

UDC 539.1.074.3:535.35

A. Y. Osetsky*, T. V. Panchenko

¹Oles Honchar Dnipropetrovsk National University, Dnipropetrovsk, Ukraine

*e-mail: osetsky.ay@gmail.com

THE OPTICAL ABSORPTION EDGE OF $\text{Bi}_{12}\text{SiO}_{20}$ DOPED BY VANADIUM

Spectral-temperature dependence of the optical absorption edge for undoped $\text{Bi}_{12}\text{SiO}_{20}$ (BSO) and doped 3d-vanadium ions (BSO:V) crystals were investigated. Crystals were grown by the Czochralski method. Research was performed within the spectral range for the following photon energy $h\nu = 2 - 3.4$ eV, temperature was varied in cycles "cooling – heating" between $330 \rightarrow 85 \rightarrow 300$ K. It was found that the optical absorption edge of BSO, BSO:V crystals obeys the Urbach rule; the temperature cycles of "cooling – heating" hysteresis are characterized by temperature dependence of the spectral absorption. The model of electron-phonon interaction (EPI) was used in order to characterize optical transitions, which form the absorption edge. In the framework of the model, the effect of vanadium ions results in an appearance of anomalies in the temperature dependence of the parameter σ (T), characterizing the EPI. It also leads to anomalies of isoabsorbing width of the band gap (pseudo-band gap) E_g^a (T).

Keywords: optical absorption edge, temperature dependencies, $\text{Bi}_{12}\text{SiO}_{20}$ crystals, vanadium doped, Urbach rule, temperature hysteresis.

Досліджено спектрально-температурні залежності крайового оптичного поглинання нелегованих кристалів $\text{Bi}_{12}\text{SiO}_{20}$ (BSO) і легованих 3d-іонами ванадію (BSO:V). Кристали вирощені за методом Чохральського. Дослідження виконані в спектральному діапазоні для таких енергій фотонів $h\nu = 2 - 3.4$ eV при варіюванні температури в циклах «охолодження - нагрівання» в діапазоні $330 \rightarrow 85 \rightarrow 300$ К. Встановлено, що крайове оптичне поглинання кристалів BSO, BSO:V підпорядковується правилу Урбаха, температурні цикли «охолодження - нагрівання» характеризуються гістерезисом спектрально-температурних залежностей поглинання. Використана модель електрон-фононної взаємодії (ЕФВ) в оптичних переходах, що формують край поглинання. В рамках даної моделі вплив іонів ванадію полягає в появі аномалій температурних залежностей параметра σ (T), який характеризує ЕФВ, а також аномалій ізоабсорбційної ширини забороненої зони - E_g^a (T).

Ключові слова: крайове оптичне поглинання, температурні залежності, кристали $\text{Bi}_{12}\text{SiO}_{20}$, леговані ванадієм, правило Урбаха, температурний гістерезис.

Исследованы спектрально-температурные зависимости краевого оптического поглощения нелегированных кристаллов $\text{Bi}_{12}\text{SiO}_{20}$ (BSO) и легированных 3d-ионами ванадия (BSO:V). Кристаллы выращены по методу Чохральского. Исследования выполнены в спектральном диапазоне для таких энергий фотонов $h\nu = 2 - 3.4$ эВ при варьировании температуры в циклах «охлаждение - нагрев» в диапазоне $330 \rightarrow 85 \rightarrow 300$ К. Установлено, что крайовое оптическое поглощение кристаллов BSO, BSO:V подчиняется правилу Урбаха, температурные циклы охлаждения – нагрев характеризуются гистерезисом спектрально-температурных зависимостей поглощения. Использована модель электрон-фононного взаимодействия (ЭФВ) в оптических переходах, формирующих край поглощения. В рамках данной модели влияние ионов ванадия заключается в появлении аномалий температурных зависимостей параметра, характеризующего ЭФВ - $\sigma(T)$, а также аномалий изоабсорбционной ширины запрещённой зоны E_g^a (T).

Ключевые слова: крайовое оптическое поглощение, температурные зависимости, кристаллы $\text{Bi}_{12}\text{SiO}_{20}$, легированные ванадием, правило Урбаха, температурный гистерезис.

