Thermoluminescence and optical studies on chromium-doped caesium chloride crystals

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Abstract. Thermoluminescence (TL), optical absorption and TL emission studies are made on CsCl:Cr^{3+} crystals at room temperature. The glow curve and optical absorption studies clearly show the participation of chromium ions in the TL process. A new high-temperature 483 K glow peak not observed in pure CsCl is ascribed to the chromium impurity. This TL glow peak gives the characteristic emission of Cr^{3+} at 730 nm.

1. Introduction

Because of unfilled d shells, the transition-metal ions have been extensively used as probes to understand the physics of defects in crystals and related phenomena using experimental techniques such as optical absorption, ESR and thermoluminescence (TL). In order to arrive at a correlation between the properties of impurity ions such as valency and ionic radius, and the effect that they produce on the luminescence and colour centres, it is necessary to have measurements in crystals doped with a variety of impurity ions. To study the TL phenomena, alkali halides seem to be quite suitable materials because, in these either relatively pure or doped materials, well defined electron and hole trapped centres are induced by irradiation. Although defects in alkali halides doped with transition-metal impurities have been of considerable interest for many years, the major part of this work has been devoted to face-centred cubic NaCl-type crystals [1–3], and systematic investigations on alkali halides with a CsCl structure doped with transition-metal impurities are very few [4]. Radhakrishna and co-workers [5–8] have carried out extensive investigations on the nature of defect centres in caesium halides doped with divalent impurities such as Pb^{2+}, Cd^{2+} and Hg^{2+}. Chowdari and Selvasekarapandian [9, 10] have studied the TL of copper and silver doped caesium halides. Neelamegam *et al* [11] have studied caesium halides doped with alkaline-earth impurities and suggested the CsBr:Ba^{2+} phosphor to be a TL dosimeter for measuring low γ doses. Recently Radhakrishnan and Selvasekarapandian [12, 13] have reported TL studies on pure and RE-doped caesium chloride.

Intense fast intrinsic luminescence (FIL) or cross luminescence (CRL) phenomena due to the intrinsic radiative transition from the X-valence band to the 5p Cs$^+$ core has been reported [14] for caesium halides which were found to be promising materials as scintillators with emission in the UV region and also as the active media of solid state lasers. Luty and co-workers [15] reported that F centres associated with certain molecular impurities such as OH$^-$ and CN$^-$ in a caesium chloride host give out vibration emission and were found to be suitable laser active materials. In the case of CsCl crystals, divalent and trivalent transition-metal impurities are reported [16] to occupy interstitial positions midway between two cation sites, and charge compensation is achieved by the introduction of Cs$^+$ vacancies along the

axial position (along the direction of the cubic axis). When the crystals are grown from aqueous solution, these vacancies may be replaced by neutral water molecules (or one water molecule and one OH^- in one of them). In the case of trivalent ions, one of the neutral molecules may be replaced by an anion, to allow complete local charge compensation. Further, because of the need for an additional charge compensator, a variety of centres larger than that observed for divalent ions can be expected. This makes the study of transition-metal impurities in CsCl crystals more interesting. In this regard, no measurement has yet been reported on the effect of trivalent transition-metal ions in luminescence and colour centres in CsCl crystals. In the present work, an attempt has been made to identify the role of chromium impurity and defect centres in the TL of CsCl using glow curves, emission spectra and optical absorption studies.

2. Experimental details

Analar BDH (Poole, England) caesium chloride was used as the starting material. Chromium-doped caesium chloride crystals were obtained by adding 3.79×10^{-3} mole fraction of $CrCl_3.6H_2O$ to a saturated solution of caesium chloride, and crystals were grown by slow evaporation. The samples chosen are usually of size 5 mm $\times$ 5 mm $\times$ 1 mm. To obtain a homogeneous distribution of impurity ions, these crystals were kept at 400 °C for 4 h and then quenched to room temperature. Samples were irradiated at room temperature using a ^{60}Co γ source of 10.3 Gy min^{-1}. The TL glow was recorded using a set-up similar to that described elsewhere [17] at a heating rate of 60 K min^{-1}. A Jarrel–Ash monochromator with omni-drive in conjunction with an R955 photomultiplier tube was used to record the TL emission spectra in the range 200–800 nm. Optical absorption spectra were measured at room temperature on a Hitachi-3010 spectrophotometer. Optical bleaching was done with an Ilford filter (603 nm) and a tungsten filament lamp (60 W).

