a redistribution of charges takes place,resulting in formation of new centres and /or enchancement of some of the already present centres.

Thermostimulated-Photostimulated Emission

The TL emission spectrum of the γ-irradiated KI:Ce^{3+} crystals at 445 K exhibit a peak at 430 nm and a prominent shoulder at 450 nm as shown in Fig. 9. The prominent shoulder at 450 nm can be attributed to the host emission. To better understand of the TL mechanism, one can record the emission spectrum under selective mobilization of charges using optical methods. This is named as photo stimulated emission (PSL). To understand the process, the irradiated samples were illuminated with light in F-band. This is expected to optically release of F-electrons and their subsequent recombination will yield a spectrum. This is different from PL in the sense that PL is
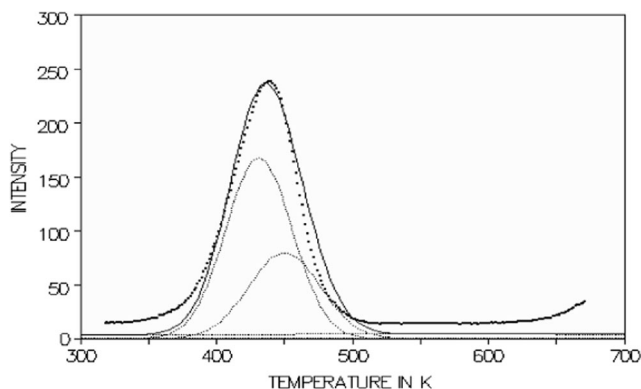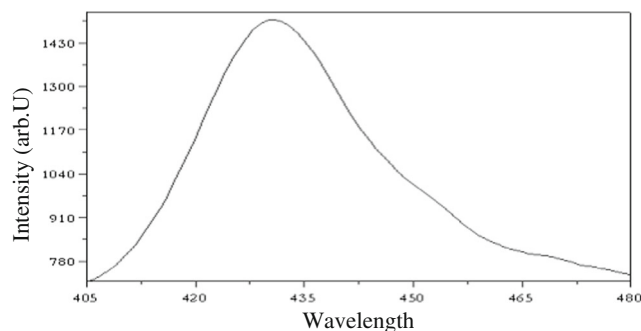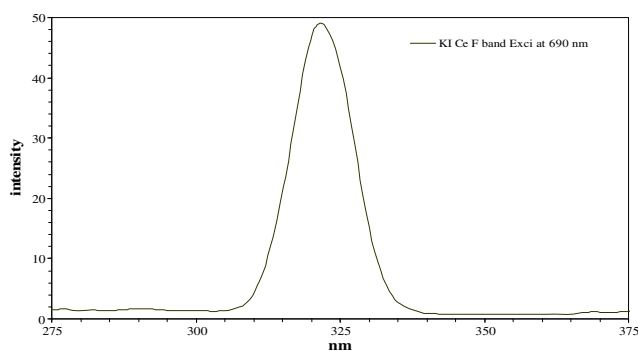
Fig. 9 TL glow curve KI: Ce^{3+} crystals F light bleached 1 min subsequent to γ -ray irradiation for 1 h

Fig. 11 PSL Emission spectra, excitation at F band 690 nm

associated with stokes shift, whereas in the PSL, the emission can be on the lower wavelength side of stimulating radiation. The photo stimulated under the F-band gives an emission spectrum with a dominant peak at 318 nm [Figs. 10 and 11]. On comparing these emissions with the TL emission, it seems more appropriate that the TL process is due to the thermal release of F-electrons and their subsequent recombination with hole centres. The emission at 430 nm in TLE and 318 nm in the PSL of the samples indicate that the cerium ions take part in the recombination process. The shift in wavelength is due to the overlapping of the neighbouring emission bands. The presence of cerium emission in the TLE and PSL are indicative of change in valence state of cerium ions during irradiation process. The excitation of the trivalent cerium may be done either optically or by ionizing radiations. Trivalent cerium may be excited to 5d state by ionizing radiation either directly by intra ionic processes within cerium or indirectly. In this case, the excited trivalent cerium emits a 5d-4f photon. The possibility is that the thermally released electrons (from perturbed F-centers) recombine at Ce^{4+} created during the irradiation process. The recombination process leaves the Ce^{3+} (formed after recombination of an e$^-$ with Ce^{4+}) in an excited state. This Ce^{3+} probably gives the emission observed at 430 nm when it returns to ground state [28–31].

Since the dominant recombination process is Ce^{4+} + e$^-$ → Ce^{3+},the electron hole recombination may be fully suppressed. The suppression of the usual electron-hole(V-Centers)

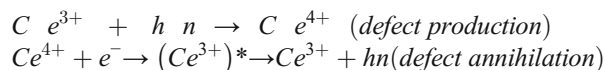**Fig. 10** TL emission curves for KI: Ce^{3+} 445 K

recombination results in the reduction in TL intensity [32]. To understand the species that is released during the TL process, the photo stimulated emission studies were made. On shining light in the F-band region, an emission band around 430 nm could be observed.

