On luminescence kinetics of scintillators used in X-ray introscopy systems

V.Ryzhikov, N.Starzhinskiy, V.Seminozhenko, B.Grinyov,
L.Nagornaya, V.Spasov, K.Katrunov, I.Zenya, O.Vyagin

Scientific and Technologycal Corporation "Institute for Single Crystals",
National Academy of Sciences of Ukraine,
60 Lenin Ave., 61001 Kharkiv, Ukraine

Data are presented on the influence of various factors upon luminescence kinetics of scintillator crystals based on activated ZnSe, CsI, CWO and GSO. It is shown that the isovalent dopant type substantially affects the decay times τ and afterglow level of ZnSe-based scintillators, and the value of τ, depending upon the dopant concentration, can vary from 1 to 150 μs. It has been determined that scintillation kinetics of ZnSe(Te) crystals has peculiar features, being characterized by a non-monotonous decrease with a region of rising luminescence intensity at the initial stage after stopping the irradiation of samples. Mechanism of energy transfer has been considered for this case. Decay times of oxide scintillators (CWO, GSO) is essentially dependent both on non-stoichiometry of their composition and on the presence of admixtures. It has been shown that the afterglow level of CsI- and CWO-based scintillators depends both on the dose of preliminary X-ray irradiation and on the density of defects introduced into the crystal mechanically. The role of X-ray irradiation and finishing thermal treatment has been considered for optimization of luminescence kinetics properties of scintillation elements.

Приводятся данные о влиянии различных факторов на кинетику люминесценции кристаллов-сцинтилляторов на основе активированных кристаллов ZnSe, CsI, CWO и GSO. Показано, что тип изовалентной примеси оказывает существенное влияние на времена высвечивания τ сцинтилляторов на основе ZnSe, и эта величина в зависимости от концентрации примеси может составлять 1–150 мкс. Определено, что кинетика высвечивания кристаллов ZnSe(Te) имеет особенности и характеризуется немонотонным спадом с наличием участка возрастания интенсивности люминесценции на начальном этапе после прекращения облучения образцов. Рассмотрен механизм энергопереноса данного явления. Инерционность оксидных сцинтилляторов (CWO, GSO) существенно зависит как от нестехиометричности состава, так и наличия неконтролируемых примесей. Показано, что уровень послесвечения сцинтилляторов на основе CsI и CWO зависит как от дозы предварительного рентгеновского облучения, так и от концентрации дефектов, введенных в кристалл механическим способом. Изучена роль финишной термообработки в оптимизации инерционных свойств сцинтилляционных элементов.

Among the main characteristics of scintillation crystals, alongside the light output, are kinetic parameters of luminescence — the decay time τ and, in particular, the afterglow level η. Just a very small group of scintillators, as for the whole complex of their main parameters — light output, τ and η — can be actually used in X-ray introscopy. Even these not numerous scintillators based on CsI, CdWO4 (CWO), Gd_2SiO_5 (GSO) often fail to provide the required performance in modern X-ray introscopy systems (XS) dealing with moving objects in the real time scale [1]. ZnSe(Te) scintillator
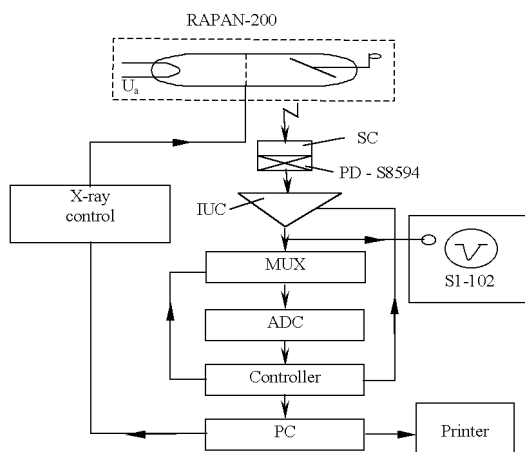
Fig. 1. Block diagram of the measuring-computing complex for measurement of the afterglow level in scintillators.

is already used in XS due to its unique properties. Rather long decay times, however, has remained its drawback [2]. Our studies of the effects of dopants upon luminescence kinetics of scintillators were aimed at broadening their field of applications. We have also considered effects of mechanical treatment and pre-irradiation upon time characteristics of various types of scintillators used in XS.

