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Radiation defects creation in CsI(Tl) crystals and their luminescence properties

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Abstract

Radiation defect creation processes in CsI(Tl) crystals have been studied. The model of color center, according to which Tl^0 is close to anionic vacancy, is considered. The absorption spectrum of $Tl^0V_a^+$ -center is a superposition of bands responsible for both transitions between the near activator exciton states and for those between the valent electron states in thallium atom perturbed by the anionic vacancy. Another center $Tl^+V_a^+$ may appear as a result of the $Tl^0V_a^+$ photoionization. Absorption bands at 3.44, 3.8, 2.64 eV of the electron trapping $Tl^+V_a^+$ in the center have exciton origin. $Tl^+V_a^+$ is also a luminescence center. The excitation in the absorption bands of this center luminescence is conditioned by the luminescence of the near activator excitons.

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1. Introduction

It is known that in alkali halide crystals doped with mercury-like ions after irradiation atomic activator color centers formed are stable at room temperature [1–5]. Despite the fact that their properties have been known for a long time there are no common conceptions at present neither on the origin of these centers nor on the mechanism of their formation. According to Goovaerts et al. and Mollenauer et al. [1,2] color centres of two types are formed in KCl(Tl) crystals:

- thallium atom perturbed by the anionic vacancy ($Tl^0V_a^+$) which appears in the irradiated KCl(Tl) crystal after illumination by light of the F-band;

- thallium atom perturbed by two anionic vacancies ($V_a^+Tl^0V_a^+$) and formed after UV illumination of the $Tl^0V_a^+$ -center.

Both defects appear as a result of the diffusion of anionic vacancies (V_a^+) towards the activator atom. The absorption spectrum of irradiated KCl(Tl) is similar to that of Cs(Tl). At the same time according to Mednikov and Shtan'ko, Smol'skaja et al., and Smol'skaja and Kolesnikova [3–5], in CsI(Tl) crystals atomic centers of another type are formed:

- Tl_2^0 appears in the process of Tl^0 diffusion along cationic or anionic vacancies;
- Tl_2^+ appears as a result of electron capture by the thallium dimer (Tl_2^+).

It is the opinion of these authors that cation or anion impurity–vacancies dipoles in the lattice leads to a more efficient formation of Tl_2^0 -centres.

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Incorporation of bivalent CO_3^{2-} or SO_4^{2-} anions into CsI crystals stimulates the radiative decay of electron excitations for several microseconds. CsI(CO_3) crystal is an effective scintillator [6]. The lattice of CsI is rather stable against radiation damage. The influence of different oxygen-containing anions on the formation of radiation damage was investigated on CsI and CsI(Tl) crystals [7–10]. It was found that only CO_3^{2-} , OH^- and BO_2^- ions in CsI(Tl) stimulate efficient formation of stable activator centers. Under the effect of ionizing radiation in CsI and CsI(Tl), there proceed chemical reactions are initiated with the participation of CO_3^{2-} and OH^- ions leading to the formation of HCO_3^- ions and electron color centers: F- and F-aggregate centres in CsI crystals and activator centres in CsI(Tl). Unlike KCl(Tl), formation of stable centers of the activator type in CsI(Tl) does not require any additional illumination of the irradiated crystal by F-light.

The purpose of this paper is the investigation of the role of BO_2^- ions in the formation of color centers, characterization of the structure of the radiation-induced activator defects and study of their luminescence properties.

2. Experimental

CsI(Tl) single crystals were grown by the Stockbarger technique in vacuum and in inert atmosphere by modified Kyropoulos technique. TlI, Cs_2CO_3 salts and boric acid were used for doping. CsI raw material as well as Cs_2CO_3 or HBO_3 were dried thoroughly by heat treatment of ingredients at 100°C and of the mixture at 250°C under continuous evacuation. The concentration of thallium in the crystals was 6×10^{-2} – $1.2 \text{ mol}\%$ and that of CO_3^{2-} anions $-5 \times 10^{-4} \text{ mol}\%$. The component of boric acid amounted 2 – $4 \times 10^{-2} \text{ mol}\%$ in the initial mixture.

