Effect of heat treatment in Zn vapor on spectral kinetic, optical and mechanical properties of ZnSe(O,Te) crystals

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Experimental data are presented on the effect of the cooling rate following the heat treatment in Zn vapor at 1250 K on the luninescence spectra within the 500–700 nm wavelength region, optical transmission as well as microhardness of ZnSe(O,Te) crystals. It has been found that in those crystals, the $V_{Zn}Zn_iO_{Se}$ complexes (the radiative recombination centers with $\lambda_{max}{\approx}600$ nm) are less stable than the $Zn_iV_{Zn}Te_{Se}$ ones (the radiative recombination centers with $\lambda_{max}{\approx}640$ nm).

Приведены экспериментальные данные о влиянии скорости охлаждения после термообработки в парах цинка при температуре 1250 К на спектры люминесценции в диапазоне длин волн 500–700 нм оптическое пропускание и кинетику высвечивания сцинтилляций, а также на микротвёрдость кристаллов ZnSe(O,Te). Установлено, что в этих кристаллах комплексы $V_{Zn}Zn_iO_{Se}$ (центры излучательной рекомбинации с $\lambda_{max}{\approx}600$ нм) менее устойчивы, чем комплексы $Zn_iV_{Zn}Te_{Se}$ (центры излучательной рекомбинации с $\lambda_{max}{\approx}640$ нм).

1. Introduction

ZnSe(O,Te) crystals comprising an isovalent impurity (oxygen or tellurium) are among materials of promise for detectors of high-intensity ionizing radiation flows. This is due to the fact that the ZnSe(O,Te) crystals are among few materials having good spectral consistence with silicon photodiode. Moreover, ZnSe(O,Te) crystals possess numerous advantages over the CsI(Tl) crystal used widely in the scintillator/photodiode type detectors. Those advantages are demonstrated by comparison of main parameters of ZnSe(O,Te) and CsI(Tl) crystals presented in Table. The main application field of the scintillator/photodiode detectors with ZnSe(O,Te) crystals is the low-energy (up to 60 keV) input channel in the X-ray nondestructive testing systems, medical X-ray tomography and radiography.

The main optical and luminescence characteristics of ZnSe(O,Te) crystals in the red-orange operating range at 300 K are known [1] to be defined by the intrinsic point defects $V_{Zn}Zn_iO_{Se}$ and $Zn_iV_{Zn}Te_{Se}$ that are present in the crystals immediately after growing. Here V_{Zn} is a zinc vacancy; Zn_i, interstital zinc; O_{Se}, Te_{Se}, oxygen and tellurium atoms, respectively, in the sites of selenium anionic sublattice. During the crystal heat treatment (HT) in zinc vapors, the concentration of those complexes becomes increased by several decimal orders, thus, the crystal scintillation efficiency increases, too. The stability of the complexes depends on the external action type. For example, the study of different nuclear radiation types effect on the X-ray luminescence (XRL) and optical transmission (OT) spectra of ZnSe(O,Te) crystals has shown [2] that

Table. Main characteristics of ZnSe(O,Te) crystals as compared to those of CsI(Tl)

Parameter	Scintillation crystal		
	CsI(Tl)	ZnSe(O,Te)	
		ZnSe(O) "fast"	ZnSe(Te) "slow"
Melting point, K	894	1773−1793	1773−1793
Density ρ, g/cm^3	4.51	5.42	5.42
Effective atomic number, Z	54	33	33
Hygroscopicity	low	none	none
Luminescence maximum λ_{max}, nm	550	600	640
Afterglow δ (after 6 ms), %	0.1−5.0	< 0.05	< 0.05
Absorption index for intrinsic emission, α (at λ_{max} = 600−640 nm), cm^{-1}	< 0.05	0.05−0.2	0.05−0.2
Light output in coupling with Si-PD relative to CsI(Tl) at 1 mm thickness under X-ray excitation at E = 40 keV, %	100	Up to 100	Up to 140
Decay time, τ, μs	1	1−8	30−70
Spectral matching coeficient with Si−PD, K_u	0.77	0.90	0.92
Refractive index, n_r	1.79	2.61	2.59
Conversion efficiency, %	Up to 15	Up to 18	Up to 22
Depth of 90 % absorption of X-rays (40 keV), mm	< 0.25	0.65	0.65

the irradiation with 18 MeV protons causes the XRL degradation. The degradation was found to be associated with destruction, first of all, of $Zn_iV_{Zn}Te_{Se}$ complexes during the interaction thereof with thermalized protons.

