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Features of the management of the rule of Urbakh in ZnSe:Yb crystals

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A comparative analysis of the edge absorption spectra measured in the temperature range of 290–470 K for two types of zinc selenide substrates has been carried out. It has been established that the self-absorption edge of pure ZnSe: Yb melt crystals is described by the "crystalline" approximation of the general Urbach rule, which is a consequence of dynamic disordering. In samples doped with ytterbium, at $T_K \approx 330°K$, a reversible transition from dynamic to static disordering was detected, which is described by the "glassy" approximation of the general Urbach rule.

Keywords: zinc selenide, Urbach rule, dynamic and static disordering.

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Introduction

Studies show that for many crystalline and non-crystalline materials, the fundamental absorption edge is described by an exponential dependence, which is commonly called the empirical Urbach rule (UR) [1]. Since today it is believed that the presence of the Urbach "tail" is associated with the presence of structural disorder in the system, UR is often used to explain its nature. Unfortunately, the application of the so-called generalized Urbach rule for this is complicated by a number of reasons, the main of which is the a priori unknown dependencies, the parameters included in it, on many external and internal factors. In this regard, the analysis of experimental Urbach "tails" is usually carried out using two extreme cases of PU - the "crystalline" and "glassy" approximations [2].

In this work, it is these approximations that are used to analyze the features of the temperature dependences of the absorption coefficient in the Urbach region, which are experimentally observed in ZnSe substrates doped with Yb impurity from the vapor phase.

I. Samples and methods of the investigated

Base plates 4 x 4 x 1 mm^3 in size were cut from a bulk ZnSe crystal grown by the Bridgman-Stockberger method from a melt of stoichiometric composition under inert gas pressure. Doping with the rare-earth element Yb was carried out in a vacuum-filled up to 10^{-4} Torr and a sealed quartz ampoule, at one end of which there was a substrate, and at the opposite end - a charge. The latter contained crushed ytterbium and a weight of selenium, the backpressure of which prevented the erosion of the sample surface and promoted the incorporation of Yb into the cation (zinc) sublattice of ZnSe. After annealing, the surface of the substrates remains the same as before loading into the ampoule, which allows their use on a par with basic ones for further studies without any additional treatments.

The optical transmission spectra T_ω were measured on an installation containing an MDR-23 diffraction monochromator, a halogen lamp with a "smooth" emission spectrum, and a Si photodiode as a receiver. The absorption spectra were α_ω calculated using a simplified

formula $\alpha_\omega = 1 - T_\omega$ and were plotted in coordinates $\ln \alpha_\omega - \hbar\omega$, the choice of which was determined by the general Urbach rule. The spectral characteristics were measured in the temperature range of 290-470 K.

In conclusion of this section, we discuss the main reasons for choosing ZnSe: Yb samples as the object of study. The main one is determined by the prospects of using this material to create effective sources of blue radiation, operating at elevated temperatures [3,4]. Secondly, the behavior of the Urbach "tails" of both pure and doped ZnSe crystals containing certain information about their structural disorder has been studied very little. Finally, the transition from dynamic to static disorder in the ZnSe: Yb samples in the temperature range under study requires separate consideration. Since this effect, like the "purification effect" observed in ZnSe: Yb crystals [5], is associated with the rearrangement of an ensemble of point defects, it is reasonable to analyze it in comparison with the behavior of the Urbach "tails" of the base substrates.

II. Discussion of results of research

As can be seen from fig. 1, the dependences α_ω of the ZnSe base substrates are described by the "crystalline" PU approximation in the entire temperature range under investigation, the analytical expression for which has the form [2]:

$$\alpha(\omega, T) = \alpha_{cr}\left[\sigma(\hbar\omega - E_f)/kT\right]. \qquad (1)$$

Here α_{cr} and E_f are the coordinates of the focal point f at which the spectral dependences of the absorption coefficient at different temperatures converge. The parameter σ characterizes the temperature-dependent slope of the spectral characteristic and, in the case of exciton-phonon and (or) electron-phonon interactions, should be described by the well-known Mara formula [6]

$$\sigma(T) = \sigma_0(2kT/\hbar\omega_p)th(\hbar\omega_p/2kT), \qquad (2)$$

where $\hbar\omega_p$ is the energy of the effective phonon, and the meaning of the parameter σ_0 will be considered in more detail later. We also pay attention to the fact that expression (1) can also be obtained in the theory of random electric fields in a crystal, but the dependence $\sigma(T)$ is no longer described by formula (2).