The absorption spectra in the UV, visible and IR regions were registered using SF-26 and UR 20 spectrophotometers. The luminescence was excited by the light of the deuterium DDS-400 lamp through monochromator MDR-2 and analyzed by the MDR-23 monochromator. The sample was mounted in a liquid nitrogen cryostat for measuring

the absorption, excitation and luminescence spectra. Crystals were irradiated by γ -ray ^{60}Co at 295 K. A high coloration intensity of CsI(Tl) containing additionally CO_3^{2-} or BO_2^- anions were attained when irradiating them by daylight, too. Illumination of colored crystals was carried out by the mercury lamp emission during 20 minutes.

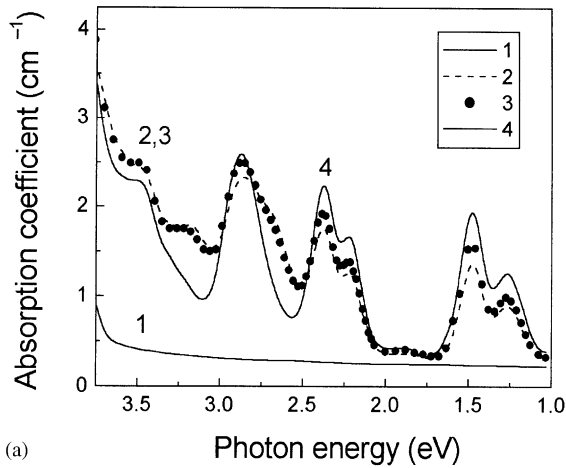
3. Transformation of radiation-induced activator centers

Radiation damage of CsI(Tl) crystals depends on both activator concentration and impurities in the lattice. Complex oxygen containing CO_3^{2-} , OH^- BO_2^- anions stimulate formation of color centers in CsI(Tl) crystals not only at exposure to ionizing radiation but also at their illumination by daylight. Irrespective of admixture composition one and the same bands are observed in the absorption spectra of CsI(Tl) crystals but the proportion of intensities between two groups of bands 3.18, 2.64 eV (i) and 2.88, 2.38, 2.21, 1.48, 1.27 eV (ii) may vary. The 3.44 eV band is not elemental. It relates to both groups.

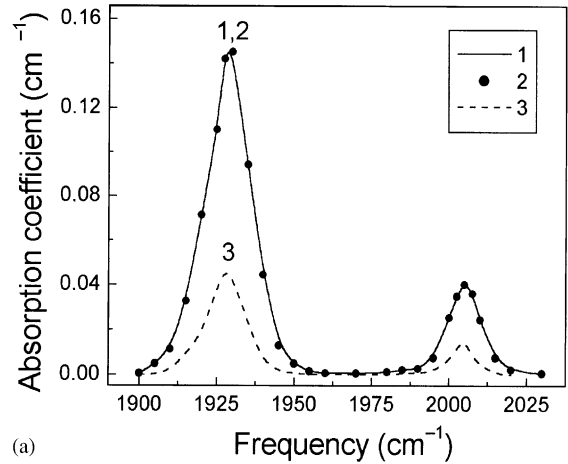
Fig. 1a shows the absorption spectra at 295 K colored by the daylight CsI(Tl) crystal. It is seen that the registered spectrum just after coloring consists of bands 3.44, 3.18, 2.88, 2.64, 2.38, 2.21, 1.48 and 1.27 eV. After keeping the crystal in darkness at 295 K one can see in its spectrum a lowering of the intensity of the bands 3.18 and 2.64 eV accompanied by rise in intensity of the bands 2.88, 2.38, 2.21, 1.48 and 1.27 eV. Lowering of the temperature of exposure in darkness down to 273 K leads to significantly smaller changes in the absorption spectrum. After illumination by light ($h\nu \geq 2.8 \text{ eV}$) of the CsI(Tl) crystal preliminarily colored by the ionizing radiation, reverse changes take place (Fig. 1b). The intensity of the bands 3.18 and 2.64 eV increases at the expense of decrease in intensity of the bands 2.88, 2.38, 2.21, 1.48 and 1.27 eV.

