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The effect of oxygen-containing anions on luminescent properties of CsI

L.N.Shpilinskaya, B.G.Zaslavsky, L.V.Kovaleva, S.I.Vasetsky, A.M.Kudin, A.I.Mitichkin,
T.A.Charkina

STC "Institute for Single Crystals", NAS of Ukraine, Kharkov, Ukraine

Abstract. It has been found that from the series of oxygen-containing impurities CO_3^{2-} , SO_4^{2-} , HCO_3^- , OH^- , IO_3^- , NO_3^- , NO_2^- , CNO^- , BO_2^- only the bivalent ions stimulate an intensive blue luminescence in CsI crystals at UV- or gamma-excitation. The blue luminescence intensity is higher in CsI(CO_3) than in CsI(SO_4) crystals. The nature of blue luminescence components has been considered and two types of centres have been suggested: the impurity type – $\text{CO}_3^{2-}\text{-V}_a^+$ (395 nm) and the structural one – $\text{V}_a^+\text{-V}_c^-$ (435 nm). A method of deep purification of the melt from oxygen-containing anions during the growth process has been proposed.

Keywords: luminescence, emission centres, cesium iodide, oxygen-containing anions.

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1. Introduction

CsI scintillation crystals are known to contain often some impurity molecular anions (MA): CO_3^{2-} , SO_4^{2-} , HCO_3^- , OH^- , IO_3^- , NO_3^- , NO_2^- , CNO^- , BO_2^- which are easily detected by the methods of IR spectroscopy. The mentioned molecular anions can serve as a source of oxides in crystals which are formed at thermal decomposition of MA in the growth process or as a result of radiation-chemical transformations in gamma-irradiated crystals [1]. Oxides in the alkali metal iodides are poorly detected by the absorption methods and their presence is detected by luminescence, related to O_2^{2-} or $(\text{O}_2^{2-}\text{-V}_a^+)$ -centres ($\lambda = 430$ nm) and O_2^- -centres ($\lambda = 530$ nm) [1]. The purpose of this paper was to study the effect of oxygen-containing impurities on luminescent properties of CsI crystals and to find out the nature of the luminescence centres.

2. Results and discussion

Photo- and radioluminescence (RL) of CsI crystals purposely doped with molecular ions CO_3^{2-} , SO_4^{2-} , HCO_3^- , OH^- , IO_3^- , NO_3^- , NO_2^- , CNO^- , BO_2^- were studied at their excitation with a deuterium lamp DDS-250 and gamma-source ^{241}Am . The presence of the mentioned impurities was controlled by the method of IR spectroscopy on a spectrophotometer UR-20 by the typical for molecu-

lar ions vibration spectra. The impurity concentration is given in mol.%.

The analysis of the RL spectra of CsI crystals with MA showed that of all the studied molecular anions only the bivalent MA ions (CO_3^{2-} и SO_4^{2-}) stimulate the appearance of the intensive blue emission (Fig. 1, curves 4-6). An insignificant contribution of other oxygen-containing impurities (OI), including oxides, to the increase of RL intensity gives evidence to the absence of a radiative channel in the processes of energy transfer from the lattice to the considered impurity centres. Besides, the effect of these impurities is reduced to a noticeable quenching of the intrinsic scintillation of CsI ($\lambda_{\text{max}} = 310$ nm).

According to [2] in CsI(CO_3) crystals the intensity of RL goes up as the content of carbonate-ions increases in the interval $4.5 \cdot 10^{-4}$ - $4.8 \cdot 10^{-3}\%$ and the maximum of a nonelementary band is shifted towards a short-wave region from 425 to 405 nm. Irrespective of CO_3^{2-} concentration in CsI(CO_3) crystals in the mentioned concentration range RL consists of two bands with the maxima 395 and 435 nm, having close halfwidths 0.6 eV. The first, to the authors' opinion, is caused by impurity-vacancy dipoles (IVD) ($\text{CO}_3^{2-}\text{-V}_a^+$) and the second – by oxygen O_2^{2-} -centres.

The carried out by the authors study of CsI(CO_3) crystals in a wider concentration range of carbonate-ions from $5.5 \cdot 10^{-5}$ to $6.5 \cdot 10^{-2}\%$ (Fig. 2) confirmed the conclusion of [2] about excitonlike nature of the luminescence centres

near the impurity-vacancy dipole ($\text{CO}_3^{2-}-\text{V}_a^+$); those centres being responsible for the short-wave luminescence band.

At the same time the nature of a longer wavelength band can be considered from other viewpoints. The study of RL crystals grown in the presence of oxygen at doping with decomposing impurities CsNO_3 and CsIO_3 (Fig. 1, curves 2, 3) did not allow to reveal any intensive RL at 435 nm, related to the oxygen O_2^{2-} -centres.

