Full Length Article

Time-resolved spectroscopy of CsI(CO₃) scintillator

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ABSTRACT

The spectral-kinetics characteristics of short-living absorption and luminescence induced by an electron pulse irradiation ($E_e = 0.25$ MeV, $t_{1/2} = 7$ ns, $W = 2 \times 10^{10} \div 4 \times 10^{12}$ electron/cm^2) in CsI(CO$_3$) crystal are studied. It is shown that the scintillation pulse of CsI(CO$_3$) crystal is caused by the radiative annihilation of perturbed two-halogen excitons of two types, which are located in nearby impurity-vacancy dipole [CO$_3^{2-} - \upsilon_a^+$] anion sites. The processes responsible for post-radiation rise and decay of both CO$_3^{2-}$-related luminescence bands with maxima at 2.8 and 3.2 eV are monomolecular with the thermal activation energy $E_{rise} = 0.1$ eV and $E_{decay} = 0.05$ eV. The cathodoluminescence pulse kinetics is discussed in the terms of the thermally assistant release of holes captured by CO$_3^{2-}$-ions and the formation of CO$_3^{2-}$-perturbed two-halide excitons.

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1. Introduction

CsI(CO$_3$) crystal is an inexpensive bright scintillation material capable of detecting ionizing radiation in a wide energy range [1–4]. CO$_3^{2-}$ activator ions do not cause any absorption bands in the near UV and visible spectral regions and their vibration absorption bands overlap the peak intensity spectral region of Planck's broadband radiation of a platinum crucible and CsI melt. This overlapping provides a better heat removal from the crystallization front during growing CsI(CO$_3$) crystal, which greatly facilitates and accelerates the production of large-size CsI(CO$_3$) boules as compared with the conventional CsI(Tl) and CsI(Na) ones [5].

Both crystals CsI(CO$_3$) and CsI(Na) have the same luminescence spectra peaking at 3 eV, but two types of the centers cause the luminescence in CsI(CO$_3$) [6], whereas only one type of the centers gives rise to the luminescence in CsI(Na) [7]. Although CsI(CO$_3$) crystals have been commercially available for a long time, the mechanism of the radio-luminescence pulse formation in these crystals have not been understood yet.

This paper deals with the spectral-kinetics properties of the luminescence and short-living absorption centers originated by electron pulse irradiation in CsI(CO$_3$) crystal. Based on the experimental results obtained by time-resolved spectroscopy we explained the mechanism of the activator luminescence in CsI(CO$_3$) crystal.

2. Experiment

CsI(CO$_3$) crystal were grown by seeding in an argon atmosphere. Cs$_2$CO$_3$ salt was used as an activator. The concentration of the activator was determined optically as it was described elsewhere [8]. The studied CsI(CO$_3$) sample containing 8.3×10^{-3} mol% CO$_3^{2-}$ ions was cut out in the form of a rectangular plate with the dimensions of $8 \times 8 \times 2$ mm^3. The luminescence and transient adsorption were excited with a pulsed electron beam generated by GIN-600 electron accelerator. The beam had the following parameters: average electron energy $E_e = 0.25$ MeV, pulse duration $t_{1/2} = 7$ ns, power density can be varied within $2 \times 10^{10} \div 4 \times 10^{12}$ electron/cm^2. The luminescence and transparency restoration after the electron pulse depletion were registered with an optical spectrometer consisting of an MDR-3 monochromator, FEU-83 and FEU-84-6 photomultipliers and LeCroy digital oscilloscope. Two oscillogram families for cathodoluminescence pulses and for transparency restoration were obtained for a certain wavelength within 250–1100 nm at a certain temperature within 80–300 K. Then the oscillogram families were converted into the kinetics curve families for luminescence and optical density in order to plot the spectra of luminescence and absorption at any time delay with a 7 ns resolution. A lamp INP-5 $\times$ 75 emitting bell-shape pulses with FWHM = 300 μs was used as a source of the probe light.

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3. Experimental results

3.1. Luminescence

CsI(CO$_3$) crystal responds with a bright pulse of blue light to irradiation with an electron pulse. An oscillogram of the cathodoluminescence pulse registed at room temperature is shown in Fig. 1. It was observed that the cathodoluminescence pulse of CsI(CO$_3$) crystal has a well pronounced rise stage (an insert in Fig. 1) and its duration is much longer than that of the irradiation pulse. The intensity of cathodoluminescence peaks at about 500 ns and then exponentially decays with time constant 1.7 μs. The following expression fits well the experimental curve:

$$I(t) = I_{max} \cdot (1 - e^{-t/\tau_{rise}}) \cdot e^{t/\tau_{decay}} \tag{1}$$

where I_{max}-peak intensity, τ_{rise}-rise time constant, τ_{decay} –decay time constant.