4. The influence of irradiation on the oscillation absorption of borate ions

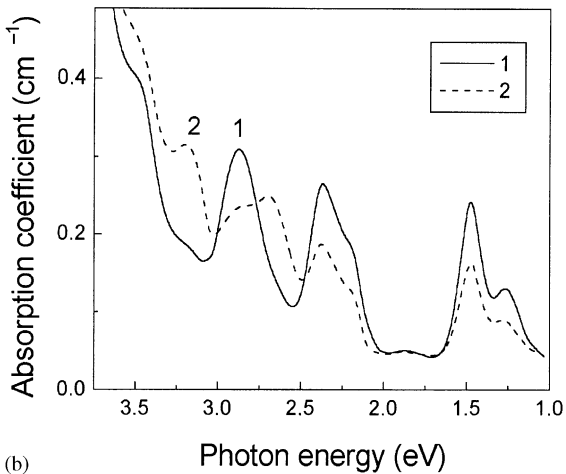
According to Hisatsune [11] BO_2^- has the form of a linear molecule 5.3 Å in size which occupies an



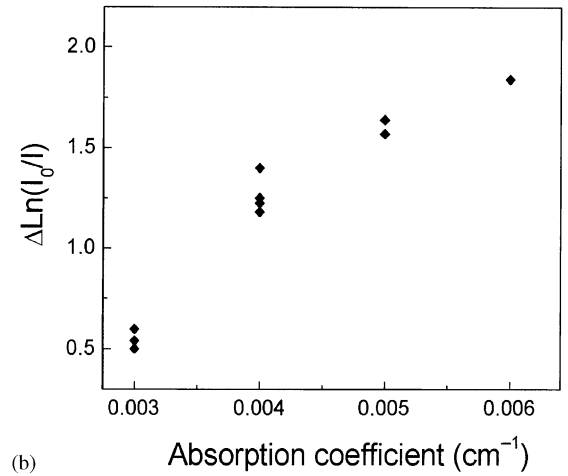
(a)



(a)



(b)



(b)

Fig. 1. (a) Absorption spectra of CsI(Tl) crystal containing BO_2^- prior to (1) and after (2) by daylight coloration with subsequent dark exposure for 17 days at 273 K (3) and 295 K (4). (b) Absorption spectra of CsI(Tl) crystal containing CO_3^{2-} immediately after irradiation (^{60}Co , 1×10^2 Gy) (1) and after the subsequent illumination at 295 K by the filtered (2.84 eV) mercury lamp emission (2). All measurements were carried out at 295 K.

Fig. 2. (a) Absorption spectra of BO_2^- ions prior to (1) and after (2) irradiation (^{60}Co , 5×10^3 Gy) and after the subsequent illumination at 295 K by daylight (3). (b) Variation of optical density at 2.25 eV versus the absorption coefficient at 1900 cm^{-1} for CsI(Tl) crystals at isodose irradiation (^{60}Co , 5×10^3 Gy) [8].

anionic site in the CsI lattice in the direction (100). Fig. 2a shows the absorption spectrum typical for partially symmetric valence ν_3 -oscillation of the BO_2^- anion consisting of two narrow bands 1930 and 2000 cm^{-1} which are related to the natural proportion of the isotopes ^{11}B and ^{10}B , respectively [11,12]. Even trace quantities of borate lead to effective coloration of CsI(Tl). Fig. 2b shows variation of optical density at 2.25 eV versus

the absorption coefficient in the region of ν_3 -oscillation of the BO_2^- anion after isodose irradiation [8]. The dependence indicates that the number of the color centers formed increases as the concentration of BO_2^- ions increases. However, as one can see from Fig. 2a (curves 1 and 2) no changes in the oscillation spectra of BO_2^- ions were revealed after exposure of CsI(Tl) crystals to the ionizing radiation. Lowering of the intensity of

BO_2^- ions' oscillation bands in the spectrum can be observed after illumination of the crystals by daylight which were preliminary colored by ionizing radiation (Fig. 2a, curve 3).

