



F centre production in CsI and CsI–Tl crystals under Kr ion irradiation at 15 K

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Abstract

We present results of simultaneous in situ luminescence and optical absorption studies in scintillator CsI and CsI–Tl crystals, exposed to very dense electronic excitations induced by ⁸⁶Kr ions (8.63 MeV/amu). Irradiation at 15 K leads to the formation of the prominent F absorption band. In addition, several other features of the broad absorption between exciton and F bands were ascribed to an anion vacancy, α centre (240 nm), self-trapped hole, V_k centre (410 nm) and interstitials, H centres (560 nm). We have found that low doping of thallium ($\sim 10^{17}$ cm⁻³) causes the F centre formation to proceed more rapidly than in pure crystal. On the other hand, we were not able to create any amount of F centres in heavily doped CsI–Tl. We have shown that point defects created by heavy ions manifested themselves in luminescence ageing. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Luminescent CsI and CsI–Tl crystals are known as very effective scintillator materials due to their widespread use in particle detectors. It is evident that radiation damage in scintillating materials do limit their applications. In general, radiation damage creates colour centres that reduce light transmission, destroys the luminescent centres in the material or prevents formation of the luminescent centres therein.

Radiation damage in alkali halides was studied in detail for many decades [1–5]. It is now well-established that primary Frenkel defects – F and H centres are formed via the non-radiative decay of self-trapped excitons. Besides, charged Frenkel defects, i.e. empty halide vacancy and interstitial halide ions, called α and I centres (arising as a result of the tunnelling recombination of primary Frenkel defects – F and H centres) are also observed. After prolonged irradiation their concentration could be quite high, e.g. in KBr crystal irradiated at 10 K the ratio of the number of α and I Frenkel pairs to the number of F and H pairs may be about four or five.

Although F centre production in alkali halides has been of considerable interest for the past four

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decades, the major portion of this interest has been devoted to studies of the face-centred cubic (NaCl-type) salts [1]. Not too much attention has been paid to radiation induced defects in alkali halides with CsCl-type structure which are important for many applications. This is of a special importance for the case of CsI crystals due to their widespread use in particle scintillator detectors [2–4]. Several studies of radiation damage in CsI and CsI–Tl crystals done at room temperature have been reported [5–12], where light output [5–11] or transmission spectra [8–12] were analysed after ^{60}Co [5,8–12], ^{137}Cs [6], PETRA [7] or 12 GeV proton [11] irradiations. As follows from [8–12], a significant F absorption band has been seen around 800 nm in both undoped CsI [10–12] and CsI–Tl [8–10]. Moreover, it has been shown that undoped CsI is substantially radiation harder than CsI–Tl [9,10]. It should be noted that radiation defect production efficiency depends strongly upon the type of lattice anions. As mentioned in [13], although point defects were produced in CsCl and CsBr by irradiation with X-rays within a few minutes, such irradiation did not produce measurable colouration in CsI, even after several hours.

2. Experimental

Three different types of CsI crystals were studied in this paper. Nominally pure CsI crystals have been grown in the Laboratoire de Spectroscopie Atomique (CNRS/ISMRA, Caen). The low-doped CsI–Tl crystals with Tl⁺ ion concentration of about 10^{17} ion/cm³ have been supplied by Dr. P. Schotanus (SCIONIX, Holland). The highly doped CsI–Tl with Tl⁺ ion concentration of about 10^{19} ion/cm³ was obtained from Dr. S. Chernov (Institute of Solid State Physics, University of Latvia). The apparatus used in this work is essentially the same as that previously described in [14,15]; we shall therefore will give only a very brief description here. Optical absorption spectra were measured before and after ion irradiation in the 200–900 nm range with a 4-nm resolution using a 16 double-beam Perkin Elmer spectrometer. The sample beam is transported, by a set of mirrors, through the sample under normal incidence.

Crystals have been irradiated at GANIL on the medium-energy beam line (SME) with ^{86}Kr ions (8.63 MeV/amu). In this study, both the irradiation and measurement temperatures were 15 K.