1. Introduction

Sillenite family crystals with common formula $\text{Bi}_{12}\text{MO}_{20}$ (BMO, where $M = \text{Si, Ge, Ti, etc.}$) have a group of unique useful properties. This causes their successful application in different fields of functional electronics. Particular attention paid to use sillenite as a light modulating element base in devices of different types, as well as devices dynamic holography and optoinformatics. Recording, processing and storage of optical information in these devices based on high photosensitivity of BMO ($\sim 10^{-5} \text{ J/cm}^2$ at the blue-green region of the spectrum near the fundamental absorption edge) in conjunction with reversible photochromic and photorefractive effects [2-5].

A large amount of work was done to expand their application possibilities in optimization BMO spectroscopic properties by doping procedure. It was shown that the intra-center electronic transitions in the impurity d-elements (Cr, Mn, Fe, Cu, Mo, Ag) affect the photochromic effect [6-10]. However, BMO are wide band gap semiconductors (band gap (BG) $\Delta E_g \approx 3.3 \text{ eV}$) and it is also important to study the possibility of changing the structure of local levels in BG by embedding the impurity introduction d-elements, i.e. varying impurity optical absorption and photoconductivity.

The role of d-electrons in formation of the energy states in BG is a complex question. For example, energy states can be formed as result of hybridization t_2 and e -states, which formed by splitting d -states of impurity ions in crystal field, with the band states [11]. Such states are ejected from the valence band in BG and could significantly affect the mechanism of electron transitions that form the fundamental optical absorption edge. However, impact of d-elements on sillenites absorption edges remains mostly unstudied.

Results of experimental investigation of the temperature dependence of optical absorption edge for undoped crystals (BSO) and crystals doped by vanadium 3d-ions (BSO:V) are presented in the paper.

2. Experiment setup

Crystals BSO and BSO:V where grown by Czochralski process along crystallographic direction [001]. Emission spectrum analyses show content of the dopant vanadium in BSO:V at 0.06 mass.%. The samples were prepared as polished plates with a thickness of 2.52 mm for BSO and of 5.02 mm for BSO:V. Sample area was $8 \times 7 \text{ mm}^2$. Optical transmission spectra $t(h\nu, T_i)$ were obtained within a spectral energy range of $h\nu = 2 - 3.4 \text{ eV}$ by using a double-beam spectrophotometer «Specord-M40» and a nitrogen cryostat with built-in crystal holder and heater. The spectral region overlaps a region where BSO crystal is transparent. Parameter T_i is the measurement temperature. It discretely changed in cycle "cooling - heating" in the range of $T = 300 \rightarrow 85 \rightarrow 300 \text{ K}$ at the rate $\approx 10 \text{ K} \cdot \text{c}^{-1}$ with a step $5 \div 10 \text{ K}$. In order to eliminate the influence of backward scattered light all manipulations (heating, placing a sample in a cryostat) were carried out with a weak red illumination that does not cause the photochromic effect. The optical absorption $\alpha(h\nu, T_i)$ spectra were calculated from the transmittance as described in [12].

3. Results and discussion

The following results were obtained. Dope of V - ions leads to change in color from yellow-brown, for undoped BSO, to light orange. This result similar to discoloration of BSO for Al^{3+} and Ga^{3+} acceptors, which replace Si^{4+} ions in centers of oxygen tetrahedrons in BSO crystal lattice. These acceptors compensate donor centers, the presence of which is due to native defects in BSO, which, in turn, reduce impurity absorption (bleaching) and photoconductivity. We can assume that levels of BG infused by vanadium ions are also acceptors.

There is no an absorption shoulder, which is correlated with a maximum of spectral impurity photosensitivity for BSO in the blue-green spectral range, in optical absorption spectra of BSO:V, poorly structured as opposed to BSO.