5. Luminescence properties of the activator defects

The number of the main Tl(I) and Tl(II) activator luminescence centers in the lattice is defined by the activator concentration. Tl(I) center is represented by the Tl^+ ion surrounded by the Cs^+ cations [13]. Tl(II) center can be considered as Tl(I) center perturbed by the neighboring Tl^+ ion.

Fig. 3a shows the luminescence of the main activator Tl(I) and Tl(II) centers before and after irradiation of the crystal. It is seen that after coloration of the crystal the luminescence centers of Tl(I) and Tl(II) are distorted by the induced absorption.

In the irradiated crystals there appears an additional luminescence (Fig. 3b). Thus, at excitation in 3.15 eV one can observe luminescence, the spectrum of which consists of two bands with the maxima 2.1 and 1.85 eV. The shape of this band 2.1 eV differs noticeably from the luminescence spectra of Tl(I) and Tl(II) centers.

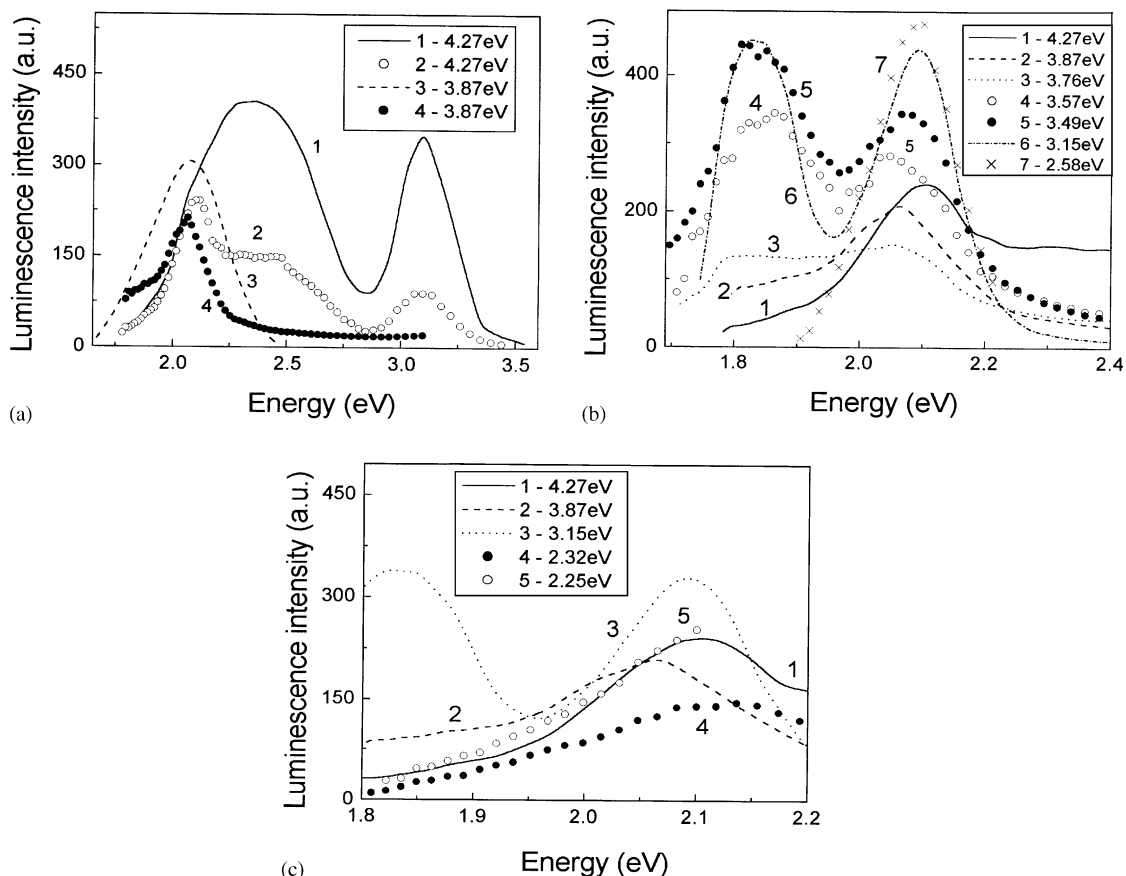


Fig. 3. (a) Emission spectra of the Tl(I) (1,2) and Tl(II) centers (3,4) in CsI(Tl) crystals before (1,3) and after (2,4) irradiation with a dose of 10^4 Gy (4) and 10^6 Gy (2). Concentrations: Tl- 8×10^{-2} mol% (1,2) and 1.2 mol% (3,4); CO_3^{2-} - 5×10^{-4} mol% (1,2) and $< 1 \times 10^{-5}$ mol% (3,4). (b) Emission spectra irradiated CsI(Tl) crystals: $E_{\text{exc}} = 4.27$ eV (1), 3.87 eV (2), 3.76 eV (3), 3.57 eV (4), 3.49 eV (5), 3.15 eV (6), 2.58 eV (7). (c) Emission spectra of irradiated CsI(Tl) crystals: Emission spectra $E_{\text{exc}} = 4.27$ eV (1), 3.87 eV (2), 3.15 eV (3), 2.32 eV (4), 2.25 eV (5). All measurements were carried out at 80 K.

The excitation spectrum of the luminescence 2.1 eV is shown in Fig. 4 (curve 1). In fact, it represents a superposition of the excitation spectra of the main and radiation-induced centers. This is connected with the fact that the luminescence spectrum of the main activator centers is strongly overlapped with the luminescence spectrum of the radiation defects. By the shape of curve 1 given in Fig. 3b it is seen that the luminescence excitation spectrum in the region of 2.27 eV can more adequately correspond to the excitation spectrum of Tl(I) centers (Fig. 4, curve 2). In this case the contribution of Tl(II) and radiation defects is significantly lower.