3. Results and discussions

3.1. Optical absorption

The optical absorption spectra of pure CsCl and CsCl:Cr^{3+} crystals before and after γ irradiation at room temperature are shown in figure 1. Pure CsCl exhibits a band at 267 nm which was found to be not affected on irradiation; this has been attributed to the OH^- ions present in the host matrix. A crystal, γ irradiated for 10 min shows the formation of an F band centred around 600 nm and a broad band between 220 and 260 nm.

The CsCl:Cr^{3+} crystal shows (figure 2) three sharp bands at 210, 238 and 267 nm in the UV region and a small broad band around 400 nm in the visible region (figure 2, curve a). γ irradiation for 10 min results (figure 2, curve b) in the formation of a characteristic F band centred around 600 nm and a new UV band at around 230 nm. In addition to this, a small decrease in the intensity of all the above bands was observed. On F bleaching the crystal following the irradiation, both F- and V-band intensities were reduced.

The sharp bands observed at 210 and 237 nm, which are not observed for pure CsCl, can probably be related to the very effective charge-transfer absorption bands of Cr^{3+} in the host matrix [18]. The small reduction in intensity of these bands on irradiation is due to the trapping of electrons by a few Cr^{3+} ions transforming to the Cr^{2+} state. Further reduction in the intensity of these bands on F bleaching subsequent to irradiation again suggests that the chromium ions act as electron traps.
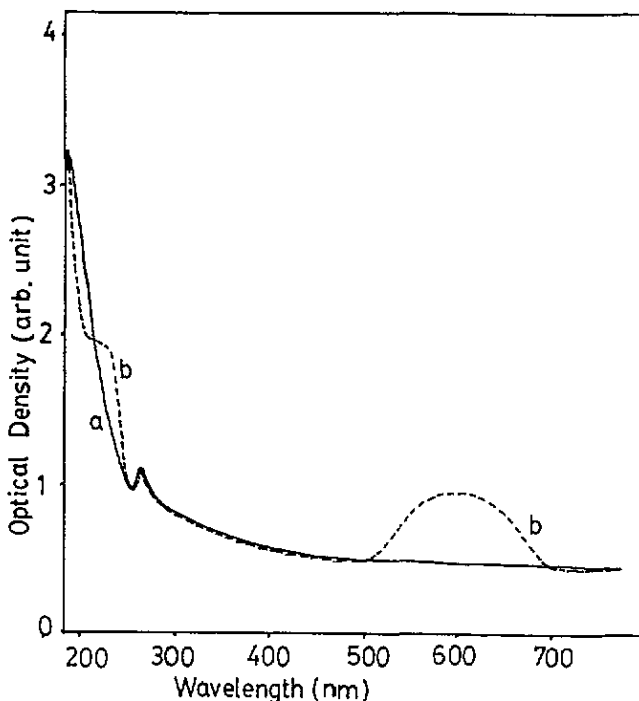
Figure 1. Optical absorption spectra of CsCl crystals measured at room temperature: curve a, before irradiation; curve b, after γ irradiation for 10 min.

It is evident that [16, 19] the Cr^{3+} ion enters the CsCl lattice interstitially, where it is hexacoordinated. From detailed ESR and optical absorption studies, Stibbe and Trappeniers [19] identified three different types of Cr^{3+} centres with tetragonal distortion and concluded that only one type of centre is effective for the observed optical bands. Trappeniers *et al* [20] have studied the optical absorption spectrum of Cr^{3+} in CsCl crystals and suggested that the site symmetry of the Cr^{3+} ion is mostly octahedral with a tetragonal distortion, chromium being surrounded by six identical ligands, in the form of either $[Cr(H_2O)_6]^{3+}$ or $[CrCl_6]^{3-}$, while neutrality might be achieved by charge vacancies at lattice sites. The Cr^{3+} ion in the CsCl matrix is expected to give three spin-allowed bands, two in the visible and one in the UV region, which were [20] assigned to the transitions from the ground $^4A_{2g}(F)$ state to the three $^4T_{2g}(F)$, $^4T_{1g}(F)$ and $^4T_{1g}(P)$ excited states, respectively. Trappeniers *et al* observed [20] only two broad bands at around 535 nm and 753 nm and attributed these to the $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$ spin-allowed electronic transitions, respectively. The latter $^4A_{2g} \rightarrow {}^4T_{1g}$ transition in the UV region was not observed by them [20] but was observed by Kikuo [21] and Rao [22] in various other lattices such as caesium sulphate and caesium nitrate in the region 260–280 nm.