Scintillator crystals used in our experiments included: CsI(Tl); CWO (undoped and doped with Bi); ZnSe, activated with isovalent dopants (IVD) O, Te, Cd, Hg; GSO doped with Ce. The dopant concentration ranged from 0.1 to 0.5 % mol. The crystals for studies were grown by known methods [1, 3–5]. Measurements of the light output and the afterglow level η (%) after a specified time were carried out using a measuring-calculating complex for studies of kinetic characteristics (MCCKC), its block diagram is presented in Fig. 1. MCCKC has been designed for measurements of afterglow intensity and automatic procession of the obtained data with determination of the amplitude-time parameters. The complex included a pulse X-ray emitter of RAPAN-200 type ($E_x = 100{-}160$ keV), a Hamamatsu S8594 photodiode, a "current to voltage" converter (IUC), a multiplexor (MUX), an analog-to-digit converter (ADC), a personal computer (PC), a S1-102 oscilloscope and a control block for the X-ray emitter (BCX).

Measurements of the afterglow level in scintillator crystals were carried out according to the amplitude-time diagram as shown in Fig. 2.
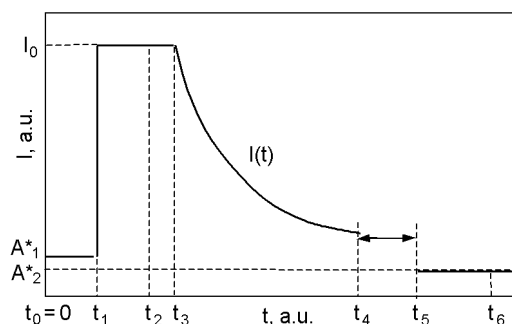

Fig. 2. Amplitude-time operation diagram of MCCKC in measurements of the afterglow level of scintillators ($t_0 - t_1$, $t_5 - t_6$ — measurement time of "substitutions" A_1^* and A_2^* IUC, $t_2 - t_3 = I_0$, $t_3 - t_4 = I(t)$, and $t_4 - t_5$ is pause).

The value of $\eta(t)$ at an arbitrary moment of time is defined as

$$\eta(t) = [I(t) - A_2^*]/[I_0 - A_1^*] \cdot 100\%, \quad (1)$$

where I_0 is the averaged signal amplitude from the irradiated sample over 256 ADC countings, $I(t)$ is the signal of the scintillator afterglow, A_1^*, A_2^* — voltage fluctuations at the output of the IUC preamplifier before and after irradiation, respectively. Experimental $I(t)$ data arrays are a function of readings with an arbitrary scale t_n, where $n = 1, 2..., N$, approximated by exponentially decreasing function of the form

$$f(t) = x_1 e^{-y_1 1^t} + x_2 e^{-y_2 2^t} + \ldots$$
$$+ x_n e^{-y_n n^t}; \quad y > 0. \quad (2)$$

Approximation parameters x_i, y_i are determined by the least squares method, i.e. by minimization of the functional

$$\Phi = \sum_{n=1}^{N} [f(t_n) - g_n]^2, \quad (3)$$

where g_n is the experimental data.

A system of normal equations obtained as a result of minimization appears to be non-linear and can be solved only numerically, by iterations. As the initial functional is not convex everywhere, and the region of the global minimum is of the ravine character, we used the quasi-Newton procedure of Broyden, Fletcher, Goldfarb and Chanot with full upper relaxation [5] as iteration method. The use of MCCKC and appropriate software for data processing allowed determination of amplitudes and decay time constants, which gave information on physics of the processes determining
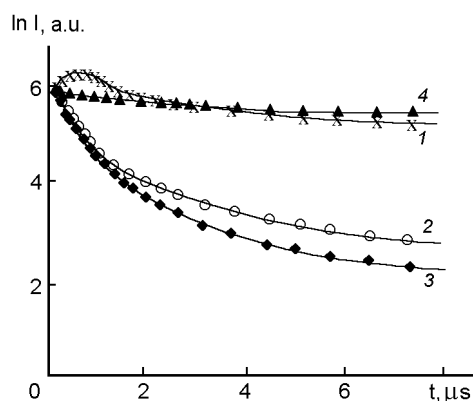
Fig. 3. Luminescence decay kinetics of doped ZnSe(Te) crystals: ZnSe(Te) (*1*), ZnSe(Cd) (*2*), ZnSe(Hg) (*3*), ZnSe(Te,Zn) (*4*) at T = 300 K.

the afterglow mechanism, as well as on relative values of the scintillator light output and X-ray sensitivity of the detectors.