The similarity in the emission spectrum for thermal stimulation (TLE) and optical stimulation (PSL) strongly suggest that the processes are identical i.e., the TL process is due to the thermal release of F-electron. The defect formation and recombination process may be represented by the following equation

$$C \ e^{3+} \ + \ h \ n \ \rightarrow \ C \ e^{4+} \ (defect \ production)$$
$$Ce^{4+} + e^- \rightarrow \left(Ce^{3+}\right)^* \rightarrow Ce^{3+} + hn(defect \ annihilation)$$

Conclusion

It is concluded that we measured strongly intense and broader emission band at 495 nm of Ce^{3+} doped KI single crystals excitation at 287 nm. The additional TL glow peak at 393 K is attributed to Ce^{3+} ions in the vicinity of an F-center.Ce^{3+} is considered to act as an electron trap and V-type defects (V$_3$ centers) as hole traps. The observed blue emission are attributed to Ce^{3+} ions. Photostimulation with F-light and the emission spectra yield similar emissions, strongly suggesting the TL process to be the thermal release of F-electrons. Z$_1$- centres are formed due to F-light bleach of KI:Ce^{3+}. The TL emission under the glow peaks contain the characteristic blue emission of the Ce^{3+} ions, in addition to the emission due to the recombination of F electrons with their counter parts. Participation Cerium ions in the recombination process is identified Photo stimulation with F light and the TL emission spectra yield similar bands, strongly suggesting the TL process to be the thermal release of F electrons.

References

1. Blasse G (1979) Handbook on the physics an chemistry of rare earths, Vol. 4, North Holland, Amsterdam
2. van Eijk CWE, Andriessen J, Dorenbos P, Visser R (1994) Nucl Instrum Methods A348:546
3. Lu FC, Song XP, Liu QL (2010) Opt Mater 33:91
4. Hollway WW Jr, Kestigian M (1969) J Opt Soc Am 59:1
5. Katelnikovas A, Bettentrup H, Uhlich D, Sakirzanovas S, Justel R, Karevia A (2009) J Lumin 129:1356
6. Meriel Maniquiz C, Kyeong YJ, Sang MJ (2010) J Electrochem Soc 157(12):H1135
7. Blasse G (1994) Chem Mater 6:1465
8. Gorodetskaya O, Reisfeld R, Orgensen OKJ (1992) Proceedings of the international congress on glass. Bol Soc Esp Ceram Vidrio 31C(4):479
9. Pedrini C, Moine B, Bouttet D, Belsky AN, Mikhailin VV, Vasilev AN, Zenin EI (1993) Chem Phys Lett 206:470
10. Zych E, Brecher C, Glodo J (2000) J Phys:Condens Matter 12:1947
11. Bangaru S, Muralidharan G (2012) Phys B: Condens Matter 407:2185
12. Bangaru S, Muralidharan G (2009) J Lumin 129:24
13. Bangaru S (2011) Phys B: Condens Matter 406:159
14. Bangaru S, Muralidharan G (2010) N Instr Phys Res B 268:1653
15. Murthi YVGS, Murthy KPN, Ramasastry C (1971) J Phys C: Solid State Phys 4:1606
16. Roth M, Halperin A (1982) J Phys Chem Solid 43:609
17. Sastry SBS, Iswanathan VV, Ramasamy C (1972) J Phys Chem 5:3552
18. Bangaru S, Muralidharan G, Brahmanadhan GM (2010) J Lumin 130:618–622
19. Vijayan C, Murthi YVGS (1989) Cryst Latt Def Amorph Mat 18:431
20. Zhou Y, Lin J, Yu M, Wang S, Zhnag H (2002) Mater Lett 56:628
21. Dorewbos P (2003) J Phys: Condens Matter 15:6249
22. Szczurek T, Schlessinger M, Jezowska B, Trzebiatowska, Legendziewicz J, Strek W (1985) (Eds) a. Rare earth spectroscopy. World scientific, Singapore
23. Vanpicterson L, Reid MF, Wegh RT, Sovenma S, Meijerink A (2002) Physiol Rev 365:04513
24. Yon H, Hong G (1997) Mater Res Bull 32:785
25. Zorenko Y, Gorbenko V, Konstankevych I, Voloshinovshki A, Stryganyuk G, Kolobanov V, Spassky D (2005) J Lumin 114:85
26. Lin J, Su Q (1995) J Mater Chem 5:1151
27. Subramanian U, Mukherjee ML (1984) Cry Latt Def Amorph Mat 10:221
28. Flor J, Pires AM, Davolos MR, Jafelicci M Jr (2002) J Alloys Compd 344:323
29. Vander Voort D, Blasse G (1990) J Solid State Chem 87:350
30. Heidepriem HE, Ehrt D (2000) Opt Mater 15:7
31. Dvan CJ, Li WF, Wu XY, Chen HH, Yang XX, Zhao JT, Fu YB, Z-mingai, Zhang GB, Shi ZS (2005) Make Sci Eng Bull 121:272
32. Vedda A, Fasoli M, Nikl M, Laguta VV, Mihokova E, Pejchel J, Yoshikawa A, Zhuravleva M (2009) Phys Rev B 80:045113