The stability of the complexes mentioned and the actual concentration thereof are influenced heavily by the parameters of HT in zinc vapors (temperature, Zn vapor pressure, the post-treatment cooling rate). By varying those parameters, it is possible to study the effect of both the complexes and their decay products on different crystal properties, including the physico-mechanical ones.

In this work, studied was the effect of the ZnSe(O,Te) crystal cooling rate after HT in Zn vapors on the XRL spectra in 600−640 nm range, the fundamental optical transmission edge, IR absorption spectrum, the scintillation decay kinetics as well as on the microhardness.

2. Experimental

The ZnSe(O,Te) crystals were grown using the Bridgman technique in vertical compression furnaces in argon atmosphere under pressure up to $5 \cdot 10^6$ Pa. The growing procedure has been described in detail in

[1]. The test samples of 1.5 mm thickness (Samples 1m, 1b, 1d, 2m, 2b, 2d) and of 5.5 mm thickness (Samples 3m, 3b, 4m, 4b) were cut out from the crystals and heat treated in Zn vapors (except f$_0$ 1d and 2d). The HT was carried out at 1250 K for 40−60 h. The post-HT cooling from 1250 to 850 K was carried out under slow cooling conditions together with the furnace at a rate of 1−3 K/min (the "m" series samples) and at high cooling rate (about 50 K/min) (the "b" series samples). The further cooling from 850 K was slow (together with the furnace). The XRL and OT spectra were measured using a KSVU-23 unit at 300 K. A REIS-1 unit was used as the X-ray source, the tube voltage was 20−40 kV. The optical transmission near the fundamental band edge was measured using a KSVU-23 unit and the IR absorption, on a UR-20 spectrophotometer. To measure the microhardness H_μ, a PMT-3 microdurometer at 300 K. The scintillation kinetics was studied using a special laboratory setup with a collimated exciting gamma radiation source (^{137}Cs, 662 keV).

3. Results and discussion

The XRL spectra of ZnSe(O,Te) crystals depending on the cooling rate ν after HT in
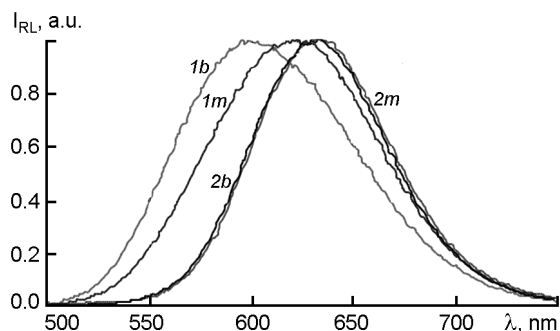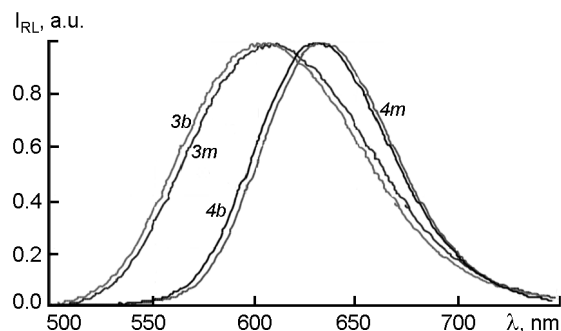
Fig. 1. Dependences of XRL spectra on the cooling speed of ZnSe(O) and ZnSe(Te) crystals after heat treatment in Zn vapors. The crystal thickness 1.5 mm. Curve numbers: for ZnSe(O): *1m*, slow cooling; *1b*, fast cooling; for ZnSe(Te): *2m*, slow cooling; *2b*, fast cooling.

