

Radiation damage factors of CsI(Tl) crystals

L.N. Shpilinskaya, D.I. Zosim, L.V. Kovaleva, A.M. Kudin, A.I. Mitichkin, T.A. Charkina

STC "Institute for Single Crystals", Lenin Avenue 60, Kharkiv, 310001, Ukraine

Abstract. The light yield deterioration of CsI(Tl) crystals subjected to ionizing irradiation is found to be due to the increase of the scintillation light re-absorption caused by the formation of F-like color centers in the diffusion process. Those centers appear due to the formation of F ones stable at ambient temperature, the stabilization of the latter is realized effectively due to radiation-chemical transformation of CO_3^{2-} and OH^- ions.

Keywords: thallium activated cesium iodide; color centers; radiation damage; re-absorption

Introduction

The radiation induced damage of CsI(Tl) scintillation crystals manifesting itself as the light yield degradation is due to the formation of color centers (CC) resulting in both transparency loss and the conversion efficiency reduction [1]. Since the absorption spectrum of formed CC overlaps the scintillation one, it is no doubt that the re-absorption contributes substantially to the light yield degradation. While the role of the conversion efficiency in the light yield loss remains still unclear. According to modern notions [2], the stable radiation induced defects in alkali halide crystals (AHC) are due to formation of Frenkel type F-H pairs having the flying apart probability exceeding that of their mutual annihilation. In the presence of impurities, near impurity (F,H) centers arise in crystals along with F,H pairs. In this case, it is not F center but H one that becomes localized near the impurity; that center transforms into H_A one and then a $(\text{V}_2)_A$ center arises due to the evolution of the latter. F_A centers can be obtained by the F band illumination of a crystal preliminary treated by ionizing radiation at temperatures close to the ambient one when the anion vacancy mobility is high enough. In the same time, the radiation induced defect formation in crystal having a CsCl type lattice activated with mercury-like ions has been explained basing on "vacancy type" mechanism. According to the latter, as a result of irradiation, electrons become localized on the activator ions under formation of A° centers; those diffuse through anionic or cationic vacancies resulting in formation of paired A_2° centers and more complex activator coagulations [3, 4]. The available experimental data on the radiation resistance of mercury-like activated CsCl type crystals, including CsI(Tl) ones doped additionally with anionic and cationic impurities cannot today be explained within the frame of the existing vacancy mechanism. In this work, the radiation induced defect formation processes involving pre-radiation defects in CsI and CsI(Tl) crystals are discussed and an attempt is made to explain the radiation damage of crystals in the frame of unified mechanism.

Experimental

The studies were carried out using samples made from CsI and CsI(Tl) crystals with different contents of thallium and molecular anions (MA) CO_3^{2-} , OH^- , SO_4^{2-} . Absorption spectra in UV, visible and IR regions were measured using SF-26 and UR-20 spectrophotometers. The light yield was measured on samples of 30 mm in diameter and different lengths (5, 20, 60 and 90 mm). The light yield degradation was characterized as the $(L_0 - L)/L_0$ ratio where L_0 and L are the light yield value prior to and after the irradiation, respectively. The re-absorption effect on the light yield reduction of irradiated crystals was estimated using the optical density change on 550 nm wavelength of $\varnothing 30 \times 60$ mm samples

measured with respect to reference by the integrating sphere technique. The crystals were colored using a ^{60}Co gamma source, UV and daylight irradiation.

Radiation-stimulated change of the CsI(Tl) detector light yield

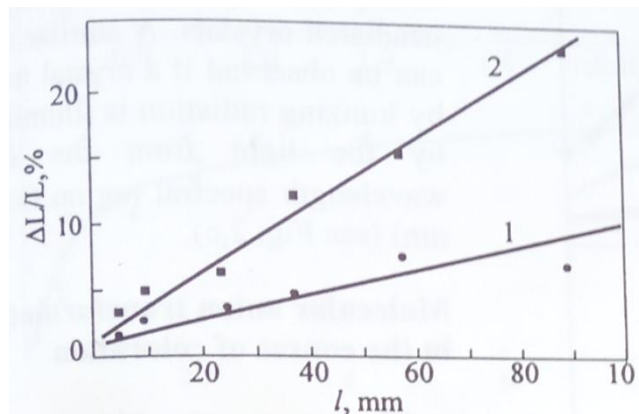


Fig. 1. The light yield degradation of $\text{Ø}30$ mm CsI(Tl) detectors as a function of its length after 0.05 Mrad (1) and 0.5 Mrad (2)

To determine the effect of the scintillation efficiency reduction on the light yield degradation of irradiated crystals, the light yield of cylindrical detectors having different heights was measured prior to and after the irradiation.