The other reason of the blue luminescence emergence can be centres of the vacancy type. The excess concentration of bivacancies can be created by, for example, quenching from a premelting temperature or by plastic deformation of crystals at room temperature. The RL spectrum of the quenched from 800 K undoped CsI crystal, the content of CO_3^{2-} ions in which did not exceed $2 \cdot 10^{-5}\%$ is shown in Fig. 2, curve 3. As compared to the spectrum of the initial crystal (curve 1) in the quenched ones a rather intensive luminescence with a maximum at 430 nm is observed. Respective emission centres are unstable and fully destroyed in the process of the sample aging. In a year the RL spectrum of the quenched sample completely corresponds to the initial sample one. Crystals

grown from melt are always quenched to some extent. A sufficiently obvious assumption can be made that in the solid solution of the nonisomorphous impurity the content of bivacancies exceeds their equilibrium concentration at the given temperature.

The study of the photoluminescence (PL) excitation spectra of $\text{CsI}(\text{CO}_3)$ crystals showed that both components of the blue luminescence at room temperature are excited in the absorption band with the maximum 242 nm (Fig. 3, curve 1). The PL spectrum at the excitation in this band is presented on the curve 2. The comparison with the spectrum of RL (curve 3) shows that the spectral composition of emission at both types of excitation is the same. It is shown [3, 4] that an efficient energy transfer to the vacancy-type emission centres takes place in the CsI lattice. The decay time of such centres varies in the range of 1.3-20 μs . Formation of the mentioned centres is stimulated by a high temperature annealing followed by quenching. A low temperature annealing of crystals at 300 K leads to a decrease of the nonequilibrium concentration of bivacancies in the diffusion process. This being so, a decrease of the quantity of the vacancy-type luminescence centres excited according to [5] at 242 nm is observed as

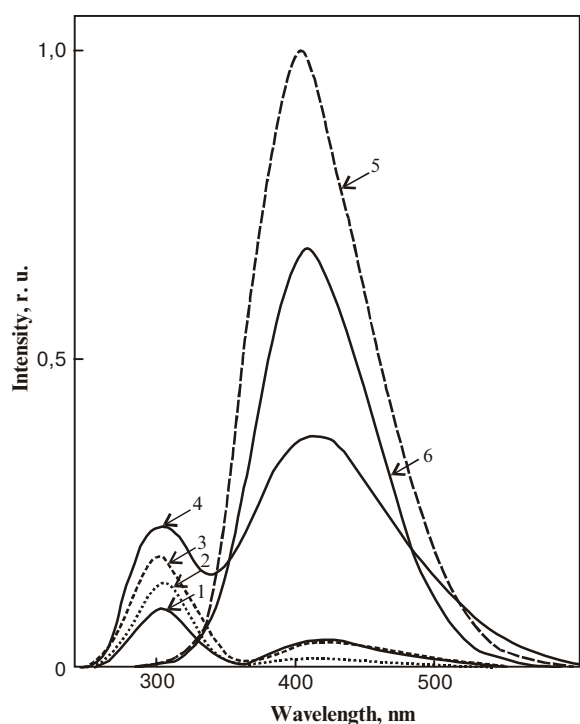


Fig. 1. Radioluminescence spectra of $\text{CsI}(\text{HCO}_3)$ (1), $\text{CsI}(\text{IO}_3)$ (2), $\text{CsI}(\text{NO}_3)$ (3), $\text{CsI}(\text{SO}_4)$ (4), $\text{CsI}(\text{CO}_3)$ (5,6) crystals: 1 – concentration of HCO_3^- and CO_3^{2-} ions in the CsI crystal $1 \cdot 10^{-4}\%$ and $2 \cdot 10^{-4}\%$, respectively; 2 – $\text{CsI}+0.07 \text{ CsIO}_3\%$ in the raw material; 3 – concentration of NO_2^- and NO_3^- ions in the CsI crystal $2.8 \cdot 10^{-3}\%$ and $2.2 \cdot 10^{-3}\%$, respectively; 4 – concentration of SO_4^{2-} ions in the CsI crystal – $3 \cdot 10^{-2}\%$, 5,6 – concentration of CO_3^{2-} ions in the CsI crystal – $1.7 \cdot 10^{-2}\%$ and $5 \cdot 10^{-3}\%$, respectively.