Fig. 2. Dependences of XRL spectra on the cooling speed of ZnSe(O) and ZnSe(Te) crystals after heat treatment in Zn vapors. The crystal thickness 5.5 mm. Curve designations: for ZnSe(O): *3m*, slow cooling; *3b*, fast cooling; for ZnSe(Te): *4m*, slow cooling; *4*b, fast cooling.
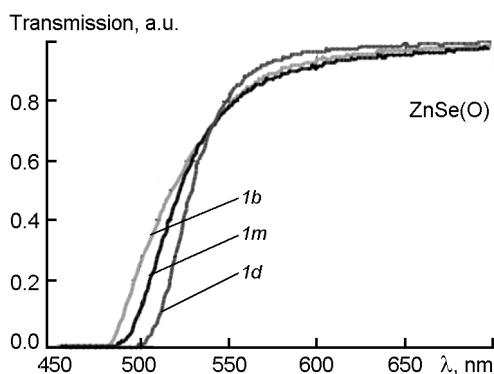

Fig. 3. Dependences of optical transmission spectra on the cooling speed of ZnSe(O) and ZnSe(Te) crystals after heat treatment in Zn vapors. Curve designations: *1m, 2m, 1b, 2b* as in Figs. 1, 2; *1d, 2d* for heat untreated samples.

Zn vapors are presented in Figs. 1 and 2. It follows from those dependences that the XRL spectrum of the ZnSe(Te) crystals is essentially independent of ν, while that of ZnSe(O) ones is ν-dependent. The ν effect on the XRL spectra increases significantly as the sample thickness is diminished (curves *1m* and *1b*, Fig. 1). For 1.5 mm thick ZnSe(O) samples after rapid cooling (50 to 100 K/min), it is $\lambda_{max} \approx 600$ nm that prevails, while after slow cooling (1 to 3 K/min), the spectrum is shifted towards longer-wave range ($\lambda_{max} \approx 620$ nm). The optical transmission measurements near the fundamental absorption edge (Fig. 3) evidence also the different effect of ν on ZnSe(Te) and ZnSe(O) crystals: the absorption edge shift ΔE is observed for both crystal types but it is much more for ZnSe(O) (0.05 eV) than for ZnSe(Te).
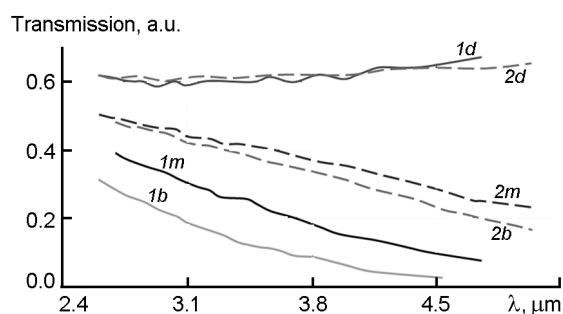

Fig. 4. IR transmission spectra for ZnSe(O) and ZnSe(Te) crystals. Curve designations as in Figs. 1–3.

Fig. 4 presents the IR thansmission spectra. Taking into account that in the wavelength range $\lambda > 3$ μm the IR absorption is due mainly to the photon interaction with the free carriers (in our case, electrons), the consideration of those spectra allows to conclude that, first, in ZnSe(O) crystals heat-
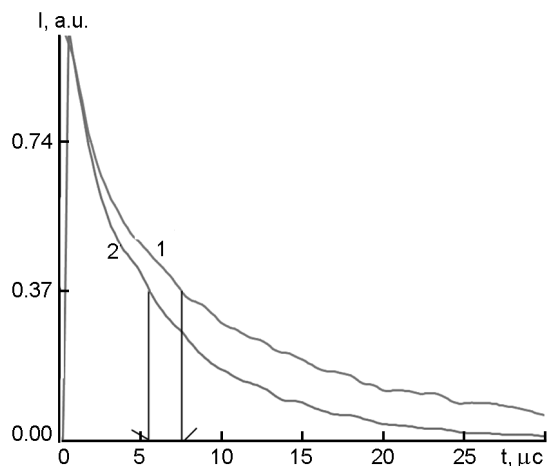
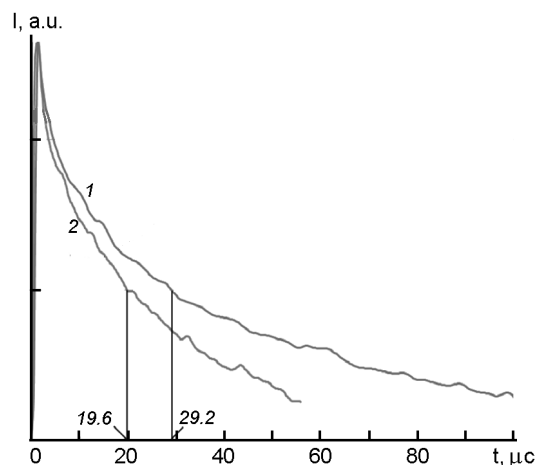Fig. 5. Decay kinetics of a ZnSe(O) crystal heat treated in Zn vapors. *1*, Sample 1m; *2*, Sample 1b.

