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The acceptors behavior in the Single and Double Doped $\text{Bi}_{12}\text{TiO}_{20}$

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Abstract: The absorption coefficient of $\text{Bi}_{12}\text{TiO}_{20}:\text{AlI}$, $\text{Bi}_{12}\text{TiO}_{20}:\text{AlII}$, $\text{Bi}_{12}\text{SiO}_{20}:\text{P}$ and $\text{Bi}_{12}\text{SiO}_{20}:\text{Al}+\text{P}$ single crystals is measured in the spectral region of Urbach's rule (1.52 – 2.92 eV) at room temperature. The parameters of electron-phonon interaction, Urbach's energy and the constants of Urbach's rule are calculated. The behavior of the acceptors Al^{3+} and P^{5+} in Urbach's rule region has been considered.

Keywords: doped sillenites, Urbach's rule, electron-phonon interaction, Urbach's energy.

Introduction

The crystals $\text{Bi}_{12}\text{TiO}_{20}$ (BTO) are large optically homogeneous photorefractive materials. Their strong photochromic effect, high photosensitivity and high carrier mobility which permit achievements of fast response time are of special interest for real-time holography, optical-phase conjugation, amplification of weak light signals, image processing, etc. [1-5]. The doping of these crystals with different impurities change their physical and chemical properties. In this work the electron-phonon interaction in doped BTO is discussed and then it is compared with the same interaction in undoped material.

Materials and Methods

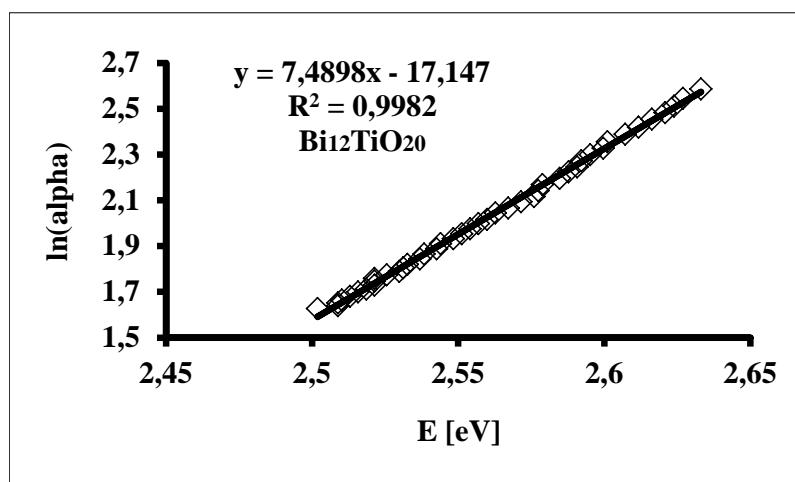
The investigated BTO crystals, either undoped or doped with Al, P and co-doped with Al+P were grown from stoichiometric melts $\text{Bi}_2\text{O}_3:\text{TiO}_2 = 11:1$ using the Czochralski method under conditions

described in detail elsewhere [6]. High purity Bi_2O_3 (99.9999%), TiO_2 (99.9999%), Al_2O_3 (99.9995%) and P_2O_5 (99.9995%) were used for synthesis and doping. The elementary sillenite crystal cell is built of two structural units – TiO_4 tetrahedra and BiO_7 octahedra [6]. The concentration of P^{5+} is $8 \times 10^{18} \text{ cm}^{-3}$ in BTO:P and the concentration of this ion is $5 \times 10^{18} \text{ cm}^{-3}$ in BSO:Al+P. The Al^{3+} ions are inculcated on the BTO:AlI and BTO:AlII with the concentrations respectively $7 \times 10^{18} \text{ cm}^{-3}$ and $5 \times 10^{19} \text{ cm}^{-3}$. These ions are inculcated on the co-doped crystal with the concentration $7 \times 10^{18} \text{ cm}^{-3}$.

The experimental set up for measurement of the absorption coefficient in the visible region consists of the following: a halogen lamp with a stabilized 3H-7 rectifier, a SPM-2 monochromator, a system of quartz lenses, a crystal sample holder, and a Hamamatsu S2281-01 detector. The experimental dependence $\ln\alpha(E)$ for all the investigated crystals is presented in Figure 1. Urbach's energy for undoped and doped BTO in the spectral region 1.52 – 2.92 eV is shown in Figure 2. The cross-section (σ_a) of the impurity absorption for the undoped and doped $\text{Bi}_{12}\text{TiO}_{20}$ is presented in Figure 3.