3. Results and discussion

Fig. 1 shows the irradiation-induced absorption spectra corresponding to several fluences (varied from 1×10^{11} to 2×10^{12} ions/cm²) under Kr ion irradiation of a pure CsI crystal at 15 K. We used the pre-irradiation optical absorption of the crystal as the baseline of zero initial optical density. This baseline was then subtracted from the absorption spectra obtained after irradiation. The tacit assumption in this procedure was that the pre-irradiation structure was not altered during the irradiation process. As follows from Fig. 1, we can easily identify the prominent F absorption band, showing, in fact, the double structure, one band at 1.65 eV (751 nm) and another – at 1.73 eV (716 nm). We have to note that at room temperature the F centre band has absorption band at 800 nm. The 50 nm difference is due to the temperature dependence of the F band peak well known for F centres in alkali halides.

Fig. 1 also gives the evidence of an α band at 5.15 eV (240 nm) observed as a shoulder on the

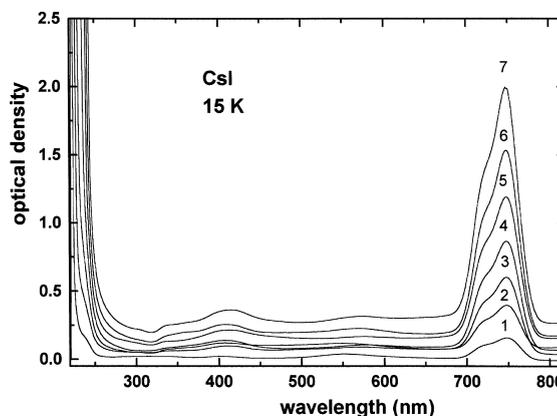


Fig. 1. Evolution of the optical absorption spectra of CsI under irradiation at 15 K with fluences 10^{11} ions/cm² (1); 3×10^{11} ions/cm² (2); 6×10^{11} ions/cm² (3); 9×10^{11} ions/cm² (4); 1.2×10^{12} ions/cm² (5); 1.6×10^{12} ions/cm² (6); 2.0×10^{12} ions/cm² (7).

fundamental absorption tail at low fluence values. In addition to the above colour centre bands, several other features of the broad absorption between α and F could be tentatively ascribed to V_k centres at 3.02 eV (410 nm) and H centres at 2.21 eV (560 nm). Such assignment is in good agreement with that made in transient absorption measurements of pure CsI excited by the pulse of 300 keV electrons at 80 K [16]. Probably, the I centres are responsible for the shoulder at 335 nm.

Fig. 2 shows the absorption spectra of the low-doped CsI–Tl (1) and pure CsI (2) after irradiation at 15 K with the fluence of 6×10^{11} ions/cm². One can see that at low Tl concentration in CsI, the concentration of F centres produced is higher than that in pure crystal. Furthermore it seems that colour centres with absorption bands ranging between 1.5 and 5 eV are also produced in higher concentration.

Fig. 3 shows the normalised F centre absorption bands of the low-doped CsI–Tl and pure CsI. The similar shape of the absorption bands shows that the individual F centres are responsible for the optical absorption. Furthermore we can conclude that there is no F centre production in the F_A configuration, i.e. when one nearest-neighbour cation of the F centre is an impurity. The reason for component structure in the F band in cesium halides has not been theoretically explained [17,18]. It seems that most probably, this is the

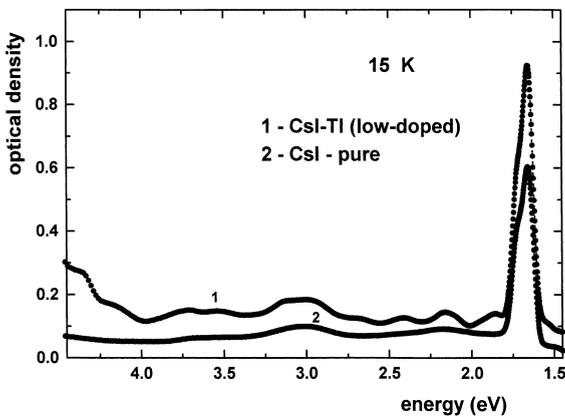


Fig. 2. Absorption spectra of the low-doped CsI–Tl (1) and pure CsI (2) after irradiation at 15 K with fluence of 6×10^{11} ions/cm².