Fig. 6. Decay kinetics of a ZnSe(Te) crystal heat treated in Zn vapors. *1*, Sample 2m; *2*, Sample 2b.
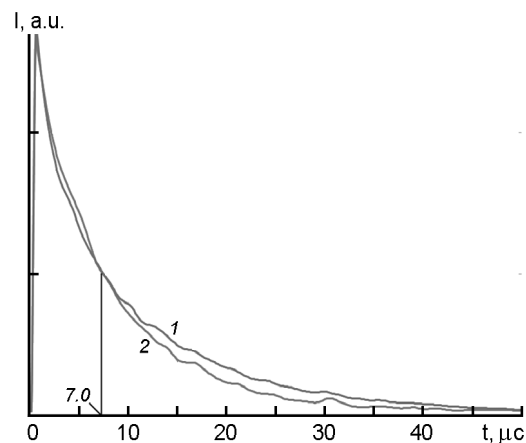
Fig. 7. Decay kinetics of a ZnSe(O) crystal heat treated in Zn vapors. *1*, Sample 3m; *2*, Sample 3b.

treated in Zn vapors the electron concentration n in the conduction band is much higher than in ZnSe(Te) ones; and, second, different v values influence the n changes in the ZnSe(O) crystals much stronger than in the ZnSe(Te) ones. The data presented in Figs. 3 and 4 show that the Burstein-Moss effect occurs in the ZnSe(O,Te) after the HT in Zn vapors. In this case, n is estimated using the Burstein-Moss formula

$$n = \frac{8\pi}{3h^3}(2m_e \Delta E)^{3/2}, \ n \leq 2 \cdot 10^{17} cm^{-3}. \quad (1)$$

As to the IR absorption range, n can be estimated using the Drude formula

$$n = \frac{4\pi^2 \alpha c^3}{\lambda^2 \ e^3} n_r \varepsilon_0 m_e^2 \mu_e, \quad n \leq 1.5 \cdot 10^{17} cm^{-3}. \quad (2)$$

Here $m_e = 0.17 m_0$, $\mu_e \approx 200$ cm^{2}V/s, $n_r = 2.45$, $\varepsilon_0 = 8.1$, $\Delta E \approx 0.05$ eV; λ is the wavelength; α, the refractive index. The calculation results show the essential coincidence of n values determined using (1) and (2) and confirm the correctness of the physical mechanism explaining the features of curves presented in Figs. 3 and 4.

In Figs. 5–7, presented are the decay kinetic curves. As to thin (1.5 mm) crystal samples, the decay time τ depends essentially on v. For ZnSe(O) crystals, τ is about 5 to 6 μs after "fast" cooling and about 7 to 9 μs after the "slow" one (v less than 2 K/min). For ZnSe(Te) crystals, τ is about 20 μs after "fast" cooling and about 30 μs after the "slow" one. As to considerably thicker (5.5 mm) ZnSe(O,Te)

crystals, τ is essentially independent of v and coincides with τ for slow-cooled thin crystals (Fig. 7).

The above effects of different cooling rate of ZnSe(O,Te) crystals cooled after the HT in Zn vapors on the spectral kinetic and optical characteristics are easy to explain basing on the model of the radiative recombination centers (RRC) in those crystals [2, 3]. According to that model, the doping of the crystals with isovalent Te impurity results in formation of stable ternary $Zn_i V_{Zn} Te_{Se}$ complexes that are the RRC at $\lambda_{max} \approx 640$ nm (RRC-1); while the doping with oxygen isovalent impurity causes the formation of stable ternary $Zn_i V_{Zn} O_{Se}$ complexes that are the RRC at $\lambda_{max} \approx 600$ nm (RRC-2). Moreover, according to the same model, the formation of ternary complexes