Results and Discussion

The behaviour of the absorption coefficient α has been investigated at the absorption edge using the Urbach's formula $\ln\alpha = A + B(\hbar\omega/T)$, where A and B are the constants, T is the temperature. The constant B is expressed by the dependence $B = \sigma(T)/k$, where $\sigma(T)$ is the parameter characterizing the slope of the absorption edge, k is the Boltzmann constant. The value of $\sigma(T)$ is 0.19 for $\text{Bi}_{12}\text{TiO}_{20}$ and $\sigma(T)$ varies from 0.12 to 0.24 in the case of doped $\text{Bi}_{12}\text{TiO}_{20}$ (Table 1). The value of the parameter $\sigma(T)$ is biggest for double doped crystal. The reason of this value is the influence of P^{5+} ions in the lattice of BTO. On the other hand, we have the next equation $W_d = kT/\sigma$ [7]. The magnitude W_d describes the broadening of the absorption edge due to the dynamic disorder. When the temperature is higher, the absorption edge is wider due to the dynamic disorder in the crystal lattice. $W_d = 136 \text{ meV}$ for undoped BTO and $W_d = 108 - 216 \text{ meV}$ for doped BTO (Table 1).



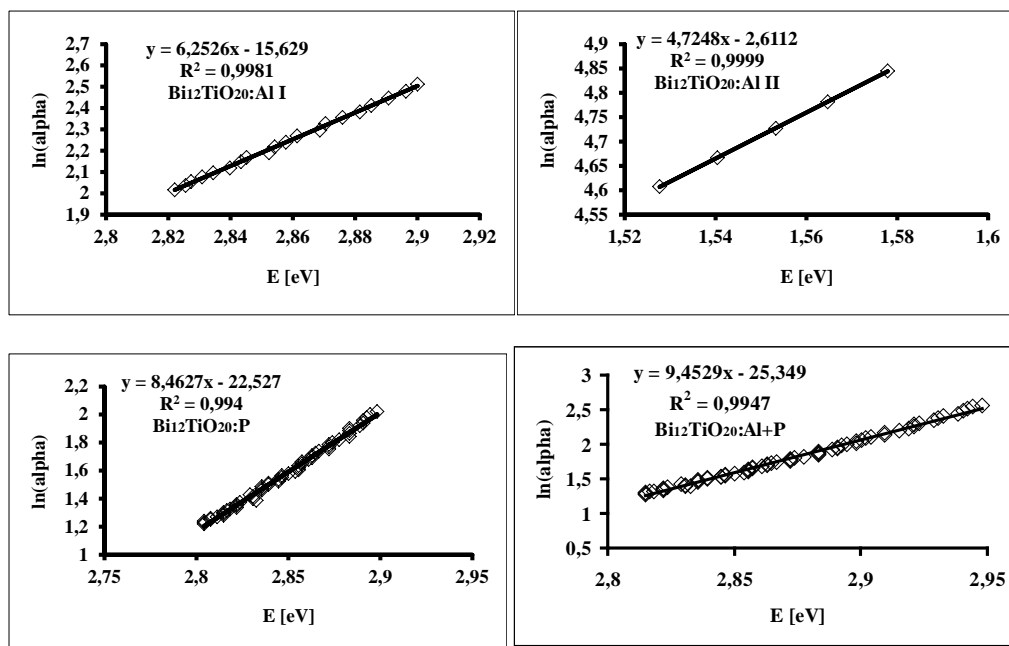


Figure 1. The experimental dependence $\ln\alpha(E)$ for all the investigated crystals

Therefore, we can generalize that the absorption edge of BTO:Al+P has smallest dynamic disorder in the crystal lattice due to the phosphorus. The Al^{3+} leads to the large dynamic disorder in the doped sillenites. The $\sigma(T)$ and W_d are calculated at room temperature ($T = 300$ K). The approximation of the experimental data shows that $\sigma(T) = \sigma_0(2kT/h\nu_0)\text{th}(h\nu_0/2kT)$, where $h\nu_0$ is the energy of the effective phonons, strongly interacting with photons, and σ_0 is the high temperature constant [8]. The magnitude $h\nu_0$ for our investigated crystals corresponds to the energy $h\nu_0 = 31.7$ meV of the longitudinal optical phonons ($\omega = 257$ cm^{-1}) which are observed in the IR absorption spectra of BSO [9]. In our case, the obtained values of σ_0 are as follows: $\sigma_0 = 0.19$ ($\text{Bi}_{12}\text{TiO}_{20}$) and $\sigma_0 = 0.12 - 0.24$ (doped $\text{Bi}_{12}\text{TiO}_{20}$) (Table 1). When we compare the values of σ_0 for our samples with the values of the same constant, obtained in [10], we can summarize that our undoped sillenite has a small surplus of Bi ions in the crystal lattice. The dependence $g = 2/3\sigma_0$ determines the strength of the electron-phonon interaction [9]. When $g > 1$, the electron-phonon interaction is strong. The value of the strength g is 3.51 for undoped BTO and $g = 1.32 - 5.56$ for doped BTO (Table 1).