Hence in the present system of CsCl:Cr^{3+}, the two bands observed at 400 nm and 267 nm could be safely attributed to the spin-allowed electronic transitions $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ and $^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$, respectively, of Cr^{3+}. The other absorption band of Cr^{3+} reported [20] in the visible region was not observed by us. On γ irradiation, the above bands are also reduced in intensity, indicating the capture of electrons that are produced on colouration by Cr^{3+} to form Cr^{2+}, which is further evidenced by the enormous decrease in the intensity of the F band compared with that for pure CsCl.
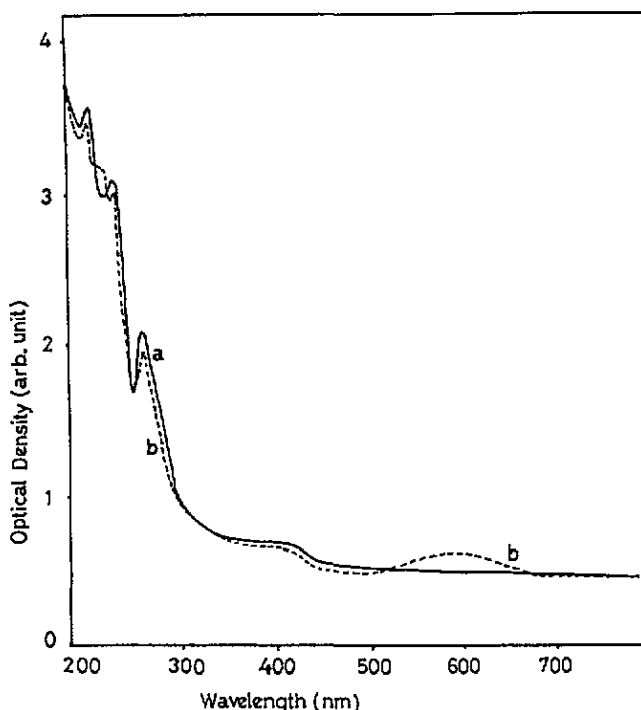
Figure 2. Optical absorption spectra of CsCl:Cr^{3+} crystals measured at room temperature: curve a, before irradiation; curve b, after γ irradiation for 10 min.

It is important to point out that, unlike the situation for CsCl, the band observed at 267 nm for the present CsCl:Cr^{3+} system is very sharp and of high intensity and hence could be related to both chromium and OH$^-$ centres. Radhakrishnan and Selvasekarapandian [12, 13] observed a band at 267 nm in undoped and europium-doped CsCl crystals, which is found to be not affected by γ irradiation. It has been attributed to the OH$^-$ ions present in the host lattice. Hence in the present Cr-doped CsCl system, this 267 nm band may be due to a complex centre associated with the chromium and hydroxyl ions present in the CsCl matrix.

Radhakrishnan and Selvasekarapandian [12] have observed a broad V band in the region between 220 and 260 nm. It consists of two bands at 252 nm and 233 nm due to V$_2$ and V$_3$ centres, respectively. In the doped system also, the band formed at around 230 nm might be due to formation of one of the V-type centres. Compared with the data for the pure system, the intensity of both the F and the V bands are found to be suppressed. It is expected [23] that the Cr^{2+} ions formed on irradiation should give rise to a new absorption band in the UV region at around 230 nm, but this band is found to fall under the increase in the V band and hence we were not able to separate out any characteristic bands attributable to Cr^{2+} ions.