Decay times of scintillator crystals were measured by oscilloscopic method using an installation comprising a MIRA-2D X-ray emitter (τ_x = 10 ns, E_x = 160 keV), the scintillator under study, a collimator, a light transducer, an S1-102 oscilloscope, and a FEU-30 PMT. For studies of the effects of preliminary irradiation upon luminescence kinetics, an IRI X-ray source was used (U_a = 150 kV, i_a = 0.1–5 mA). Mechanical defects were introduced into samples by their grinding or deformation up to destruction threshold.

Depending upon the activating dopant type, changes in X-ray luminescence kinetics are observed for all the scintillators studied. In the case of oxide scintillators CWO, BGO, variations of the dopant composition (introduction of Bi, Tb) mainly affect the values of η. For ZnSe-based scintillator crystals, the type of the activator dopant can substantially affect both decay times and the afterglow level. For ZnSe(Te) crystals, kinetics of X-ray luminescence decay is described by a non-monotonous dependence with a region of rise at the initial time moment after ending the sample irradiation (Fig. 3).

Accounting for the fact that in ZnSe(Te) concentration of the free electrons n_0 is, though sufficiently high ($\approx 5 \cdot 10^{17}$ cm^{-3}), by an order of magnitude lower than in ZnSe with cationic dopants Cd and Hg, let us consider a simple scheme of electronic transitions with one recombination level (E_a). The corresponding kinetic equations will have the following form

$$dp/dt = g - C_p\,p(N - p_a), \qquad (4)$$

$$dp_a/dt = C_p\,p(N - p_a) - C_n\,np_a. \qquad (5)$$

Here g is the rate of electron-hole pair generation under inter-zone excitation, p — concentration of non-equilibrium free holes on the valence zone, p_a — concentration of non-equilibrium holes localized on recombination centers, $C_{p,n}$ — capture coefficients of holes and electrons, respectively, on the admixture center, τ_p — hole capture time on the recombination center, τ_n — recombination time of a free electron with a free hole, N — concentration of the capture-recombination centers. The luminescence intensity is $I_{XL} = C_n np_a$, and $g = (N - p_a)I_{XL}$.

Under conditions of $p_a \ll N$ inequality, solution of system (4)–(5) gives

$$p_a(t) = \left\{ \left[p_\infty / (\tau_p/\tau_n - 1) \right] \cdot \exp(-t/\tau_p) \right\}$$

$$+ \left[(p_a)_\infty - p_\infty / (\tau_p/\tau_n - 1) \right] \cdot \exp(-t/\tau_n), \quad (6)$$

where p_∞, $(p_a)_\infty$ are stationary (initial) concentrations of free and localized non-equilibrium holes, respectively; $\tau_n = 1/nC_n$, $\tau_p = 1/C_pN$.

As seen from (6), the law of the luminescence decay in the general case is not exponential. Let us consider two specific cases. For the case $\tau_p \ll \tau_n$, we have $p_a(t) \sim \exp(t/\tau_n)$, i.e., X-ray luminescence kinetics is determined by the free electron concentration, and for crystals ZnSe(Cd) and ZnSe(Hg) it will be described by a dependence close to exponential (Fig. 3, plots 2, 3), which is characteristic for "fast" centers of radiative recombination of $\{Zn_iV_{Zn}Cd_{Zn}\}$ and $\{Zn_iV_{Zn}Hg_{Zn}\}$ type. At $\tau_p \gg \tau_n$, the first term of the right-hand side of (6) would be predominant, i.e., the luminescence decay time would be determined by the concentration of recombination centers.