The values of these constants are independent of the electron beam density in the range from 2×10^{10} to 1×10^{12} electron/cm^2.

The spectrum of cathodoluminescence pulse is a broad asymmetrical band, ranging from 2.2 to 3.8 eV with a maximum at about 3.0 eV (Fig. 2). The sum of two Gaussians with maxima at 2.8 and 3.2 eV and their half-widths (FWHM) equal at about 0.5 eV (dash lines in Fig. 2) fits the spectrum. This tallies with the results of authors [6] who found that the luminescence spectrum registered under a steady-state γ-excitation of CsI(CO$_3$) crystal consists of two bands peaking at 2.85 and 3.15 eV. Note, that kinetics parameters of the rise and decay of the cathodoluminescence pulse are the same for the both bands and therefore the normalized oscillograms of the cathodoluminescence registered at different wavelength throughout the spectrum matched after normalization.

It was found, that the time constants of the kinetics Eq. (1) greatly depend on the irradiation temperature of the sample. Lowering the temperature from 295 to 170К slows down the rise
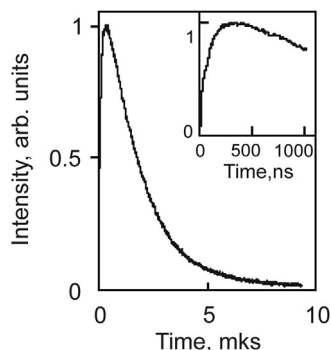
and decay of cathodoluminescence pulse intensity, as the oscillogram family registed at various temperatures demonstrates in Fig. 3. The temperature dependences of the rise and decay time constants are shown in Arrhenius coordinates in Fig. 4. The energy of thermal activation E_a, estimated by the slope $\tau_{rise}(1/T)$ and $\tau_{decay}(1/T)$ dependences amounts to 0.1 eV and 0.05 eV, respectively.

3.2. Short-living optical absorption

It was found that the pulse irradiation colors the crystal with high efficiency. The spectrum of the induced absorption stretches from 1.0 to 2.5 eV; the long-wave part of the spectrum fits a Gaussian with maximum at $E_{max} = 1.45$ eV and half-width FWHM $= 0.5$ eV (Fig. 5).

With respect to spectral parameters this band closely matches the absorption band of F centers in CsI crystal [9]. The optical

Fig. 3. Oscillograms of CsI(CO$_3$) cathodoluminescence recorded at 3 eV under 295 K (1), 225 K (2) and 170 К (3).

Fig. 4. Kinetics parameters of CsI(CO^3) cathodoluminescence pulse at 3 eV vs. reciprocal temperature: 1-rise time constant τ_{rise}, 2-decay time constant τ_{decay}.

Fig. 1. Cathodoluminescence oscillogram of CsI(CO$_3$) crystal at $T = 295$ К.
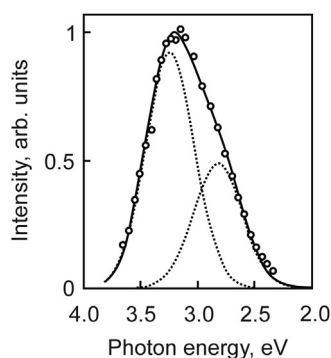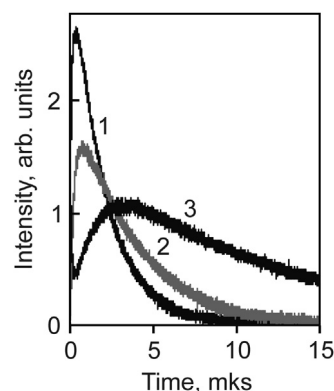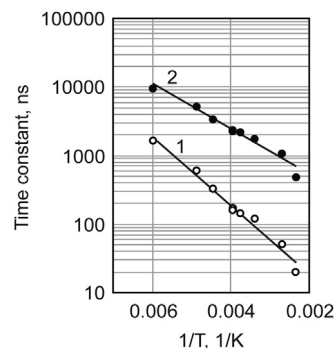