Table 1. The parameters which are characterized the Urbach's rule region

| samples | σ | σ_0 | g | W_d [meV] |
|---|----------|------------|------|-------------|
| $\text{Bi}_{12}\text{TiO}_{20}$ | 0.19 | 0.19 | 3.51 | 136 |
| $\text{Bi}_{12}\text{TiO}_{20}:\text{AlI}$ | 0.16 | 0.16 | 4.17 | 162 |
| $\text{Bi}_{12}\text{TiO}_{20}:\text{AlII}$ | 0.12 | 0.12 | 5.56 | 216 |
| $\text{Bi}_{12}\text{TiO}_{20}:\text{P}$ | 0.22 | 0.22 | 1.32 | 118 |
| $\text{Bi}_{12}\text{TiO}_{20}:\text{Al+P}$ | 0.24 | 0.24 | 2.78 | 108 |

Hence, we can conclude that the impurity ions change by different way the electron-phonon interaction in the crystal lattice. The P^{5+} ions make the electron-phonon interaction very weak in the sillenites. Thus the electron-phonon interaction is weaker in BSO:Al+P. On the other hand, the Al^{3+} ions lead to the strong electron-phonon interaction in BTO:AlI and BTO:AlII. The Urbach's region for BTO:AlI, BTO:P and BTO:Al+P are almost identical (Figure 2).