As in the case of ZnSe(Te) the tellurium atoms included into radiative recombination centers $\{Zn_iV_{Zn}Te_{Se}\}$ [1, 4] can play the role of isoelectron traps [6], it can be assumed that large values of τ_p, non-monotonous and delayed character of the X-ray luminescence (Fig. 3, plot 1) are due to an initial partial capture of non-equilibrium holes on Te atoms with their subsequent transition to V_{Zn} and further radiative recombination with free electrons according to the scheme presented in Fig. 4.
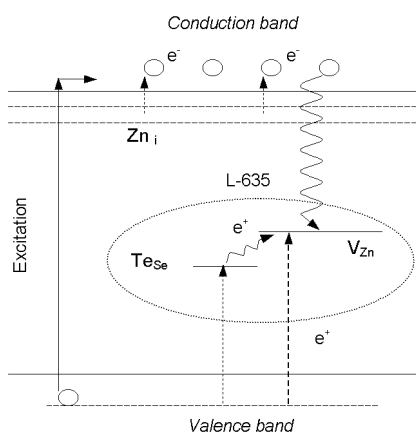
Fig. 4. Scheme of non-radiative and radiative transitions in ZnSe(Te) crystals.

Fig. 5. Changes in the afterglow level η after 20 ms in scintillator crystals at different doses of preliminary X-ray irradiation: CsI(Tl)–M (*1*), CWO(Bi) (*2*), CsI(Tl) (*3*), CWO (*4*).

Very large values of kinetic constants τ and η for ZnSe(Te,Zn) crystals can be explained as follows. When extra Zn is introduced into the initial raw charge ZnSe–ZnTe, this over-stoichiometric component can, under growth conditions of temperatures up to 1900 K and pressures of tens of atmospheres, either enter the crystal lattice, filling the vacancies in the cation sublattice sites and hindering formation of $V_{Zn}Te_{Se}$ complexes, or cause generation of vacancies in the anion sublattice V_{Se} (and interstitial Se_i), forming deep levels with $E_a = 0.3-0.45$ eV in the band gap [7] serving as charge carrier traps.

Various kinds of mechanical treatment (grinding, deformation, etc.) or other factors similar in their consequences for the crystal lattice (thermal or radiation shock, etc.) can also change the X-ray lumines-
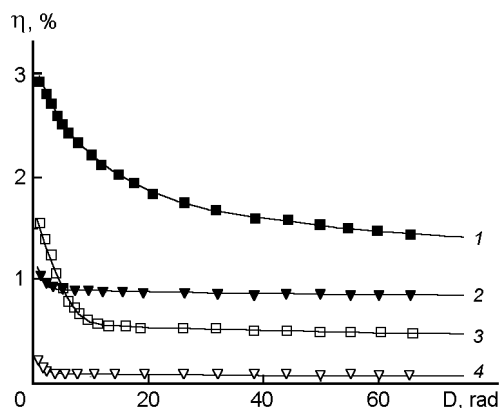
cence kinetics. Experiments have shown that, to smaller or larger degree, for all crystals studied the afterglow level η is increased proportionally to the depth of the affected surface layer or to the plastic deformation value. These factors are the most important with CWO- and CsI-based scintillators. With CsI(Tl) crystals, it is possible to nearly double the η value by plastic deformation, which is shown in Fig. 3, plots 1, 3 (see η values at $D = 0$; notation CsI(Tl)–M corresponds to a sample after mechanical treatment). The presence of such effects can be explained by a mechanostimulated increase in concentration of point and extended defects that affect the energy level structure in the band gap and play the role of traps for charge carriers causing secondary processes of capture-release-radiative

Table. Kinetic characteristics of luminescence in scintillator crystals based on ZnSe, CsI, CWO and GSO

Crystal	τ, μs	η, % (after ms)		
		5	10	20
ZnSe(Te)	50–120	2.009	0.073	0.027
ZnSe(Te,Zn)	>200	38	31	27
ZnSe(Cd)	2–8	0.018	0.012	0.011
ZnSe(Hg)	3–10	0.064	0.035	0.021
CWO	10–15	0.03	0.014	0.011
CWO(Bi)	10–20	0.34	0.076	0.037
CsI(Tl)	0.4	3.983	2.511	1.259
CsI(Na)	0.4	3.34	2.73	2.16
GSO(Ce)	0.03	0.032	0.020	0.019
GSO(Ce,Tb)	0.05	6.9	0.55	0.14

recombination and, as a consequence, increased afterglow values.