For the specification of the excitation spectra of radiation defects, the luminescence spectra were measured at excitation by photons of different energies most typical for the absorption spectrum were measured (Fig. 3b). It is seen that the spectral composition of the luminescence depends on the excitation energy. At excitation in the region of 3.76–3.15 eV of the induced by irradiation absorption one can observe the luminescence the spectrum of which consists of bands with the maxima 2.1 and 1.85 eV (Fig. 3b). It should be noted that the emission at 1.85 eV becomes the most intense at excitation in (i) absorption bands except for the lowest energy ones at 2.64 eV (Fig. 4, curve 3). The luminescence with the maxima 2.1 eV of the

radiation defects is excited in any band of (i) group. In the intensive absorption bands of the (ii) group, only weak luminescence was excited (Fig. 4). The bands of the main activator centers were revealed in its spectra.

6. Discussion

According to Nagirnyi et al. [13] the luminescence with the maxima 2.55 and 2.25 eV was caused by the emission of the localized exciton perturbed by Tl^+ . The luminescence 3.09 eV is connected with the electronic transitions between the Tl^+ ion states. As the concentration of Tl^+ increases the edge of the activator absorption is shifted towards the long-wave region and the luminescence of Tl(II) complex activator centers with the maximum 2.1 eV appears [14]. In Ref. [15] the luminescence with the maximum 2.75 eV is related to the electron transition between the states of Tl^+ ion perturbed by the neighboring Tl^+ . By analogy with Tl(I) centers, the luminescence with the maximum 2.1 eV can be attributed to the luminescence of the exciton localized near the Tl(II) center.

In the CsI(Tl) crystals colored by the ionizing radiation or daylight there appears an additional luminescence 2.1 and 1.85 eV. According to Babin et al. [16] a durable irradiation in the absorption bands of Tl(I) centers at 4.2 K can lead to a dissociation of localized near activator excitons with the formation of both the closest $\{\text{Tl}^0, V_{\text{KA}}\}$ pairs and Tl^0 and V_{KA} at different distances from each other. This is accompanied by the appearance of an afterglow. Its spectral composition is typical for the luminescence of the main activator centers.