Functions $\alpha(h\nu, T_i)$ for both of crystals (BSO and BSO:V) rises quickly and monotonically with increasing the photon energy $h\nu$ as it is close to the absorption edge. In addition, they are shifted to longer wavelengths ("red" shift) with a temperature increase. Such kind of behavior $\alpha(h\nu, T_i)$ is similar to the Urbach rule [1]:

$$\alpha(h\nu, T_i) = \alpha_0 \exp\left[\sigma(T) \frac{h\nu - E_0}{kT}\right], \quad (1)$$

α_0 , E_0 are coordinates of the convergence point of $\ln(\alpha(h\nu, T_i))$, parameter $\sigma(T) = \Delta \ln(\alpha(h\nu, T_i)) / \Delta(h\nu)$ is a steepness of the dependences, k is the Boltzmann constant. The representation of dependencies $\alpha(h\nu, T_i)$ in semilogarithmic $\ln(\alpha(h\nu, T_i))$ scale confirms the performance of the Urbach rule (Fig.1).

Extrapolation to the high values of $h\nu$ linear sections of these dependencies meet in a point with coordinates α_0 and E_0 . It should be noted that this points were different not only for different crystals but also for heating and cooling cycles (Table 1). At the same time E_0 correlate with BSO BG at low temperatures.

Table 1

Urbach rule parameters

Temperature cycle	Crystal	Parameters					
		α_0, cm^{-1}	E_0, eV	σ_0	g	$A \cdot 10^4, \text{eVK}^{-1}$	θ, K
Cooling	BSO	307,9	3.1	0,29	2,3	2,64	107,8
Heating	BSO	445,9	3.1	0,33	2	3,41	104,2
Cooling	BSO:V	42,9	2.65	0,17	4	2,98	78
Heating	BSO:V	35,5	2.65	0,3	2	4,05	73,9

In a model interpretation of the Urbach rule the $\sigma(T)$ dependences are explained by participation of excitons or phonons in the interband valence band \rightarrow conduction band transitions. In the case of the phonon participation, the dependence should be as follows

$$\sigma(T) = \sigma_0 \left(\frac{2kT}{h\nu_p} \right) \tanh\left(\frac{h\nu_p}{2kT} \right), \quad (2)$$

where $h\nu_p$ is an effective phonon energy in a single oscillator model, σ_0 is a parameter associated with constant g , which determine a value of the electron-phonon interaction (EPI) as $g = (2/3)(\sigma_0)^{-1}$.

The obtained dependences $\sigma(T)$ well converge for undoped BSO, where they are virtually identical in the cycles of cooling and heating. Anomalous jumps in the $\sigma(T)$ dependencies were observed at $T_1 = 200$ and $T_2 = 270$ K for BSO:V crystal. Besides, dependences $\sigma(T)$ are significantly different for cycles cooling and heating (Fig. 2).

The values of σ_0 , $h\nu_p$ and g are given in table 1. For both crystals EPI force place a major, $g > 1$, which is typical fore for predominance of ion-covalent bonds. In binary semiconductors of A^{III}B^V type, were $g \ll 1$ covalent bonds are predominant. Furthermore, the influence of vanadium appears in increase of EPI (relatively to BSO) in cooling cycles, while cycles of heating performs the same value of g .

For many of semiconductors and dielectrics anomaly temperature dependences of $\sigma(T)$ are accompanied with the temperature anomalies of so-called optical pseudo-gap $E_g^\alpha(T)$, which is determined as an energy coordinate at the same absorption coefficient α , and is measured at different temperatures. In interpretation with a significant role of phonons the dependence is approximated by the following expression