3.2. Thermoluminescence glow

In figure 3 the glow curves of γ irradiated CsCl crystals for different doses are shown. Three glow peaks at 368, 383 and 398 K are observed.
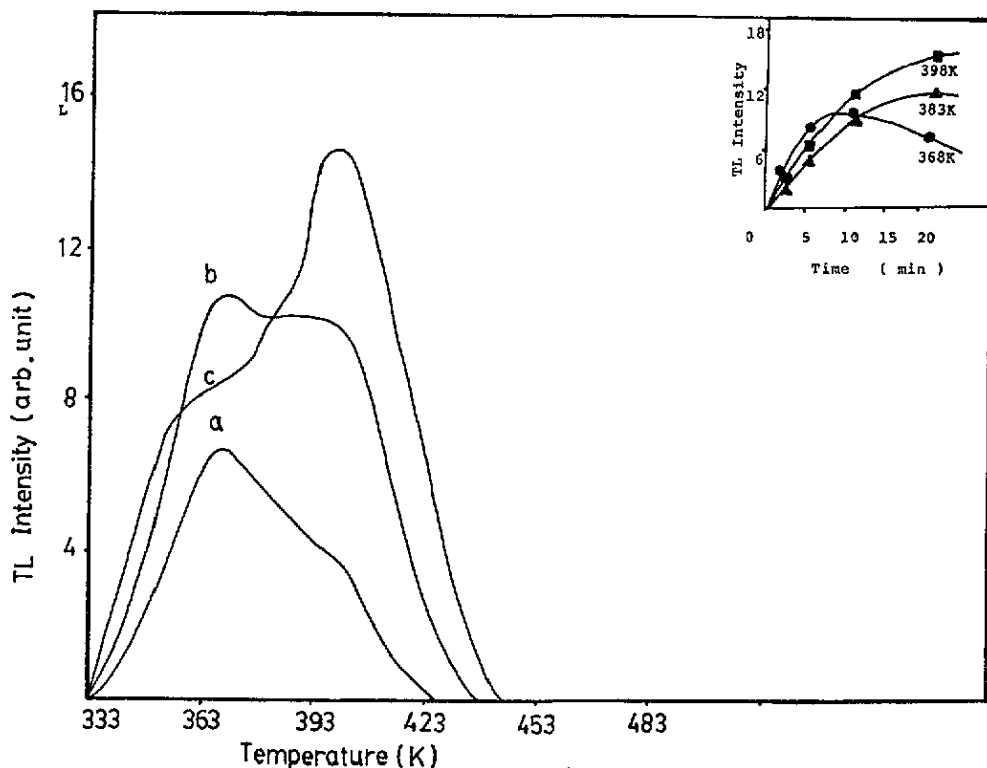
Figure 3. TL glow curves of CsCl crystals: curve a, γ irradiated for 2 min; curve b, γ irradiated for 10 min; curve c, γ irradiated for 20 min. The inset shows the increase in glow peaks with increasing irradiation time.

The TL glow of a CsCl:Cr³⁺ crystal γ irradiated for different doses of irradiation is shown in figure 4. Three glow peaks at 363, 398 and 483 K are observed. From the figure (curve a), it is clear that, after irradiation for 2 min, the 363 K glow peak is found to be sharp followed by a shoulder in the high-temperature region at around 398 K, while the 483 K glow peak appears as a weak and broad TL glow. As the irradiation time is increased from 2 to 5 min, the intensity of all the observed glow peaks increases. After irradiation for 10 min, the glow peak which appears as a shoulder at 398 K has grown into a well defined peak and the 363 K glow peak now appears as a weak shoulder on the low-temperature side (curve b). The 483 K glow peak also increases appreciably in intensity and appears as a well defined sharp glow peak. When the irradiation time is increased to 15 min, increases in the intensities of both the 398 and the 483 K glow peaks to a high value are observed and the low-temperature shoulder is no longer visible (curve c). A further increase in irradiation time to 20 min makes the 398 K glow peak decrease in intensity while the other peak keeps on increasing (curve d).