At excitation of the non-irradiated crystals at room temperature by photons with the energy that corresponds to the long-wave edge of the activator absorption, there appears a durable afterglow, the spectra of which coincided with those of the main activator Tl(II) centers. The intensity of the afterglow rises as the activator concentration becomes higher [17].

The number of activator color centers linearly increases, as the activator concentration becomes higher [10]. The absence of the superlinear

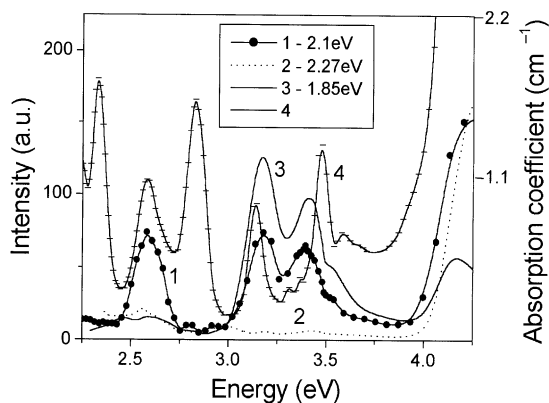


Fig. 4. Excitation (1–3) and absorption spectra (4) of irradiated CsI(Tl) crystal (^{60}Co , 10^6 Gy). $E_{\text{em}} = 2.1$ eV (1), 2.27 eV (2), 1.85 eV (3). Concentrations: $\text{Tl} = 8 \times 10^{-2}$ mol%; $\text{CO}_3^{2-} = 5 \times 10^{-4}$ mol%. All measurements were carried out at 80 K.

dependence indicates that formation of color centers cannot be explained by trapping of electrons by dimers initially existing in crystals. It was supposed in Refs. [3–5] that Tl_2^0 centers are formed in the process of Tl^0 diffusion along anionic or cationic vacancies of impurity–vacancy dipoles including $O^{2-}-V_a^+$. The latter can be formed during doping of crystals with oxygen-containing impurities. However, neither doping of CsI(Tl) with univalent oxygen-containing anions IO_3^- , NO_3^- which decompose with formation of oxygen, nor growth of crystals in oxygen-containing gas atmosphere enhances coloration. Besides, if Tl_2^0 centers are formed due to a diffusion of atoms towards each other, there is a high probability of formation of Tl_2^+ analogously, but not only due to a direct trapping of an electron by thallium dimer.

In the scope of the color center model, according to which the absorption is conditioned by transitions in the thallium atom perturbed by the anionic vacancy ($Tl^0V_a^+$ -center) [1,2] the linear dependence of the number of color centers on content of the activator and origin of some absorption bands can be interpreted.

The electronic configuration of a thallium atom is $[Xe] 4f^{14}5d^{10}6s^26p^1$. The main term is $^2P_{1/2}$. In the isolated atom the following transitions are allowed [18]:

$$6^2P_{1/2} \rightarrow 7^2S_{1/2} \quad (3.28 \text{ eV}),$$

$$6^2P_{3/2} \rightarrow 7^2S_{1/2} \quad (2.31 \text{ eV}).$$

In the color center, Tl^0 perturbed by the field of the neighboring defect due to a deterioration of symmetry, the forbidden between the levels of different multipletness the $^2P_{1/2}$ and $^2P_{3/2}$ transition become allowed and $6^2P_{3/2}$ transition becomes the first excited level [1]. The bands 0.89 and 1.3 eV revealed in CsI(Tl) crystals by the photostimulation method are related just to the transition $6^2P_{1/2} \rightarrow 6^2P_{3/2}$ in the Tl^0 centre perturbed by the V_k [19]. Proceeding from this the long-wave bands 1.48 and 1.27 eV (Fig. 1) can be attributed to the defect $Tl^0V_a^+$.