First of all, we note that the energy position of the focal point f turned out to be 2.81 eV and is consistent with the band gap E_g of zinc selenide at 0 K [7,8]. This, as well as the temperature-dependent slope of the Urbach "tails," indicate the prevalence of dynamic disorder in ZnSe substrates. Meanwhile, the experimental and theoretical dependences $\sigma(T)$ differ not only quantitatively but also qualitatively, the inset in Fig. 1. (The value of the parameter $\sigma_0 = 0.28$ is determined by the formula (2) after substituting into it the experimental value σ at T=293 K and the energy of the longitudinal optical phonon $\hbar\omega_p = 30$ meV of zinc selenide [7,9].) The observed differences, in our opinion, are due to the presence of random electric fields, caused by the chaotic distribution of intrinsic point defects (IPD) - positive single-charge selenium vacancies $V_{Se}^{\bullet}$ (shallow donors) and negative two-charged zinc vacancies $V_{Zn}^{''}$ (deep acceptors). The basis for this is the results of work [10], according to which the concentration of STD data in molten pure ZnSe crystals in the region of room temperature is ~$6\cdot10^{21}$ cm^{-3}. As a result, the temperature dependence of the parameter is not consistent with the Mara formula, and its decrease T with growth is associated with an increase in the concentration of charged IPD and a corresponding increase in the contribution to the dynamic disorder of a chaotic electric field.

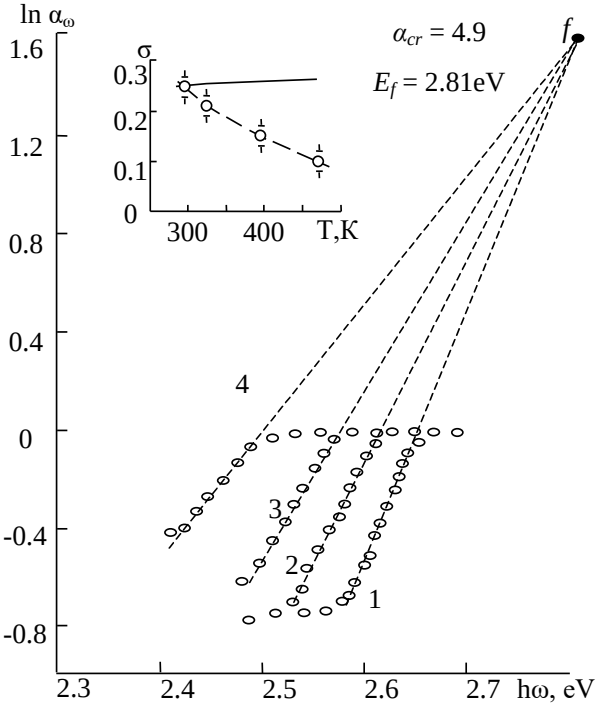

Fig. 1. Absorption spectra of ZnSe substrates at different temperatures: 1 - 293, 2 - 323, 3 - 393, 4 - 468 K. On the inset is the temperature dependence of the parameter σ: points - experiment, solid line - calculated by formula (2) at $\sigma_0 = 0.38$ and $\hbar\omega_p = 30$ meV.