The nature of the centres responsible for the observed glow peaks in the pure and doped crystals could be studied [13] by observing the bleaching kinetics of these centres. In pure crystals, bleaching with F light results in decreases in the intensities of all the glow peaks (not shown in the figure). One such typical glow cure of CsCl:Cr³⁺ crystals γ irradiated for 10 min and F bleached for 30 min is shown in figure 5. (The inset shows the intensity variation of glow peaks with time of F bleaching.) It is observed that the glow peaks at 363
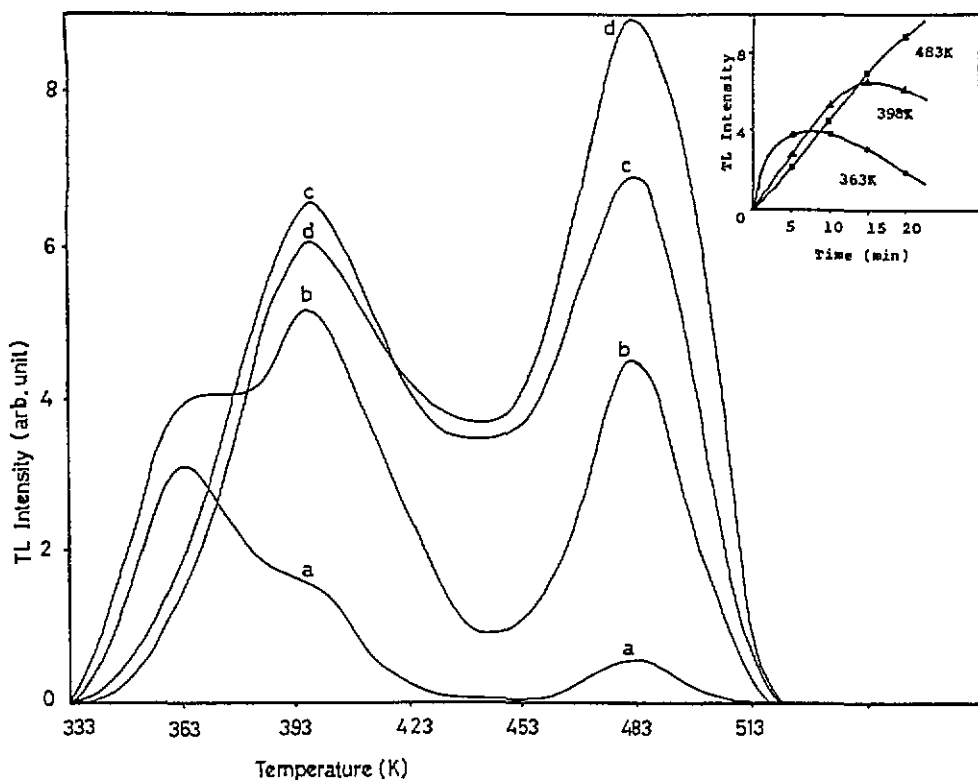
Figure 4. TL glow curves of CsCl:Cr^{3+} crystals: curve a, γ irradiated for 2 min; curve b, γ irradiated for 10 min; curve c, γ irradiated for 15 min; curve d, γ irradiated for 20 min. The inset shows the increase in glow peaks with increasing irradiation time.

and 398 K decrease in intensity very drastically while that of 483 K is not much affected. The lower-temperature peak is bleached more rapidly than is the higher-temperature peak. Prolonged F bleaching results in the elimination of this new 483 K peak also. Similar results have been observed for the higher-temperature glow peak attributed to impurities in the case of the CsCl:Eu^{2+} system also [13]. X-ray irradiation also produced TL glow curves very similar to those observed with γ irradiation but with a lower intensity, indicating that the same processes are involved in both types of excitations.

The intensities of the glow peaks in CsCl:Cr^{3+} crystals are found to be lower by approximately two orders of magnitude than those of pure CsCl, clearly indicating the participation of chromium ions in the TL processes. This result is consistent with the strong quenching effect of the transition-metal impurity ions in the host of many phosphors [24] which is opposite to the effect of RE impurities such as europium in CsCl crystals [13].

It is quite interesting to note that, while all the low-temperature glow peaks follow the typical evolution process of an early rapid growth and saturation which is followed by a decrease when the irradiation dose increases, the additional high-temperature peak at 483 K shows a nearly continuous increase in intensity within the radiation dose range studied.