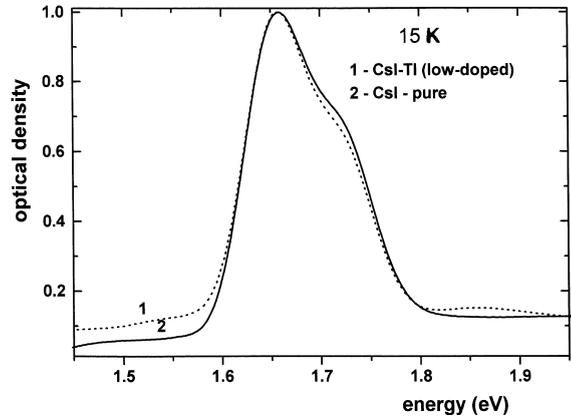


Fig. 3. Normalised F center absorption bands of the low-doped CsI–Tl and pure CsI.

spin-orbital splitting due to the presence of the cesium ion.

When pure CsI and low-doped CsI–Tl crystals are exposed to ion irradiation, the F centre concentration increases prominently. Plots of F centre concentration versus Kr ion fluence are shown in Fig. 4. The following conclusions can be drawn here. At low Tl doping the F centre formation is accelerated compared to a pure crystal. On the other hand, we did not able to create any amount of F centres in highly doped CsI–Tl. It seems clear that in the last case the complete suppression of the F centre production is due to the fact that almost

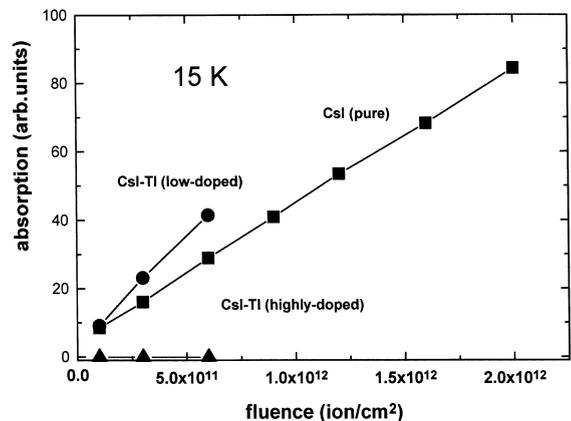


Fig. 4. Ion fluence dependence of the F center optical absorption for the three studied crystals.

all $e-h$ recombinations occur on the Tl^+ sites or nearby thus relaxing via the production of Tl^+ centre luminescence. Such competition between luminescence and defect creation processes has been studied in detail at 300 K for KBr doped with In or Tl ions [19]. In order to explain why the small concentration of Tl ions enhances greatly the number of stable F centres, that appear as a result of irradiation at temperatures near LHeT, we have to consider the stabilization and trapping of mobile interstitials (H and I centres) by Tl ions. Apparently it is well known that the introduction of minor concentration of mercury-like ions into alkali halides leads to a significant increase of the yield of stable F centre under irradiation at 80 K [20] or 300 K [19,21]. This phenomenon is explained by the trapping of H centres by the activator ions giving a decrease of the portion of F centres recombining in non-correlated F–H pairs [1,22].

It is of interest to compare the production efficiency (eV/centre) of F band absorption for all cesium halides. Rabin and Schulman have reported the values of $(6-15) \times 10^2$ and 8.1×10^2 eV/centre in CsCl and CsBr at LHeT, respectively [23]. Taking into account that in our case the F centres are created in a crystal layer of a thickness that corresponds to the ion range R of 83.4 μm and using the oscillator strength of 0.4, we can obtain the value of 2.5×10^7 eV/centre. Such a quite high value defines the appropriate radiation hardness of CsI scintillators.

