The electron-phonon interaction in $Bi_{12}SiO_{20}$ doped with Fe^{3+}, Cr^{3+} and P^{5+} ions

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The absorption coefficient of $Bi_{12}SiO_{20}$:Fe, $Bi_{12}SiO_{20}$:P and $Bi_{12}SiO_{20}$:Cr+P single crystals is measured in the spectral region of Urbach's rule (2.5–3.1 eV) at room temperature. The parameters of electron-phonon interaction, Urbach's energy and the constants of Urbach's rule are calculated. It is established the behavior of the donors Fe^{3+} and Cr^{3+} and this of the acceptor P^{5+} in Urbach's rule region.

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

INTRODUCTION

The crystals $Bi_{12}SiO_{20}$ are piezoelectric, electro- and magnetooptic materials. The optical activity, photoconductivity and photorefractivity are a characteristic for BSO and their combination allow the use of these materials in various acousto and opto-electronic devices (piezo sensors, space-time light modulators etc.) [1, 2, 3, 4]. The doping of these crystals with different impurities change their physical and chemical properties. Therefore, the electron-phonon interaction is discussed in doped BSO and then it is compared with the same interaction in these materials in the frame of this work.

EXPERIMENTAL

The investigated BSO crystals, either undoped or doped with Cr, P and co-doped with Cr+P were grown from stoichiometric melts Bi_2O_3:SiO_2 = 6:1 using the Czochralski method under conditions described in detail elsewhere [5]. High purity Bi_2O_3, SiO_2, Cr_2O_3 and P_2O_5 were used for sythesis and doping. The concentration of P^{5+} is 1.6×10^{20} N/cm^{-1} in BSO:P and the concentration of this ion is 1.13×10^{20} N/cm^{-1} in BSO:Cr+P. The Cr^{3+} ions are inculcated on the BSO:Cr with the concentration 8.6×10^{18} N/cm^{-1} and these ions are inculcated

on the co-doped crystal with the concentration 8.1×10^{16} N/cm^{-1}. The thickness of the samples is as follows: $d_{BSO:Cr+P}$ = 0.101 cm, $d_{BSO:P}$ = 0.062 cm.

The Fe^{3+} ions were inculcated on the crystal lattice as Fe_2O_3 oxide. The concentration of Fe dopant 1.4×10^{18} N/cm^{-3} into the grown crystal was determined by flame (Zeeman 3030) and electro-thermal atomic (Varian 240) absorption spectrometry. The thickness of BSO:Fe is $d_{BSO:Fe}$ = 0.152 cm and the thickness of the undoped sample is d_{BSO} = 0.04 cm. 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 polarizer, a crystal sample holder, and a Hamamatsu S2281-01 detector.

The experimental dependence lnα(E) for all the investigated crystals is presented in Fig. 1. Urbach's rule for undoped and doped BSO in the spectral region 2.5–3.1 eV is shown in Fig. 2. Urbach's energy for the undoped and doped $Bi_{12}SiO_{20}$ is presented in Fig. 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 0.27 for $Bi_{12}SiO_{20}$ and $\sigma(T)$ var-

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

sillenites at T = 300 K	σ	σ$_0$	g	W$_d$ [meV]	E$_0$ [meV]	σ$_a$[cm^2]
Bi$_{12}$SiO$_{20}$	0.27	0.27	2.47	96	301	–
Bi$_{12}$SiO$_{20}$:Fe	0.32	0.32	2.08	81	239	1.83×10^{-18}
Bi$_{12}$SiO$_{20}$:Cr+P	0.52	0.52	1.28	50	154	7.91×10^{-17}
Bi$_{12}$SiO$_{20}$:P	0.88	0.88	0.76	29	97	4.87×10^{-17}

ies from 0.32 to 0.88 in the case of doped Bi$_{12}$SiO$_{20}$ (Table 1). The BSO:Fe has a value of σ(T) close to that of undoped sample. The value of the parameter σ(T) is biggest for P^{5+} ions. This is the reason for the bigger value of this parameter for co-doped BSO.

On the other hand, we have the next equation W$_d$ = kT/σ [6]. 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$_d$ = 96 meV for undoped BSO and W$_d$ = 29–81 meV for doped BSO (Table 1). Therefore, we can generalize that the absorption edge of BSO:P has smallest dynamic disorder in the crystal lattice due to the phosphorus. Therefore this fact, the dynamic disorder has small value in BSO:Cr+P. The Fe^{3+} leads to the large dynamic disorder in the doped sillenites. The σ(T) and W$_d$ are calculated at room temperature (T = 300 K).

The approximation of the experimental data shows that σ(T) = σ_0(2kT/hν_0)th(hν_0/2kT), where hν_0 is the energy of the effective phonons, strongly interacting with photons, and σ_0 is the high temperature constant [7]. The magnitude hν_0 for our investigated crystals corresponds to the energy hν_0 =

31.7 meV of the longitudinal optical phonons (ω = 257 cm^{-1}) which are observed in the IR absorption spectra of BSO [8].