It should be pointed out that pure CsCl crystals under a similar kind of irradiation display glow peaks at 368, 383 and 398 K only and all of these have been attributed to the thermal decay of isoelectronic F centres (i.e. F centres in different local environments) [25]. In doped CsCl, since the intensities of the 363 and 398 K glow peaks are reduced
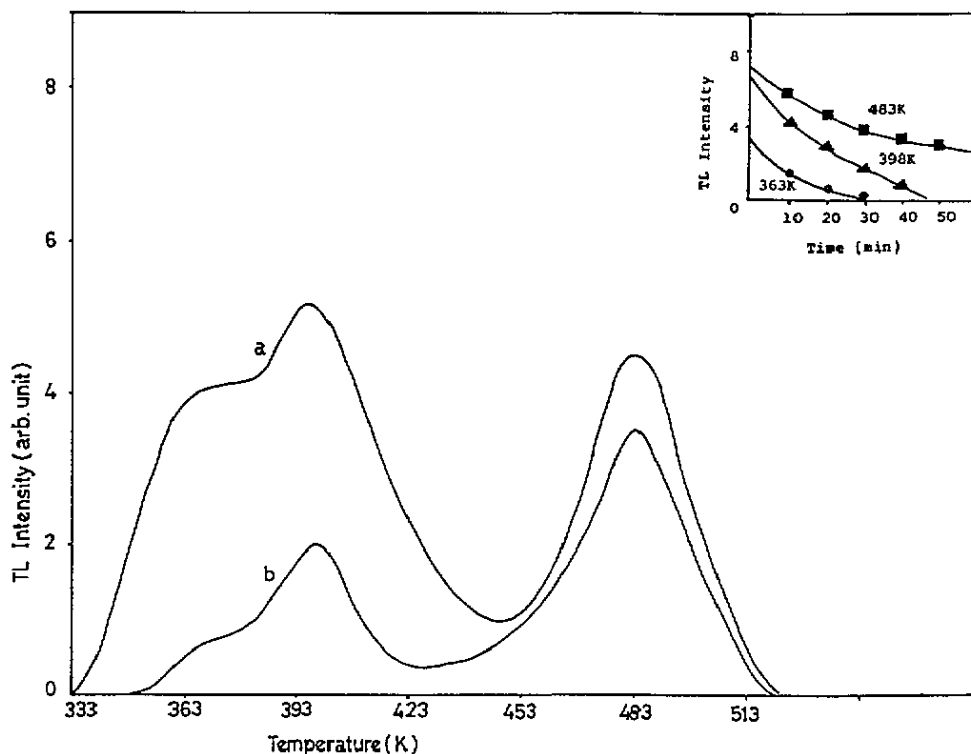
Figure 5. TL glow curves of CsCl:Cr^{3+} crystals before and after F bleaching: curve a, γ irradiated for 10 min; curve b, γ irradiated for 30 mm subsequent to γ irradiation for 10 min. The inset shows the intensity variation in various glow peaks with F bleaching time.

drastically on F bleaching as observed in pure crystals, both of these are attributed to the thermal decay of F centres. The high-temperature glow peak at 483 K is observed only in the doped samples and found to decrease in intensity only on prolonged F bleaching. It is obvious that an F centre perturbed by the crystalline field of an impurity would give rise to a glow peak with more thermal stability than that of an isolated F centre [26]. From this viewpoint the 483 K glow peak which arises out of the incorporation of chromium impurities could be attributed to chromium ions in the vicinity of F centres, which are perturbed by the strong crystalline field (because of an incomplete 3d shell) of the Cr impurity in the form of F–Cr complexes. The shift observed in the first-glow-peak position and the suppression of the 383 K glow peak between the pure and chromium-doped samples may be due to the effect of impurities. The total decrease in the TL output might result from the capture of electrons by the impurity ions which in turn annihilate the majority of F centres responsible for TL glow.