Considering the above, we should expect a transformation of the dependences α_ω associated with the restructuring of the defect subsystem due to doping of ZnSe substrates with ytterbium. First of all, this is manifested in the absence in the luminescence spectra of the ZnSe: Yb samples of the R band, due to the complexes considered above $\left(V_{Zn}^{''}, V_{Se}^{\bullet}\right)$ [5,11]. In turn, this should cause a weakening of the role of random electric fields in the formation of Urbach "tails", which is indirectly confirmed by a smaller parameter value of $\alpha_{cr} \approx 2.2$ samples of ZnSe: Yb compared to $\alpha_{cr} \approx 4.9$ base substrates, fig. 1 and 2. We also pay attention to the fact that the "crystalline" approximation of PU describes the experimental dependences α_ω of Yb-doped substrates in a narrower (~40 K) temperature range, Fig. 2. However, since the value E_f in this case is also consistent with E_g zinc selenide at 0 K, the stated facts indicate a change in the mechanism of dynamic disordering, most likely due to the exciton-phonon interaction. This is confirmed by the exciton nature of the edge B band, which is dominant in

the luminescence spectra of ZnSe: Yb crystals up to 470 K [3].

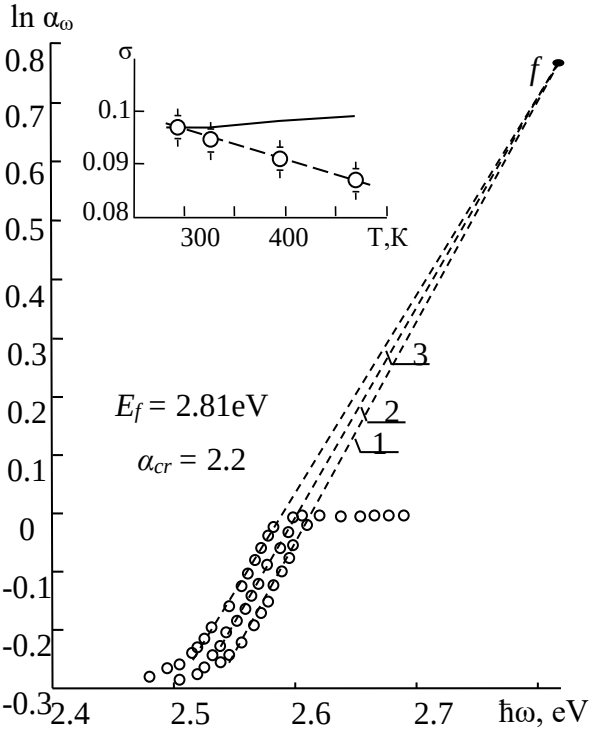

Fig. 2. Absorption spectra of ZnSe: Yb substrates at different temperatures: 1–293, 2– 304, 3– 328 K. The inset shows the temperature dependence of the parameter σ: points – experiment, solid line – calculated by formula (2) at $\sigma_0 = 0.15$ and $\hbar\omega_p = 30$ meV.

Despite this, satisfactory agreement between the experimental and calculated values σ by formula (2) is observed only up to a temperature of $T_K \approx 330$ K, above which the slope of the Urbach "tails" becomes temperature independent, fig. 3. This indicates a decrease in dynamic disordering compared with static, which is indirectly confirmed by a decrease in the intensity of the exciton luminescence band of ZnSe: Yb samples with increasing T [3]. As a result, after exceeding a certain degree T_K, static disorder becomes predominant, in which the absorption edge is already described by the "glassy" UR approximation [2]

$$\alpha(\omega, T) = \alpha_{st} exp\left[\left(\hbar\omega - E_g\right)/E_0\right] \qquad (3)$$

Here α_{st} is the constant, and $E_0^{-1} = d\ln\alpha_\omega / d(\hbar\omega)$ is the temperature-independent slope of the spectral characteristic constructed on a semi-log scale. Temperature changes in the absorption coefficient are caused in this case by the temperature dependence of the width of the forbidden band, for which T the linear dependence is valid at high [7]

$$E_g(T) = E_g(0) - \beta T \qquad (4)$$

Under conditions of a parallel shift of the absorption edge, its temperature dependence must completely coincide with the change $E_g(T)$, that is, taking into $\hbar\omega(T)$ account (4), the function can be written as

$$\hbar\omega(0) - \hbar\omega(T) = E_g(0) - E_g(T) = \beta T \qquad (5)$$

As can be seen from fig. 3 (inset), the temperature dependence of the absorption $\ln\alpha_\omega = 0$ edge at 340–470 K is approximated by a straight line with an energy slope of $7\cdot10^{-4}$ eV/K. This value is in good agreement with the temperature coefficient of change E_g of zinc selenide [7,12]. The deviation of the experimental points from the straight line at $T \le 340$ K (Fig. 3) is due to the increasing role of dynamic disordering, at which the dependence α_ω is described by the "crystalline" approximation of the UR considered earlier, Fig. 2.