Fig. 2. Cathodoluminescence spectrum of CsI(CO$_3$) measured at 295 К with delay $t = 400$ ns after the irradiation pulse depletion. Dots - experimental data; dash lines – fitting curves; solid lines – the sum of fitting curves.
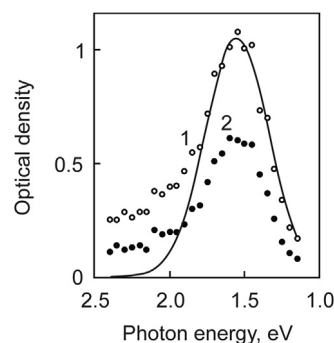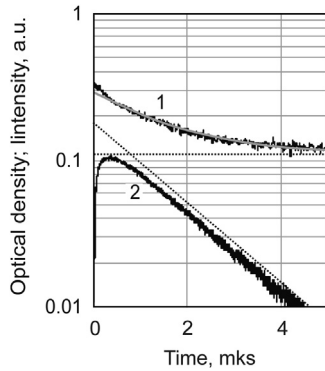

Fig. 5. Short-living absorption spectra of CsI(CO$_3$) crystal measured at $T = 295$ К with 250 ns (1) and 1.5 mks (2) delay after the irradiation pulse depletion. The fitting curve for the long-wave part of the spectrum is shown in the solid line.

Fig. 6. Oscillograms of optical density at 1.45 эВ (1) and cathodoluminescence at 3 eV (2) for CsI(CO₃) crystal at $T=295$ К. The fitting curves for optical density decay curve are calculated according to (2) expression. Dash lines – the exponential and hyperbolic components, the solid line – the sum of the components.

density decay curve after the irradiation pulse depletion is shown in semi-logarithmic scale in Fig. 6 (curve 1). The optical density decay curve fits the sum of exponential and hyperbolical components:

$$D(t) = D_1 \cdot \exp(-t/\tau_{abs}) + D_2 \cdot (1 + \alpha \cdot t)^{-1} \tag{2}$$

where τ_{abs} and α are time constants exponential and hyperbolic absorption decay component, respectively. The fitting curve obtained by the expression (2) is shown in Fig. 6 in solid line.

As one can see in Fig. 6, the decay time constants of both: the optical density exponential component at 1.45 eV (the fitting curve in dashed line) and the activator luminescence pulse at 3 eV (the oscillogram in broken line) match $\tau_{abs} = \tau_{lum}$.

4. Discussion

Studying the effect of thermal treatment on vibrational absorption and luminescence of CsI(CO₃) crystals authors [6] concluded that at least one of the two activator luminescence bands is caused by impurity-vacancy complexes $[CO_3^{2-} - \upsilon_a^{+}]$, where an anion substituting CO_3^{2-} ion and an charge-compensating iodine vacancy occupy neighboring anion sites.

The below stated regularities observed in this research significantly facilitate understanding the luminescence processes in these crystals.

- The time constants of exponential rise and decay kinetics of luminescence after the irradiation pulse depletion do not depend on the density of electron beam (i.e. on concentration of band charge carriers caused by a single pulse). It means that that both the processes responsible for the rise and decay of activator luminescence are monomolecular.
- The matching values of the exponential decay time constants for F-band absorption and 3 eV band of luminescence show that there is a direct correlation between process of F center disintegration and the process formation of the activator luminescence pulse.
- The presence of two close bands with the same values of FWHM and the time constants of the rise and decay stages indicates that luminescence centers responsible for these bands are formed and disintegrated by the same mechanisms.

It is known that the luminescence pulses in CsI(Tl) and CsI(Na) crystals is formed by the recombination of thermally released charge carriers with the recombination centers which can be electron color centers (Na⁰ in CsI(Na) [7]) as well as hole color centers (V_{kA} in CsI(Tl) [10]). The regularities for CsI(CO₃) crystal

can be described in the scope of following model. The band charge carriers arising under irradiation are captured by $[CO_3^{2-} - \upsilon_a^{+}]$ complexes, which due to recharge transform to $[CO_3^{-} - \upsilon_a^{+}e^{-}]$ complexes consisting of singly charged CO_3^{-} radical and $(\upsilon_a^{+}e^{-})$ electron color center known as F center:

$$[CO_3^{2-} - \upsilon_a^{+}] + \ldots + e^{-} + \ldots + h^{+} \rightarrow [CO_3^{-} - \upsilon_a^{+}e^{-}] \tag{3}$$

At low temperatures, when both F centers and CO_3^{-} ions are thermally stable, the system can relax into an equilibrium state due to electron tunneling from F centers to CO_3^{-} ions:

$$[CO_3^{-} - \upsilon_a^{+}e^{-}] \xrightarrow{\text{tunneling}} [CO_3^{2-} - \upsilon_a^{+}] \tag{4}$$
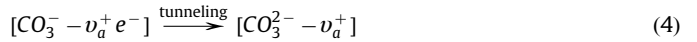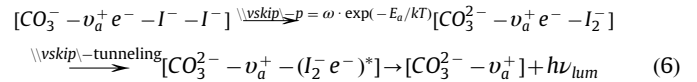
According to [11], the probability of the electron tunnel transition from donor to acceptor is determined by overlapping both the electron and hole wave functions and exponentially decays with increasing distance:

$$p = \tau^{-1} \sim \exp(-r/a_B) \tag{5}$$

where a_B is the half Bohr radius of a charge carrier.