results in appearance of n free electrons in the conduction band, where $N \approx n$, N being the concentration of complexes. The decay time τ of the RRC-1 is of the order of 30 to 80 μs while for RRC-2, it is 1 to 8 μs. Such differences in τ for ZnSe(O) and ZnSe(Te) crystals agree with the radiative transition scheme in ZnSe(O,Te) crystals presented in [1]. According to that scheme, in the band-gap of a ZnSe(Te) crystal, there is a metastable trap associated with the Te isovalent impurity that retards the radiative recombination process in the crystal. As follows from the same scheme, no similar trap exists in the band-gap of a ZnSe(O) crystal, therefore, the decay time is shorter in that crystal.

According to the model proposed in [3–5], the $Zn_iV_{Zn}O_{Se}$ complexes are thermodynamically less stable than $Zn_iV_{Zn}Te_{Se}$ ones. Therefore, it is to expect that the different cooling rates of ZnSe(O,Te) crystals should influence considerably their optical properties, spectra, and scintillation decay kinetics as well as the mechanical properties of the crystals, that is, the characteristics that depend on the relative contributions from the $Zn_iV_{Zn}O_{Se}$ and $Zn_iV_{Zn}Te_{Se}$ complexes.

The results of this work confirm this statement. In fact, the strong dependence of the luminescence spectrum maximum position for ZnSe(O) crystal on the cooling speed v after the HT in Zn vapors and the absence of such a dependence for ZnSe(Te) (Fig. 1); the strong dependence of the fundamental absorption edge shift for ZnSe(O) on v and the weak similar dependence for ZnSe(Te) (Fig. 3); the strong effect of v on the IR absorption for ZnSe(O) and much weaker similar effect for ZnSe(Te) (Fig. 4) — all these effects observed in experiment are explainable in a noncontradictory manner when assuming that at the fast cooling, the excess non-equilibrium concentration of $Zn_iV_{Zn}O_{Se}$ and $V_{Zn}Zn_iTe_{Se}$ complexes is "frozen". This results in increased real concentration of those complexes and thus in increasing luminescence intensity. In the conduction band, n increases considerably, thus resulting in the Burstein-Moss effect. The "freezing" of complexes must influence first of all the concentration of less stable $Zn_iV_{Zn}O_{Se}$ ones: their fraction in the total amount of $Zn_iV_{Zn}O_{Se}$ and $V_{Zn}Zn_iTe_{Se}$ complexes increases. This results in shortened effective value of the luminescence quenching time as well as in a short-wave shifting of λ_{max}. At slow cooling, a fraction of the complexes becomes decomposed, so n decreases.

In real ZnSe(O) crystals, some residual tellurium always is present due to technological features of preparation thereof; thus, there is always a certain amount of $V_{Zn}Zn_iTe_{Se}$ complexes. Similarly, there is a residual amount of oxygen in real ZnSe(Te) crystals, thus, some $V_{Zn}Zn_iO_{Se}$ complexes are present. That is why the dependence of physical characteristics on v is observed to a certain extent in real ZnSe(Te) crystals.

As the $Zn_iV_{Zn}O_{Se}$ complexes are less stable than the $V_{Zn}Zn_iTe_{Se}$ ones, it is to expect that the different cooling rates of ZnSe(O,Te) crystals should affect considerably the scintillation decay kinetics. Judging from the radiative transition scheme in ZnSe(O,Te) crystals presented in [1], the radiative recombination related to the $Zn_iV_{Zn}O_{Se}$ complexes proceeds faster than that associated with $V_{Zn}Zn_iTe_{Se}$ ones. It follows therefrom that the increasing fraction of the $Zn_iV_{Zn}O_{Se}$ complexes in the total $Zn_iV_{Zn}O_{Se}$ and $V_{Zn}Zn_iTe_{Se}$ content observed at the fast cooling of the crystals, should result in a shortened effective decay time.