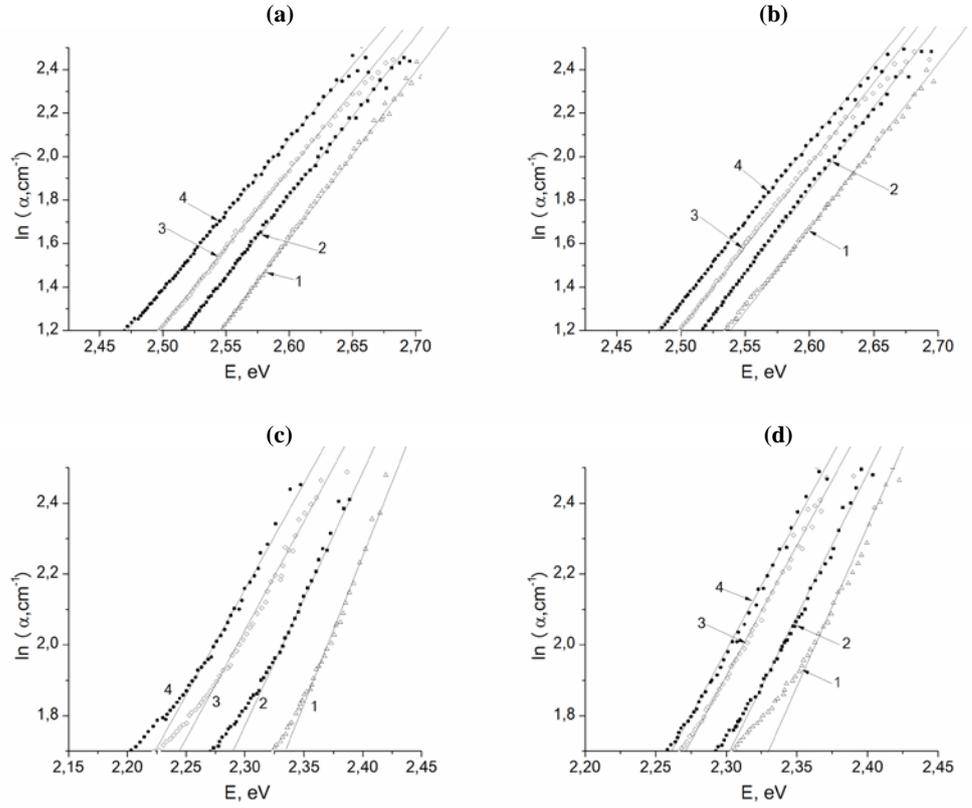


Fig. 1. Dependences $\ln(\alpha(h\nu, T_i))$ for crystals BSO (a, b) and BSO:V (c, d) for cycles: cooling (a, c) and heating (b, d) at $T = 85$ (b,1;c,1;d,1), 173 (a,1;c,1;d,2), 203(b,2), 233 (a,2;b,3;c,2), 253 (a,3;c,3;d,3), 273 K (a,4;b,4;c,4;d,4).

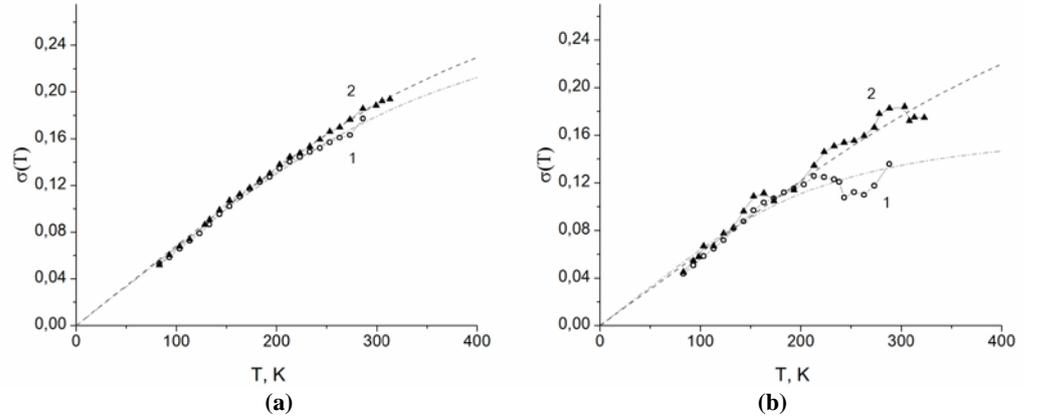


Fig. 2. Dependences $\sigma(T)$ for crystals (a) - BSO: cooling (1), heating (2) ; (b) - BSO:V : cooling (1), heating (2)

$$E_g^\alpha(T) = E_g^\alpha(0) + \frac{AT^2}{\theta + T}, \quad (3)$$

A and θ – empirical constants, and θ must correlate with the value of the Debye temperature for these materials, $E_g^\alpha(0)$ – extrapolated value of $E_g^\alpha(T)$ at $T = 0$ K. The obtained dependencies $E_g^\alpha(T)$ showed at Fig.3, we see that they are well approximated by (3),

only for the heating cycle of the crystals. For the cooling cycle, there are anomalies that do not correlate with the temperature dependences of anomalies $\sigma(T)$. Effect of vanadium is shown in the values A and θ (Table. 1) and a greater degree of deviation dependencies $E_g^\alpha(T)$ described in the expression (3).