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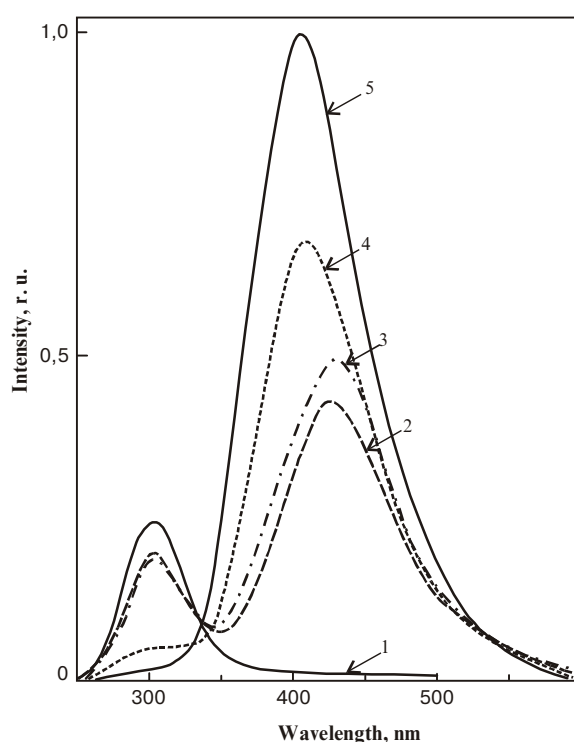


Fig. 2. Radioluminescence spectra of crystals CsI (1,3) and $\text{CsI}(\text{CO}_3)$ (2,4,5). CsI crystal before (1) and after (3) quenching; $\text{CsI}(\text{CO}_3)$ crystals with the concentration of CO_3^{2-} ions $2 \cdot 10^{-4}\%$ (2), $5 \cdot 10^{-3}\%$ (4), $2 \cdot 10^{-2}\%$ (5).

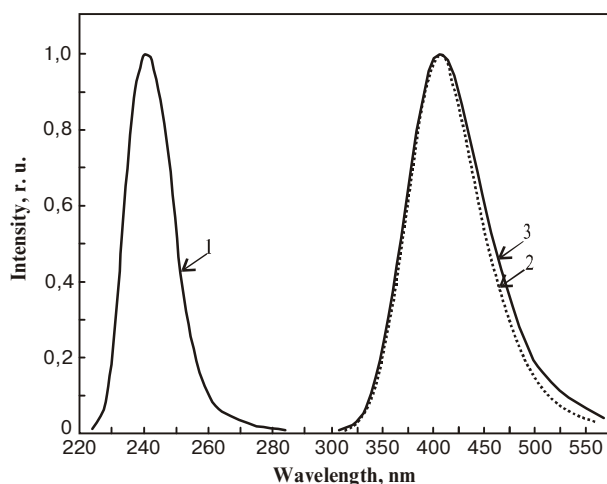


Fig. 3. Excitation spectra (1), photo-(2) and radioluminescence (3) of the $\text{CsI}(\text{CO}_3)$ crystal; concentration of CO_3^{2-} ions is $2 \cdot 10^{-4}\%$.

well. The described facts allow to assume that the luminescence centres with the maximum 435 nm and decay time $3.4 \mu\text{s}$ can be related not to O_2^{2-} [2] but to the luminescence centres of the $(\text{V}_a^+ - \text{V}_c^-)$ type.

Molecular ions CO_3^{2-} , SO_4^{2-} , HCO_3^- , OH^- , IO_3^- , NO_3^- and other oxygen-containing impurities are always present in the raw material composition. Concentration of all impurities except for SO_4^{2-} ions can be essentially decreased by thermal treatment of the raw material and melt. The content of sulfate-ions in crystals reaches the values of $5 \cdot 10^{-5}$ - $5 \cdot 10^{-4}\%$. This makes the contribution of a slow component of RL higher in the undoped CsI crystals used as fast scintillators.

For an additional purification of melt from the oxygen-containing impurities, including SO_4^{2-} and BO_2^- ions, an efficient technique was developed for treating melt with

metals which form low soluble oxides in it [6]. The most advantageous appeared to be usage of metallic titanium which owing to its high melting temperature (1725°C) and chemical activity allows to treat the melts efficiently in the process of automated growth of large crystals. The analysis of the vibration MA spectra of crystals grown in such way showed that the level of the most difficult to eliminate impurities - SO_4^{2-} and BO_2^- ions is below the sensitivity level of the absorption method.

Conclusions

1. It has been found that among the studied molecular anions (CO_3^{2-} , SO_4^{2-} , HCO_3^- , OH^- , IO_3^- , NO_3^- , NO_2^- , CNO^- , BO_2^-) only the bivalent ions stimulate an intensive blue luminescence in CsI crystals at UV and gamma-excitation.

2. The nature of two components of the blue luminescence has been considered and two types of the centres have been suggested: the impurity-type $\text{CO}_3^{2-} - \text{V}_a^+$ (395 nm) and a structural one - $\text{V}_a^+ - \text{V}_c^-$ (435 nm).

3. A method of a deep purification of melt from the oxygen-containing anions in the process of automated growth of crystals has been proposed.

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