In fact, the study results of the scintillation kinetics (Figs. 5–7) confirm completely the considerations concerning different effect of the cooling rate on the ZnSe(Te) and ZnSe(O) crystals kinetic characteristics. Comparing the curves 1 and 2 (Fig. 5), it is seen that the fast-cooled thin ZnSe(O) sample exhibits a shorter τ value ($\tau \approx 5$ μs) than the slowly cooled one ($\tau \approx 7$ μs). This effect is pronounced at a thin crystal (1.5 mm in our case) when the low heat conduction does not hinder the fast cooling. At a significantly thicker crystal, the effective cooling rate (depending on the heat conduction) is considerably lower and could be insufficient to "freeze" the excess concentration of the "fast" $Zn_iV_{Zn}O_{Se}$ complexes. This means that τ after the fast cooling should not to differ considerably from that after the slow cooling. In fact, as is seen in Fig. 6, the τ values for curves 1 and 2 at the crystal thickness of 5.5 mm are essentially the same, and in that case, τ has the same value as for slowly cooled thin sample (curve 1 in Fig. 5).

In Fig. 7, presented are the decay kinetics curve for a ZnSe(Te) crystal after slow (curve 1) and fast (curve 2) cooling of the thin sample. For the curve 1, $\tau \approx 29.2$ μs while for the curve 2, it is about 19.6 μs, thus exceeding considerably the τ value for

ZnSe(O) crystals, as expected. It is seen also that after the fast cooling, τ is considerably shorter than after the slow one. This can be explained by the fact that (as is noted above) the technology of ZnSe(Te) growing does not exclude the residual oxygen impurity and the presence of some $Zn_i V_{Zn} O_{Se}$ complexes, that is manifested as a shortened effective τ value. For a 5.5 mm thick sample, $\tau \approx 30$ μs and does not depend on the cooling rate.

An unuisual effect was observed when measuring the microhardness of one 5.5 mm thick ZnSe(O) crystal sample fast-cooled after HT in Zn vapors prior to the measurements. In the course of H_μ measurements on that sample at the indentor load over 100 g, an accumulation of volume defects up to several micrometers appeared near the indentation; after unloading, those defects disappeared during several hours at $T = 300$ K. Under 200 g load, the same sample exhibited a superplasticity effect manifested as the H_μ reduction by a factor of 1.7 as compared to the slowly cooled samples having $H_\mu \approx 160$ kg/mm^2. Three days later, the H_μ has been recovered to ≈ 160 kg/mm^2. The mechanism of the defects observed can be explained by the coopertive motion character of dislocations generated under the mentioned loads and providing considerable plastic strains as well as by the coagulation of vacancies (decomposition products of the excess non-equilibrium amount of $Zn_i V_{Zn} O_{Se}$ complexes) concentrated about those dislocations and the subsequent (after unloading) emission of vacancies from the pores towards the indentations along thje accelerated diffusion paths, such as dislocation tubes [6].

4. Conclusion

The study results concerning the effect of the cooling rate after HT in Zn vapor on the physical characteristics of ZnSe(O,Te) crystals are completely consistent with the physical mechanism of the luminescence nature in that type crystals developed before. According to the mechanism, the decisive part in the luminescence of those crystals is played by the radiative recombination centers associated with $Zn_i V_{Zn} O_{Se}$ and $V_{Zn} Zn_i Te_{Se}$ complexes. The conclusion about a lower thermodynamical stability of $Zn_i V_{Zn} O_{Se}$ as compared to $V_{Zn} Zn_i Te_{Se}$ is also substantiated. The results obtained are to be taken into consideration when developing a reproducible technology to obtain scintillation materials basing on ZnSe(O,Te) crystals.

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Вплив термічної обробки у парах цинку на спектрально-кінетичні, оптичні та механічні характеристики кристалів ZnSe(O,Te)

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Наведено експериментальні дані про вплив швидкості охолодження після термічної обробки у парі цинку при температурі 1250 К на спектри люмінесценції у діапазоні довжини хвиль 500–700 нм, оптичне пропускання та кінетику висвічування сцинтиляцій, а також на мікротвердість кристалів ZnSe(O,Te). Встановлено, що в цих кристалах комплекси $V_{Zn} Zn_i O_{Se}$ (центри випромінювальної рекомбінації з $\lambda_{max} \approx 600$ нм) є менш стабільними, ніж комплекси $V_{Zn} Zn_i Te_{Se}$ (центри випромінювальної рекомбінації з $\lambda_{max} \approx 640$ нм).