The distance between the donor and acceptor are the same in all $[CO_3^{-} - \upsilon_a^{+}e^{-}]$ complexes and equals the lattice parameter ($r=a$), therefore, according to (6) the disintegration of F centers with time occurs by monoexponential law. We think that the tunnel recharge process (4) is non-radiative, for at once after the irradiation pulse depletion the F-band intensity is maximal whereas luminescence intensity is minimal (Fig. 6).

The components in $[CO_3^{-} - \upsilon_a^{+}e^{-}]$ complex are likely to thermally dissociate at higher temperatures. We believe that it is the thermal release of hole from CO_3^{-} ion that causes the rise stage in the luminescence kinetics and the two bands in the luminescence spectrum. The released hole localizes on iodine ion in anion site nearby F center as V_k center with I_2^{-} structure, forming donor-acceptor pair $[F, V_k]$. When electron tunnel from F to V_k center perturbed two-halide exition $(I_2^{-}e^{-})^{*}$ arises, and its annihilation results in luminescence:

$$[CO_3^{-} - \upsilon_a^{+}e^{-} - I^{-} - I^{-}] \xrightarrow{p = \omega \cdot \exp(-E_a/kT)} [CO_3^{2-} - \upsilon_a^{+}e^{-} - I_2^{-}]$$
$$\xrightarrow{\text{tunneling}} [CO_3^{2-} - \upsilon_a^{+} - (I_2^{-}e^{-})^{*}] \rightarrow [CO_3^{2-} - \upsilon_a^{+}] + h\nu_{lum} \tag{6}$$

where ω-frequency factor; E_a-hole thermal releasing activation energy determined by the slope $\tau_{rise}(1/T)$ dependence (Fig. 4) amounts to 0.1 eV.

A lattice fragment with possible locations of V_k centers against F center in the complex is shown in Fig. 7. One can see that when F-electrons tunnel to free levels of V_k center, two-halide exitons $(I_2^{-}e^{-})^{*}$ of two types are likely to arise nonequivalent in relation to carbonate ions: in the centers of type I (1, 2 position in Fig. 7) this distance equals the lattice constant a; in the centers of type II (3, 4 position in Fig. 7) – $a\sqrt{2}$. It is obvious that the perturbation degree of these two type excitons by negatively charged carbonate ions is different. The origin of the two bands with almost the same
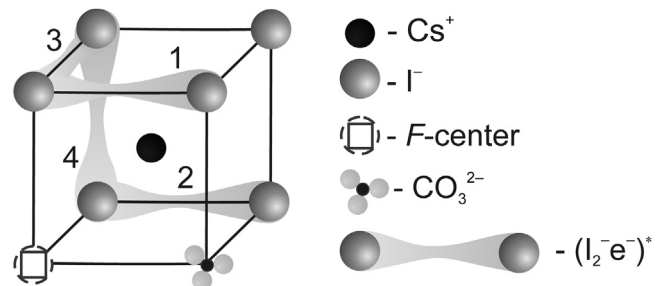
Fig. 7. A fragment of CsI crystal lattice in the vicinity of the impurity-vacancy dipole $[CO_3^{2-} - \upsilon_a^{+}]$.

spectral parameters in the luminescence spectrum appears to be caused by this difference.

5. Conclusion

The above results can be summarized briefly as follows. Radioluminescence of CsI(CO_3) crystal is caused by radiative annihilation of the perturbed two-halogen excitons of two types, which are located in nearby impurity-vacancy dipole $[CO_3^{2-} - \upsilon_a^+]$ anion sites. The excitons arise due to electron tunneling from F to V_k centers originated by thermal liberation of holes captured by CO_3^{2-} ions under irradiation. The formation process of CO_3^{2-}-perturbed excitons is responsible for post-radiation rise of the luminescence pulse and the tunnel recombination in the short-interspace donor-acceptor pairs $[F,V_k]$ causes the exponential decay of the luminescence pulse.

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