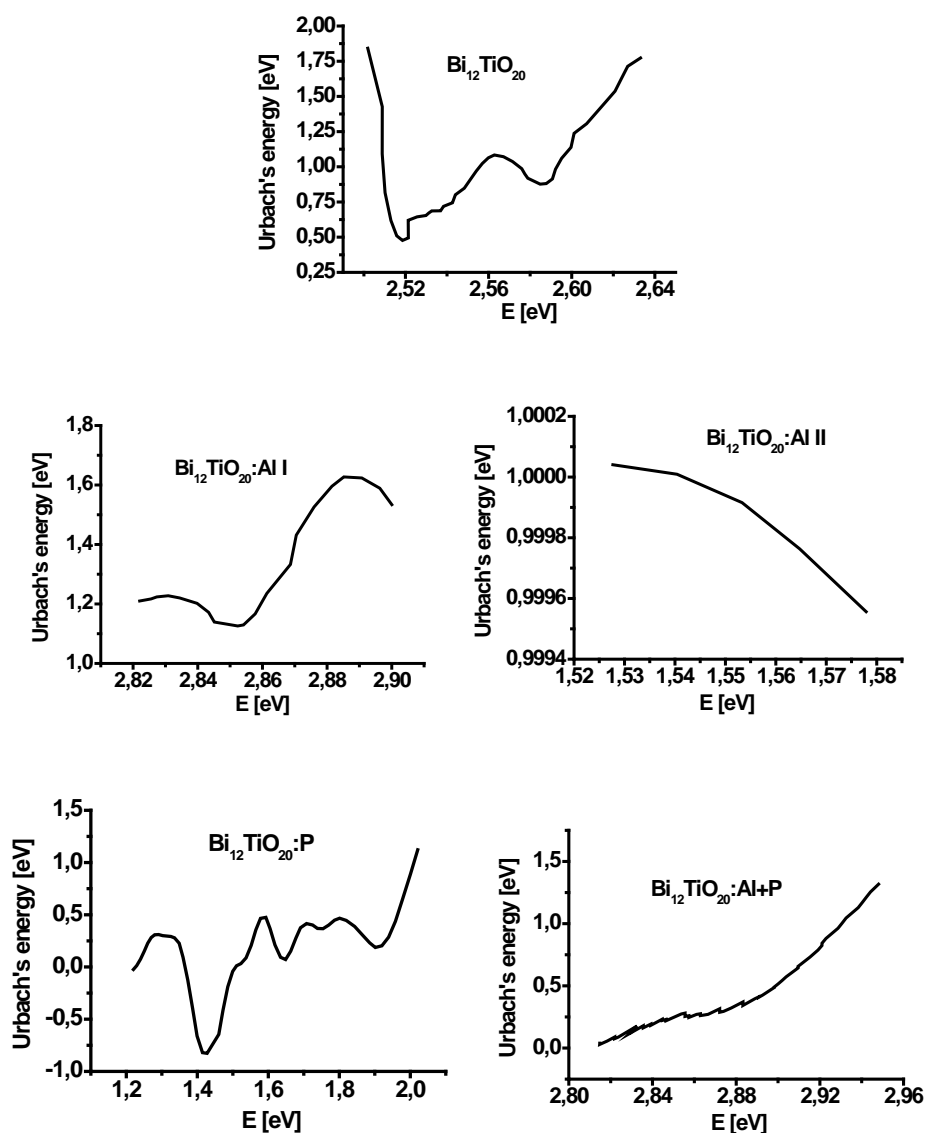


Figure 2. Urbach's energy for the undoped and doped $Bi_{12}TiO_{20}$

The Urbach's region is shifted to the lower energies for BTO:AlII and BTO:P. Hence the Urbach's region is shifted to the higher energies for BTO:AlI and BTO:Al+P (Figure 2). The Urbach's energy is connected with the carrier impurity interaction, the carrier-phonon interaction and the structural disorder [11]. That is why this energy is calculated by the formula $E_u = \alpha(E)/(d\alpha/dE)$. The E_u is not a constant for undoped and doped crystals in the spectral region 1.52 – 2.92 eV. The values of the

Urbach's energy E_u decrease for all doped samples (Figure 3). Next step in the calculations is the determination of the cross-section of the impurity absorption [12]. It is very important to establish how the radiation is absorbed by the impurity ions in the crystals. The total cross-section σ_a of the impurity absorption is defined by the integration within the absorption band of the impurity ions

$$\sigma_a = (1/N) \int_{E_1}^{E_2} \alpha(E) dE,$$

where N is the number of the impurity ions in the unit volume, α is the impurity absorption coefficient typical of an energetic interval from E_1 to E_2 . $E_1 = 1.52$ eV and $E_2 = 2.92$ eV for the investigated crystals here. The cross-section σ_a can vary significantly from one absorption band to another (Figure 3).