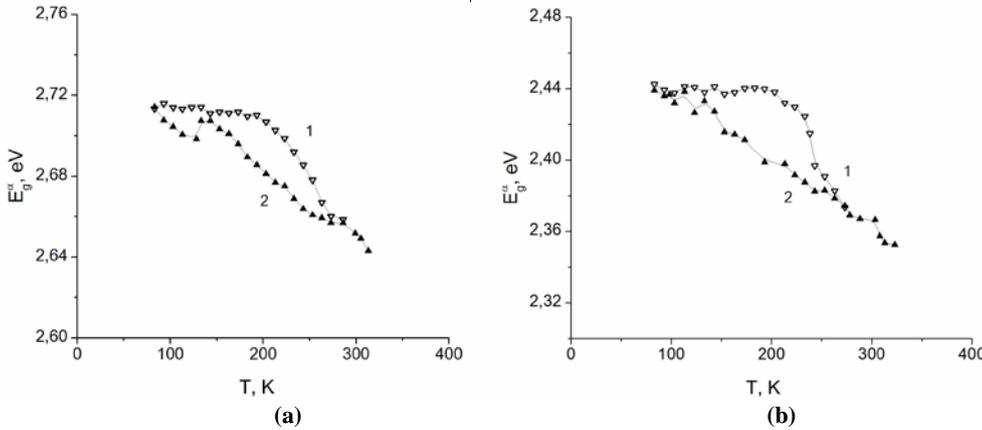


Fig. 3. Dependencies $E_g^\alpha(T)$ for $\alpha = 12,1 \text{ cm}^{-1}$ crystals (a) - BSO: cooling (1), heating (2) ; (b) - BSO:V : cooling (1), heating (2)

4. Conclusions

The results show a significant temperature hysteresis, which presents itself in different spectra of $\alpha(h\nu, T)$ dependencies $\sigma(T)$ and $E_g^\alpha(T)$ measured at the same temperature T_i cycles of cooling and heating. This situation can be explained by assuming that the electronic optical transitions occur between the "tails" of acceptor ionization states density (shallow levels), near valence band top and conduction band. In undoped BSO such a kind of acceptors could be present as Bi^{3+} , replacing Si^{4+} ions in the centers of oxygen tetrahedrons. Their presence is confirmed with neutron spectroscopy research [13]. Vanadium ions as acceptors can displace antisite bismuth and create own "tails" density of states, the shape and size of these "tails" determine the difference of spectral dependencies $\alpha(h\nu, T)$. The long-optical shift of the curves $\alpha(h\nu, T)$ with temperature rise, are mostly, due to, temperature dependence of BG, which is close to linear. Anomalies of dependencies $\sigma(T)$ and $E_g^\alpha(T)$ may be caused by additional ionization of acceptors due to the level-depopulation of some shallow donor levels near the bottom of the conduction band with temperature decreases. In this case the subsequent heating cycle will take place without the redistribution of electrons between the donor and acceptor and anomalies will disappear, as it takes place for BSO crystals. However, for BSO crystals anomalies do not vanish completely. Perhaps they have other nature.

Similar anomalies of Urbach rule parameters were observed in many materials with exponential shape of the absorption edge: SbSI , Sb_2S_3 , $\text{Gd}_2(\text{MoO}_4)_3$, KH_2PO_4 , KTN , KTaO_3 , PbZrO_3 , BaTiO_3 , CdTiO_3 , SrTiO_3 , PbTiO_3 , NaNbO_3 , LiNbO_3 . In [14] these anomalies are associated with phase transitions of a particular nature (such as "melt - crystal", "non-polar phase - ferroelectric phase"). However, there are no phase transitions in the studied temperature range for tested sillenite crystals. So, additional studies are required to resolve the nature of these anomalies.