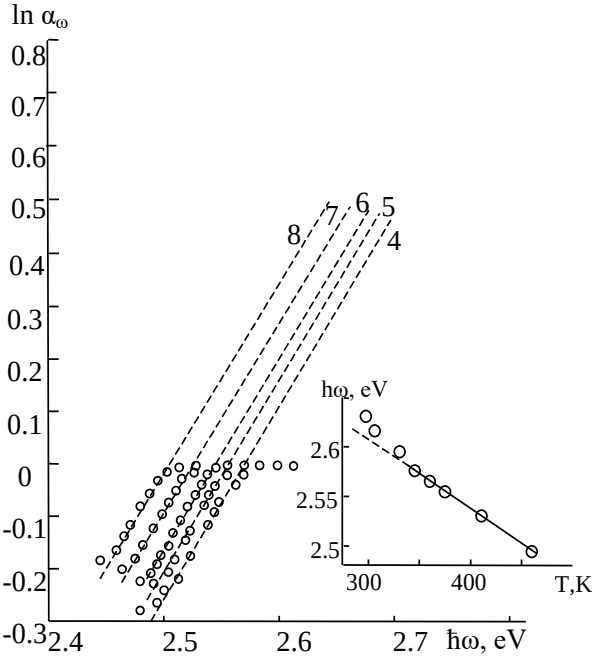

Fig. 3. Absorption spectra of ZnSe: Yb substrates at different temperatures: 4–343, 5–358, 6–373, 7–406, 8–468 K. The inset shows the temperature dependence of the absorption edge at $\ln\alpha = 0$.

In conclusion, we note that the nature and absolute values of the experimental curves $\alpha(\omega, T)$ of the ZnSe and ZnSe: Yb samples, as well as the temperature T_K values, do not depend on the direction of change (increase or decrease) of the measurement temperature. This is a consequence of the lack of influence of the latter on the composition of the defective subsystem, which is formed at much higher growing temperatures (~1800 K) and doping (~1400 K) of the objects of research.

Conclusion

The conducted studies allow us to draw the following conclusions.

1. The absorption edge of pure molten ZnSe crystals in the temperature range of 290–470 K is described by the "crystalline" UR approximation, and the dynamic disorder in this case is due to the presence of random electric fields caused by the chaotic distribution of intrinsic point defects $V_{Zn}^{''}$ and $V_{Se}^{\bullet}$.

2. Doping of ZnSe substrates with Yb impurity causes

restructuring of the ensemble of point defects and the corresponding qualitative and quantitative transformation of Urbach "tails".

3. The observed reversible transition from dynamic disorder to static in ZnSe: Yb samples at $T_K \approx 330$ K is caused by the temperature dependence of the relative contribution of these mechanisms to the formation of Urbach tails.

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Особливості прояву правила Урбаха в ZnSe:Yb

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Проведено порівняльний аналіз спектрів крайового поглинання виміряних в температурному діапазоні 290-470 К для двох типів підкладинок селеніду цинку. Встановлено, що край власного поглинання бездомішкових розплавних кристалів ZnSe:Yb описується "кристалічним" наближенням загального правила Урбаха, що є наслідком динамічного розупорядкування. В зразках, легованих ітербієм, при $T_K \approx 330°K$, виявлено зворотній перехід від динамічного до статичного розупорядкування, який описується "склоподібним" наближенням загального правила Урбаха.

Ключові слова: селенід цинку, правило Урбаха, динамічне і статичне розупорядкування.