3.3. Thermoluminescence emission spectra

In order to obtain a better understanding of the TL process, the spectral distribution of TL glow is studied for both pure and doped crystals. The emission spectra of all the glow peak positions of a pure CsCl crystal γ irradiated for 10 min are shown in figure 6. For all the glow peaks the emission is found to be the same with a peak at 407 nm followed by a shoulder at 470 nm.
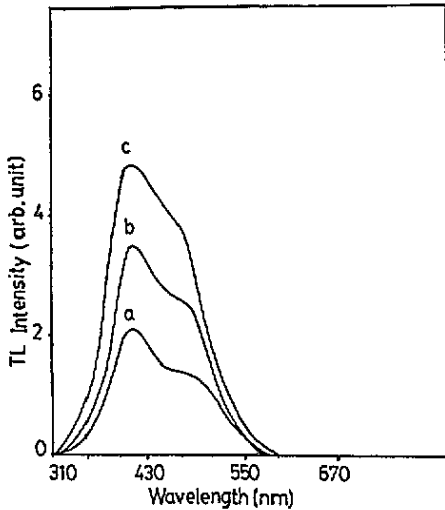
Figure 6. TL emission spectra of CsCl crystals: curve a, TL emission under 368 K glow peak; curve b, TL emission under 383 K glow peak; curve c, TL emission under 398 K glow peak.
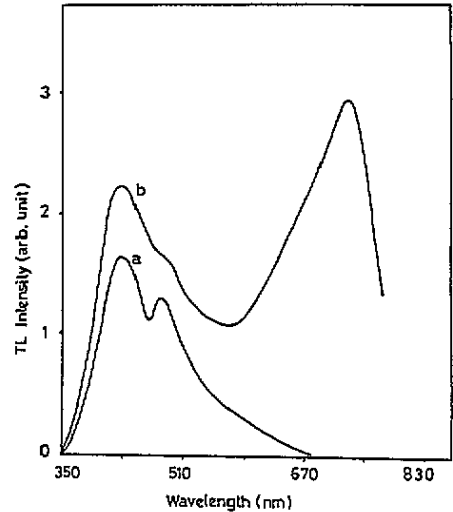
Figure 7. TL emission spectra of CsCl:Cr^{3+} crystals: curve a, TL emission under 363 and 398 K glow peaks; curve b, TL emission under 483 K glow peak.

Figure 7 shows the TL emission spectra corresponding to the glow peaks at 363, 398 and 483 K for CsCl:Cr^{3+} crystals. The spectra consists of a band at 430 nm and a well defined shoulder at 470 nm for the two glow peaks at 363 and 398 K. For the 483 K glow peak (which is assigned to F–Cr complex centres) an intense band peaking at 730 nm has been observed in addition to the above bands.

For pure CsCl crystals, the identical emission spectra observed under all the glow peaks indicate that the recombination centres are the same for all the glow peaks. The possible mechanism suggested by Radhakrishnan and Selvasekarapandian [12] was the thermal excitation of F-centre electrons and its recombination with V$_2$- and V$_3$-type centres having absorption bands at 252 and 233 nm.

In CsCl:Cr^{3+} crystals the emission at 470 nm is that observed in pure CsCl and hence may be attributed to the recombination of thermally detrapped F electrons with V$_3$ centres. For the MgO:Cr^{3+} system, Wertz *et al* [27] observed a blue emission in addition to the characteristic R line of Cr^{3+} ions. The blue emission was attributed to Cr^{2+} ions. Hence in the present system also the 430 nm blue emission observed at all glow peaks is believed to be associated with the formation of Cr^{2+} ions. The emission at 470 nm corresponding to the direct recombination of F electrons with the V$_2$ centres is found to be absent in the doped system. This may be due to the utilization of this recombination energy in exciting the neighbouring Cr^{2+} ions (formed on irradiation) which then emit their characteristic radiation (430 nm) on returning to the ground state.

The 730 nm emission is undoubtedly related to Cr^{3+} emission and it has been observed in almost all types of lattice and is referred to as the R line of Cr^{3+} [28–30]. The occurrence of this 730 nm emission in the present system can be explained by the following mechanism. During TL read-out, the thermally activated electrons from Cr^{2+} centres recombine at V-type centres, leaving the Cr^{3+} ions in an excited state, which on subsequent relaxation to the ground state gives out the characteristic R-line emission of Cr^{3+}.

The interpretation can be summarized by the following reaction.

$$Cr^{2+} \xrightarrow[TL]{e^-} Cr^{3+} \rightarrow Cr^{3+} + h\nu(\text{R line}).$$
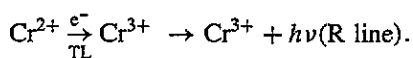
4. Conclusions

(1) The chromium ion displays its characteristic absorption and also charge-transfer bands. On irradiation, a valence conversion of the chromium from trivalent to divalent occurs.

(2) The additional TL glow peak at 483 K is attributed to chromium ions in the vicinity of an F centre.

(3) Cr^{3+} is considered to act as an electron trap, and V-type defects as hole traps. The observed blue emission and red emission are attributed to Cr^{2+} and Cr^{3+} ions, respectively.

(4) A strong quenching effect of luminescence due to Cr^{3+} has been observed for the CsCl:Cr^{3+} system, which is opposite to the effect of RE impurities in the CsCl:Eu^{2+} system.

Acknowledgments

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