References

1. **Ihor Studenyak.** Urbach Rule in Solid State Physics / Ihor Studenyak , Mladen Kranjčec , Mykhailo Kurik // International Journal of Op-tics and Applications - 2014, 4(3) - p.76-83.
2. **Roman V. Romashko** Fast photogalvanic response of a $\text{Bi}_{12}\text{GeO}_{20}$ / Roman V. Romashko, Alexander I. Grachev, Yuri N. Kulchin, and Alexei A. Kamshilin //Optics Express 20 - December 2010. - vol. 18, No. 26 2714
3. **Yoshimasa Kawata** Randomly accessible, multilayered optical memory with a $\text{Bi}_{12}\text{GeO}_{20}$ crystal/ Yoshimasa Kawata, Takuo Tanaka, and Satoshi Kawata//Applied Optics -10 September 1996.- Vol. 35, No. 26
4. **Asja Veber.** Synthesis and Characterization of $\text{Bi}_{12}\text{GeO}_{20}$ Thin Films. // LAP Lambert Academic Publishing, (2011-08-06) - Number of pages:132.
5. **Malinovskij V.K.** Fotoinducirovannye yavleniya v sillenitax / Malinovskij V.K., Gudaev O.A., Gusev V.A., Demenko S.I.// Novosibirsk: Nauka, 1990. - 160 s.
6. **W. Wardzynski** “ The center of orthorhombic symmetry in chromium doped $\text{Bi}_{12}\text{GeO}_{20}$ and $\text{Bi}_{12}\text{SiO}_{20}$ single crystals”/ W. Wardzynski, H. Szymzak //J. Phys. Chem. Solids. V.45, № 8/9, pp. 887 – 896, 1984
7. **W. Wardzynski** “Ling-induced charge transfer processes in Mn-doped $\text{Bi}_{12}\text{GeO}_{20}$ and $\text{Bi}_{12}\text{SiO}_{20}$ single crystals”/ W. Wardzynski, H. Szymzak, M.T.Borowiec, K.Pataj. // . J. Phys. Chem. Solids. v.46, № 10, pp. 1117 – 1129, 1985.
8. **Panchenko T.V.** Fotoxromnyj effekt v kristallax $\text{Bi}_{12}\text{SiO}_{20}$, legirovannyx Cu i Ag. / Panchenko T.V., Strelec K.Y. //FTT. 50, 1824-1830 (2008).
9. **Panchenko T.V.** fotoxromnyj effekt v kristallax $\text{Bi}_{12}\text{SiO}_{20}$, legirovannyx molibdenom,/ Panchenko T.V., Strelec K.Y.// FTT. 51, 277-281 (2009).
10. **P. Petkova.** λ -modulation absorption spectra and photochromic effect in $\text{Bi}_{12}\text{SiO}_{20}$: Fe single crystal / P. Petkova, B. Kostova, V. Marinova and J. Tacheva. // IOP Conf. Series: Materials Science and Engineering 15 (2010).
11. **Sokolov V.I.** novyj sposob identifikacii struktury energeticheskogo sostoyaniya 3d- pri-mesi v poluprovodnikax. / Sokolov V.I., Surkov T.P. // Optika i spektroskopiya t.65, vyp.2, s 482-484. – 1988.
12. **Panchenko T.V.** Termoopticheskoe issledovanie glubokix urovnej v legirovannyx kristal-lax $\text{Bi}_{12}\text{SiO}_{20}$ // FTT 40, 452- 457 (1998).
13. **Radaev S.F.** Struktura sillenitov i atomnye mexanizmy izomorfnyx zameshhenij v nix/ Radaev S.F., Simonov V.I. // Kristallografiya 37, 914-944 (1992).
14. **V. I. Zamktin.** Absorption Edgo Anomalies in Polar Semiconductors// phys. stat. sol. – 1984. - (b) 124, 625

Received 15.06.2015.