The bands 2.31 eV in the isolated Tl atom [18] and 2.14 eV in the isolated Tl^0 center in the CsI(Tl) crystal correspond to the transition between terms

$6^2P_{3/2}$ and $7^2S_{1/2}$ [19]. The band at 2.21 eV can be interpret as the transition $6^2P_{3/2} \rightarrow 7^2S_{1/2}$ in the Tl^0 center perturbed by the anionic vacancy. Both the position of the band in the absorption spectrum and a shift of its maximum towards higher energy region 2.23 eV, as the temperature goes down from 295 K to 80 K given evidence to it. The intensive band with the maxima 2.88 and 2.38 eV cannot be attributed to any electron transition in the isolated thallium atom and probably have an exciton origin even though they are related to the $Tl^0V_a^+$ center. This is confirmed by the shift of these bands towards the low energy region 2.83 and 2.33 eV, respectively, as the temperature goes down from 295 K to 80 K.

One of the possible reasons for absorption in the region of 3.44 eV is the transition between the states $6^2P_{1/2}$ and $7^2S_{1/2}$ in the thallium atom perturbed by the anionic vacancy. Due to the thermal motion the electron from the upper excited level $7^2S_{1/2}$ can move to the conduction zone. Thus, the activator defect $Tl^+V_a^+$ is formed corresponding to which are the absorption bands of the exciton origin 3.44, 3.18, 2.64 eV. The close $Tl^+V_a^+$ pairs observed only ion the irradiated crystals.

The defect $Tl^+V_a^+$ can be considered as an α -center (V_a^+) localized near the activator ion. Due to their high mobility at room temperature α -centers are not stable. Anionic and cationic vacancies easily combine forming bivacancies and vacancy clusters [20]. The lowering of mobility of the α -center localized near Tl^+ ion can be explained by mixing of the states into a quasi-molecule which includes close thallium ion and the anionic vacancy surrounded by ions of cesium and iodine. The same way as for Tl^+ ; for Tl(I) the defect $Tl^+V_a^+$ is the nucleus of the luminescence center.

The structure of the $Tl^+V_a^+$ defect is such that the localized near it excitons can differ in the electron and hole components. The electron component of the near-activator exciton of one type can be connected with the excited 6p state of the Tl^+ ion perturbed by the anionic vacancy. In this case the hole component is V_k center. In the near-activator exciton of the second type the hole component is localized near Tl^+ (V_{kA} center), the

electron component is distributed between the excited 6s state of the Cs⁺ ions which create an effective positive charge of the anionic vacancy. This can explain the presence of two bands in the luminescence spectrum connected with $Tl^+V_a^+$ defect.

The role of the impurity BO_2^- ions in the process of radiation-chemical coloration of crystals CsI(Tl) cannot supposed comprehensible. Despite the fact that there is a direct dependence of the content of borate on the color centers' formation under the effect of radiation, no changes in the oscillation spectrum of BO_2^- ions after coloration of the crystal by the ionizing radiation were revealed. However, further illumination of CsI(Tl) by photons with the energy 3.44 eV resulted in the decrease of the bands' intensity in the oscillation spectrum of the borate. The number of the formed $Tl^0V_a^+$ centers increased with rise in the concentration of BO_2^- ions and transformation of $Tl^0V_a^+$ into $Tl^+V_a^+$ centers after additional UV illumination has accompanied by decomposition of the borates. All this indicated the possibility of participation of BO_2^- ion in the radiation-chemical transformations with the formation of the defects under irradiation. However, for the elucidation of mechanism of these transformations additional investigations are necessary.

Conclusions

The absorption spectrum of the colored CsI(Tl) crystals can be considered as a superposition of bands responsible for both: transitions between the states of the exciton localized near the radiation defect as well as near the color center and for those between the states of the valent electron in Tl^0 perturbed by the anionic vacancy. The ionized color center is the luminescence center, which is responsible for the radiation damage luminescence in the investigated region 1.77–3.76 eV. The appearance of the main activator centers' luminescence under excitation in the region of the induced by irradiation absorption of 1.77–3.76 eV due to delocalization of the excitons and subsequent formation of both the closest $\{Tl^0,$

$V_{k\} \}$ pairs and Tl^0 and V_{kA} at different distances from each other.