It is seen from Fig.1 that the light yield degradation depends linearly on the detector height and can be approximated to zero thus evidencing that the conversion efficiency changes affect the light yield degradation only slightly. The re-absorption influence in the crystals was estimated from the optical density change in the 540 nm

region corresponding the scintillation spectral maximum. The radiation-stimulated re-absorption increase is due to the presence of color centers in the crystals.

Color center formation in CsI(Tl) crystals

The color centers stable at ambient temperature and having the absorption bands in the activator absorption and emission region are known to be formed in CsI(Tl) crystals due to ionizing radiation and, in some cases, under the daylight action [5]. Fig. 2a presents the absorption spectra of gamma-irradiated CsI(Tl) crystal at different concentrations of Tl and CO_3^{2-} , OH^- , SO_4^{2-} molecular anions. The absorption bands are seen to increase in intensity as the Tl concentration rises. At the same Tl concentration, it is just crystals containing CO_3^{2-} ions as an additional impurity. In Fig. 3, the optical density variations of $\text{Ø}30 \times 60$ mm CsI(Tl) crystals at the same irradiation dose are shown as functions of Tl and CO_3^{2-} ions. Neither new bands nor intensity increase of any bands as compared to non-irradiated samples are observed in absorption spectra of gamma-irradiated CsI(Tl) crystals doped additionally with SO_4^{2-} ions (Fig. 2,a) as well as with IO_3^- ones [5]. The Tl concentration being the same, the 430, 520, 560, 840, 975 nm bands intensities are higher in crystals with higher CO_3^{2-} ion content. According to [3], the absorption bands with maxima at 430 and 520 nm are due to Tl_2^0 centers, weaker 390 and 465 nm bands, to Tl_2^+ ones while IR bands (840 and 975 nm), to more complex linear and three-dimensional associates of atomic thallium.

A high coloration intensity of CsI(Tl, CO_3) crystals can be attained irradiating them by UV and visible light, too; in both those cases, the absorption spectra are identical to those of gamma-irradiated crystals (Fig. 2,a,b). In contrast, CsI(Tl) crystals grown in vacuum using the Bridgman technique, having the activator concentration from $2 \cdot 10^{-5}$ to $5 \cdot 10^{-1}$ % and an additional SO_4^{2-} impurity are stable against light. A specific feature of CsI(Tl, CO_3) crystals colored by daylight consists in that at first the 355, 430, 520, 560, 840, 975 nm are appeared in the absorption spectrum and then, as the irradiation duration increases, the 390 and 465 nm ones arise (Fig. 2,b). The accumulation kinetics of color centers is of an usual character. As the irradiation duration grows, the intensity of all bands observed increases and then becomes saturated. A comparison of absorption spectra for crystals colored by gamma-irradiation (Fig.