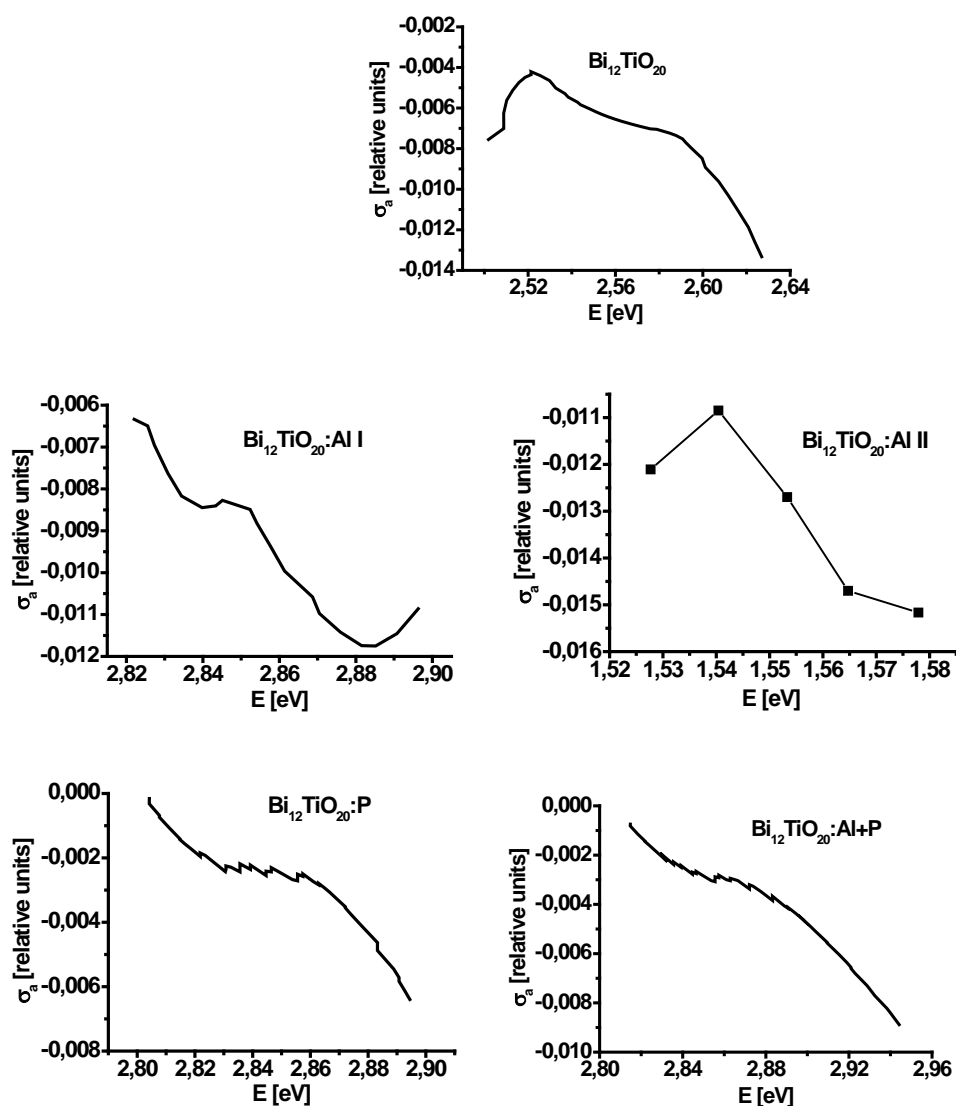


Figure 3. The cross-section (σ_a) of the impurity absorption for the undoped and doped $\text{Bi}_{12}\text{TiO}_{20}$

Conclusions

1. The curve of Urbach's energy describes: 1) maximum for BTO, 2) minimum for BTO:AlI, 3) convex slope for BTO:AlII, 4) concave slope for BTO:Al+P and 5) some impurity structure for BTO:P.
2. The Al^{3+} ions (BTO:AlI) have influence in the spectral region 2.82-2.9 eV and the Al^{3+} ions (BTO:AlII) have their influence in the spectral region 1.52-1.58 eV. The P^{5+} ions (BTO:P) have influence in the same spectral region as the Al^{3+} ions (BTO:AlI) and phosphorus has dominant influence in the comparison with aluminium (BTO:Al+P) in the spectral region 2.8-2.96 eV.

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References

- [1] Georges M.P., Lemaire Ph.C., Phase-shifting real-time holographic interferometry that uses bismuth silicon oxide crystals, *Appl. Opt.*, **1995**, 34, 7497.
- [2] Pouet B., Krishnaswamy S., Dynamic holographic interferometry by photorefractive crystals for quantitative deformation measurements, *Appl. Opt.*, **1996**, 35, 787.
- [3] Rajbenbach H., Huignard J.P., Refregier P., Amplified phase-conjugate beam reflection by four-wave mixing with photorefractive $\text{Bi}_{12}\text{SiO}_{20}$, *Opt. Lett.*, **1989**, 14, 128.
- [4] Vainos N.A., Gower M.C., High-fidelity image amplification and phase conjugation in photorefractive $\text{Bi}_{12}\text{SiO}_{20}$, *Opt. Lett.*, **1991**, 16, 363.
- [5] Tonchev D., Zhivkova S., Miteva M., Holographic interferometric microscope on the basis of BTO monocrystals, *Appl. Opt.*, **1990**, 29, 4753.
- [6] Marinova V., *Optical Materials*, **2000**, 15, 149-158.
- [7] Kunets V., Kulish N., Kunets Vas., Lisitsa M., *Semiconductor Physics, Quantum Electronics & Optoelectronics*, **2002**, 5, 9.
- [8] Kurik M., *Phys. Status Solidi (a)*, **1971**, 8, 9.
- [9] Woidovsky W., Lukasiewicz T., Nazariwicz W., Zmija J., *Phys. Status Solidi (b)*, **1979**, 94, 649.
- [10] Panchenko T., Kopylova S., Osetskié Yu., *Solid State Physics*, **1995**, 37, 1415.
- [11] Faruque Ahmed Sk., Moon Myoung-Woon, Lee Kwang-Ryeol, *Thin Solid Films*, **2009**, 517, 4035.
- [12] *Optical Properties of Condensed Matter and Applications*, Edited by Jai Singh, John Wiley & Sons **2006**.