It is known that kinetic characteristics of scintillators can be improved not only by the correct choice of dopants, but also by applying thermal or radiation annealing in optimized conditions. Thus, for scintillator crystals on the basis of zinc selenide, an effective way is annealing in Zn vapor [1, 4]. The afterglow level η of CWO and GSO crystals after annealing in an oxygen-containing atmosphere at $T = 0.7T_M$ falls by nearly two times (it should be noted, however, that similar thermal treatment of CWO(Bi) and CsI(Tl) crystals leads to a noticeable — by 30–100 % — increase in η. Small doses of X-ray radiation ($D \leq 100$ rad) at $E_x < 100$ kV lead to increases in time characteristics of nearly all scintillator crystals under study, which is especially characteristic for oxide and alkali-halide scintillators (Fig. 5). Similar effects after radiation annealing of the defects are observed in ZnSe(Te) and ZnSe(Te,O) crystals, when low-energy neutrons are used [8]. It is natural that at high D values and high energies of the exciting radiation, when the defect formation and accumulation processes are predominant, worsening of time characteristics is more probable, as well as a decrease in light output.

Thus, the luminescence kinetics (parameter η) of zinc selenide-based scintillators can be controlled within 1–2 orders of magnitude by introduction of various cation (Cd, Hg) or anion (O, Te) dopants. The afterglow level and radiation stability of oxide scintillators of undoped crystals (CWO, GSO) is essentially dependent upon the dopant composition and the post-growth annealing conditions. In fabrication of scintillation elements on the basis of al-kali-halide crystals, one should account for noticeable effects of mechanically introduced structural defects upon the decay time, which can be avoided by a finishing thermal treatment of the scintillator crystals. When alkali halide crystals and oxide scintillators are used in X-ray introscopy systems, changes in the parameter η at the initial stage of irradiation should be taken into account.

References

1. L.V.Atroshchenko, V.D.Ryzhikov, N.G.Starzhinskiy, Crystal Scintillators and Detectors Base Thereon, Naukova Dumka, Kiev (1998) [in Russian].

2. V.D.Ryzhikov, L.P.Gal'chinetskii, N.G.Starzhinskiy et al., *Int. J. Inorg. Mater.*, No.3, 1227 (2001).

3. V.K.Komar', V.M.Puzikov, Single Crystals of A^2B^6 Group: Growing, Properties, Application, Inst. for Single Crystals Publ., Kharkiv (2002) [in Russian].

4. V.D.Ryzhikov, N.G.Starzhinskiy, L.P.Gal'chinetskii, V.I.Silin, Semiconductor Scintillators on the Basis of $A^{II}B^{VI}$ Compounds, in Book: Functional Materials and Technology, Inst. for Single Crystals Publ., Kharkiv (2001) p.76 [in Russian].

5. M.E.Globus, B.V.Grinyov, Inorganic Scintillators: New and Traditional Materials, Akta Publ., Kharkiv (2000) [in Russian].

6. J.D.Watkins, in: Inst. Phys. Cont., Ser.No.31, Chapter 1, p.95 (1997).

7. S.Kishida, K.Matswura, H.Nagase, H.Mori, *Phys. St. Sol.(a)*, **95**, 155 (1986).

8. V.Ryzhikov, N.Starzhinskiy, L.Gal'chinetskii et al., *IEEE Trans. Nucl. Sci.*, **48**, 1561 (2001).

Про кінетику люмінесценції сцинтиляторів, що використовуються у рентгеноінтроскопічних системах

В.Рижиков, М.Старжинський, В.Семіноженко, Б.Гриньов, Л.Нагорна, В.Спасов, К.Катрунов, І.Зеня, О.Вягін

Наводяться дані про вплив різних факторів на кінетику люмінесценції кристалів-сцинтиляторів на основі активованих кристалів ZnSe, CsI, CWO та GSO. Показано, що тип ізовалентної домішки впливає на час висвітлення і сцинтиляторів на основі ZnSe, і ця величина у залежності від концентрації домішки може складати 1–150 мкс. Визначено, що кінетика висвітлення кристалів ZnSe(Te) має особливості і характеризується немонотонним спадом з наявністю ділянки зростання інтенсивності люмінесценції на початковому етапі після припинення опромінювання зразків. Розглянуто механізм енергопереносу цього явища. Інерційність оксидних сцинтиляторів (CWO, GSO) суттєво залежить як від нестехіометричності сполуки, так і від неконтрольованих домішок. Показано, що рівень післясвітіння сцинтиляторів на основі CsI і CWO залежить як від дози попереднього рентгенівського опромінення, так і від концентрації дефектів, що введені у кристал механічним способом. Вивчено роль фінішної термообробки в оптимізації інерційних властивостей сцинтиляційних елементів.