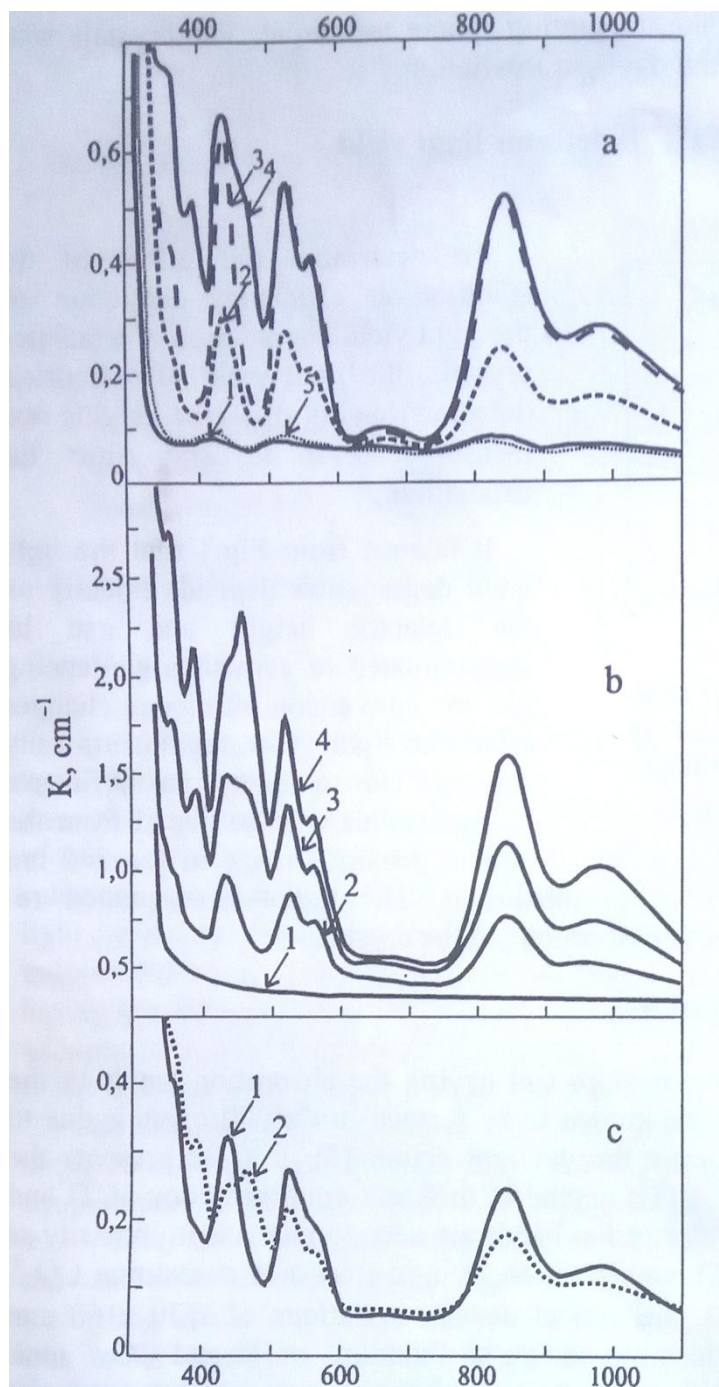


Fig. 2.

- a) Absorption spectra of γ -irradiated CsI(Tl) crystal (0.01 Mrad). Tl concentration is equal to $1.1 \cdot 10^{-2}$ (1, 2, 4, 5); $6 \cdot 10^{-2}$ (3). Concentration of CO_3^{2-} ions is $6 \cdot 10^{-4}$ (3, 4); $6 \cdot 10^{-5}$ (2); less than $2 \cdot 10^{-5}$ (1, 5). Concentration of SO_4^{2-} is $1 \cdot 10^{-4}$ (5); less than $2 \cdot 10^{-5}$ mole % (1, 2, 3, 4).
- b) Absorption spectra of CsI(Tl,CO₃) crystal prior to (1) and after (2, 3, 4) daylight irradiation during 3 hour (2), 9 days (3), 35 days (4). Concentrations of Tl is $6 \cdot 10^{-2}$ mole %; of CO_3^{2-} is $6 \cdot 10^{-4}$ mole %.
- c) CsI(Tl,CO₃) crystal absorption spectra immediately after γ -irradiation of CsI(Tl) crystal (0.01 Mrad) and after the subsequent illumination by the filtered (430 nm) mercury lamp emission (2).

2, a) and by daylight (Fig. 2b) shows that even at low Tl concentrations ($\leq 10^{-2}$ %) intense 390 and 465nm bands characteristic for Tl_2^+ centers appear in absorption spectra of daylight irradiated crystals. A similar effect can be observed if a crystal treated by ionizing radiation is illuminated by the light from the short-wavelength spectral region ($\lambda \leq 430$ nm), see Fig. 2,c.

Molecular anion transformation in the course of coloration

The appearance of bands due to activator type CC in the electron absorption spectra of colored CsI(Tl,CO₃) crystals is accompanied by substantial change in vibration spectra (Fig.4). As the intensity of bands typical for CC grows, that of CO_3^{2-} ion vibration bands decreases and a series of additional ones (593, 663, 745, 830, 947, 1223, 1315, 1679, 3318 cm^{-1}) ascribed to HCO_3^- ion appears. As in the case of CsI(CO₃) crystals [6], the effect of HCO_3^- ion formation has a volume character. No changes were observed in vibrational spectra of CsI and CsI(Tl) crystals containing SO_4^{2-} ions after gamma or daylight irradiation. A study of electron absorption spectra of isodose irradiated (10^3 rad) CsI(SO₄) and CsI(CO₃) crystals with the same MA content has shown that no F-absorption bands are observed in CsI(SO₄) crystals in contrast to CsI(CO₃) ones.

Discussion

The estimation of the re-absorption and of the scintillation efficiency reduction to the light yield degradation of gamma-colored CsI(Tl) crystals has shown that the light yield decrease is due to the transparency loss to the

Conclusion

1. The predominant importance of re-absorption in the radiation resistance degradation of CsI(Tl) detectors has been established.
2. The increased scintillation light re-absorption in irradiated yield CsI(Tl) crystals is caused by formation of F-like activator color centers (F_{AA}) in the course of F center diffusion towards paired ($Tl^+ - Tl^+$) centers.
3. The formation of stable F centers is possible under presence of CO_3^{2-} molecular anions and OH^- ions involved in radiation-chemical reactions in CsI and CsI(Tl) crystals.
4. The photochemical instability of CsI(Tl, CO_3) crystals is due to the

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