Acknowledgements

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References

- [1] E. Goovaerts, J. Andriessen, S.V. Nistor, D. Schoemaker, *Phys. Rev. B* 24 (1980) 29.
- [2] L.F. Mollenaer, N.D. Vieira, L. Szeto, *Phys. Rev. B* 27 (1982) 5332.
- [3] A.K. Mednikov, V.I. Shtan'ko, *Proceedings of the Conference on Technology, Processes, Instruments and Quality of Industrial Luminophores*, Stavropol, 1978, p. 61 (in Russian).
- [4] L.P. Smol'skaja, T.A. Kolesnikova, V.N. Salomatov, L.V. Kovaleva, L.L. Nagornaja, *Single crystals and scintillators, their production and property*, vol. 8, monokristallov, Kharkov, Ukraine, 1979, p. 11 (in Russian).
- [5] L.P. Smol'skaja, T.A. Kolesnikova, *Iz. Akad. Nauk SSSR, Ser. Fiz.* 50 (1986) 547.
- [6] L.N. Shpilinskaja, B.G. Zaslavsky, L.V. Kovaleva, S.I. Vasetsky, A.M. Kudin, A.I. Mitichkin, T.A. Charkina, *Semicond. Phys. Quantum Electron. Optoelectron.* 3 (2000) 178.
- [7] L.N. Shpilinskaja, D.IZ osim, L.V. Kovaleva, A.M. Kudin, A.I. Mitichkin, T.A. Charkina, *Proceedings of fifth International Conference on Inorganic Scintillators and Their Applications*, Moscow, 1999, p. 538.
- [8] B.G. Zaslavsky, V.S. Suzdal, A.M. Kudin, S.I. Vasetsky, L.N. Shpilinskaja, T.A. Charkina, J.A. Nesterenko, A.I. Mitichkin, L.V. Kovaleva, V.N. Zviagintsev, *Proceedings of Fifth International Conference on Inorganic Scintillators*, Moscow, 1999, p. 663.
- [9] B.V. Grinev, L.N. Shpilinskaja, A.M. Kudin, L.V. Kovaleva, A.I. Mitichkin, T.A. Charkina, *Opt. Spectrosc.* 89 (2000) 50.
- [10] L.N. Trefilova, A.M. Kudin, L.V. Kovaleva, T.A. Charkina, A.I. Mitichkin, L.E. Belenko, *Radiat. Meas.* 33 (2001) 687.
- [11] C. Hisatsune, N. Haddock Soares, *Inorg. Chem.* 3 (1964) 168.
- [12] D.F. Smith, *Spectrochim. Acta* 32 (1976) 319.
- [13] V. Nagirnyi, A. Stolovich, S. Zazubovich, V. Zepelin, E. Mihokova, M. Nikl, G.P. Pazzi, L. Salvini, *J. Phys.: Condens. Matter* 7 (1995) 3637.
- [14] L.P. Smol'skaja, T.A. Kolesnikova, *Iz. Akad. Nauk SSSR Ser. Fiz.* 41 (1977) 1409.
- [15] V. Babin, A. Krasnikov, S. Zazubovich, H. Wiczorek, *J. Lumin.* 96 (2002) 75; V. Babin, A. Krosnikov,

- S. Zazubarich, H. Wieczorek, Abstracts of Sixth International Conference on Inorganic Scintillators, Chamonix, 2001, SM-P-30.
- [16] V. Babin, K. Kalderr, A. Krasnikov, S. Zazubovich, *J. Lumin.* 96 (2002) 75.
- [17] Z.L. Morgenshtern, I.P. Schukin, *Opt. Spectrosc.* 1 (2) (1956) 190.
- [18] El'jashevicz, *Atomic and Molecular Spectroscopy*, Phys-Math Lit., Moscow, 1962 p. 304 (in Russian).
- [19] S.A. Chernov, L. Trinkler, A.I. Popov, *Radiat. Eff. Def. Solids* 143 (1998) 345.
- [20] A. Gektin, N. Shiran, V. Serebrjanny, T. Charkina, A. Kudin, *Opt. Spectrosc.* 72 (5) (1992).