In order to check whether the amount of scintillation light, emitted by a crystal, changes as a result of radiation, we have measured the emission spectra during Kr ion irradiation. As an example, in Fig. 5 we present luminescence spectra of pure CsI taken in the beginning of ion irradiation and after irradiation with the fluence of 2.0×10^{12} ions/ cm^2 . As follows from Fig. 5, well-known self-trapped exciton (STE) triplet emission band at 340 nm (3.65 eV) [24] dominates over the entire investigated spectral range. Luminescence band at 295 nm seems to be complex due to the superposition of two other excitonic bands at 289 nm (4.3 eV) and 300 nm (4.1 eV). A new emission band at 2.33 nm (5.32 eV) has been observed for the first time. This emission band has also been detected in

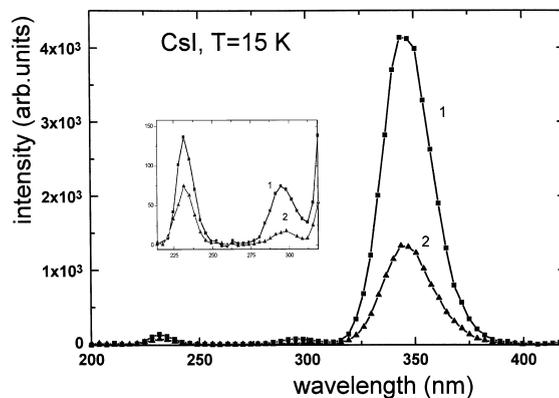


Fig. 5. Luminescence spectra of pure CsI taken at 15 K in the beginning of ion irradiation (1) and after irradiation with fluence of 2.0×10^{12} ions/ cm^2 (2). Inset shows both spectra in more detail for the spectral range of 200–300 nm.

low-doped CsI–Tl, but not in highly doped crystal. We believe that this emission arises from metastable state of one-centre self-trapped excitons (OSTE). Study of the temperature dependence of this luminescence band confirms the above interpretation [25]. Recently, broad bands tentatively ascribed to the metastable OSTE, have been detected in the VUV region for KCl, KBr, NaCl, RbCl and RbBr crystals [26–29]. The relative Stokes shift $\mu = (E_A - E_L)/E_A$ for these emissions are 0.13–0.15 for alkali chlorides and 0.08–1.0 for bromides (the maximum of long-wavelength exciton absorption band is taken as the E_A and E_L is the maximum of luminescence band). The relevant values for iodides should be smaller. We can find easily that relative Stokes shift for 5.32 eV in CsI is 0.06 which is in good correspondence with the above values.

Another conclusion which can be drawn from Fig. 5 is that the ion irradiation leads to the significant ageing of all exciton luminescence bands. No emergence of new emission bands was found. Estimation of the reabsorption of luminescence by the radiation defects cannot explain the observed values of the luminescence decrease. Probably, the luminescence ageing can be understood taking into account the STE-radiation defect interaction.

Preliminary results for NaCl and KBr have been published in [15]. In low-doped CsI–Tl we have observed significant ageing of the excitonic

and Tl ion luminescence. More detailed results on CsI–Tl ion luminescence will be published in the forthcoming paper [25].

4. Conclusion

We have presented the results of in situ luminescence and optical absorption studies in scintillator CsI and CsI–Tl crystals exposed to very dense electronic excitations induced by ^{86}Kr ions (8.63 MeV/amu). Irradiation at 15 K leads to the formation of the prominent F absorption band. We have found that low doping of thallium ($\sim 10^{17} \text{ cm}^{-3}$) accelerates the F centre formation as compared to a pure crystal. We were not able to create any amount of F centres in highly doped CsI–Tl. The production efficiency of F centre in CsI at 15 K was found as high as 2.5×10^7 eV/F centre.

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