In our case, the obtained values of σ_0 are as follows: σ_0 = 0.27 (Bi$_{12}$SiO$_{20}$) and σ_0 = 0.32 – 0.88 (doped Bi$_{12}$SiO$_{20}$) (Table 1). When we compare the values of σ_0 for our samples with the values of the same constant, obtained in [9], we can summarize that our undoped sillenite has a small surplus of Bi ions in the crystal lattice.

The dependence g = 2/3σ_0 determines the strength of the electron-phonon interaction [8]. When g > 1, the electron-phonon interaction is strong. This strength has a highest value (g = 2.47) for undoped BSO and g = 0.76 – 2.08 for doped BSO (Table 1). Therefore, we can conclude that the impurity ions reduce this interaction in the crystal lattice. The P^{5+} ions make the electron-phonon interaction very weak in the sillenites. Therefore the electron-phonon interaction is a weaker in BSO:Cr+P. On the other hand, the Fe^{3+} ions lead to the strong electron-phonon interaction in BSO:Fe.

The Urbach's region for undoped BSO is almost the same as for the sample BSO:Fe (Fig. 2). The Urbach's region is shifted (2.8–3.1 eV) for BSO:P
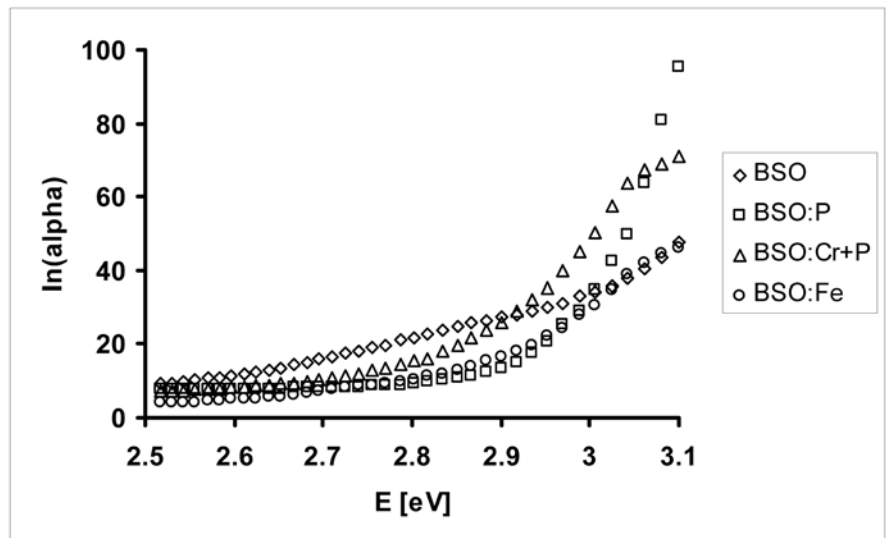

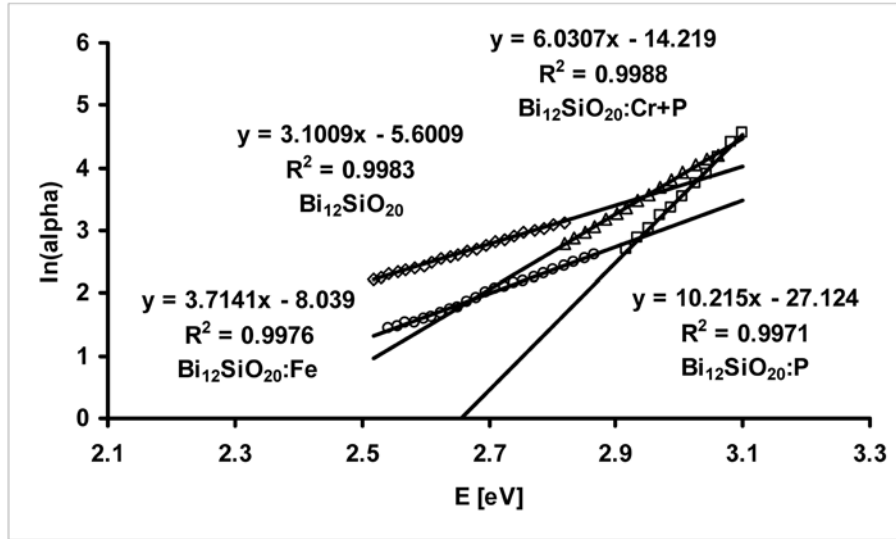**Fig. 1.** The experimental dependence lnα(E) for all the investigated crystals

and BSO:Cr+P. It is interesting that the phosphorus shifts the Urbach's region to the biggest energies. Therefore the absorption edge is shifted to the smallest wavelengths for BSO:P (Fig. 1).

The Urbach's energy is connected with the carrier impurity interaction, the carrier–phonon interaction and the structural disorder [10]. That is why this energy is calculated by the formula Eu = α(E)/(dα/dE). The Eu is not a constant for undoped and Fe doped crystals in the spectral region 2.5–3.1 eV. The values of the Urbach's energy of the BSO:Fe are smaller than the Eu of the BSO (Fig. 3a). The parameter $E_0 = 1/[d(ln\alpha)/d(h\nu)]$ is known as Urbach's slope [11]. We can see the values of E_0 at T = 300 K in Table 1 for undoped, doped and co-doped BSO. Next step in the calculations is the determination of
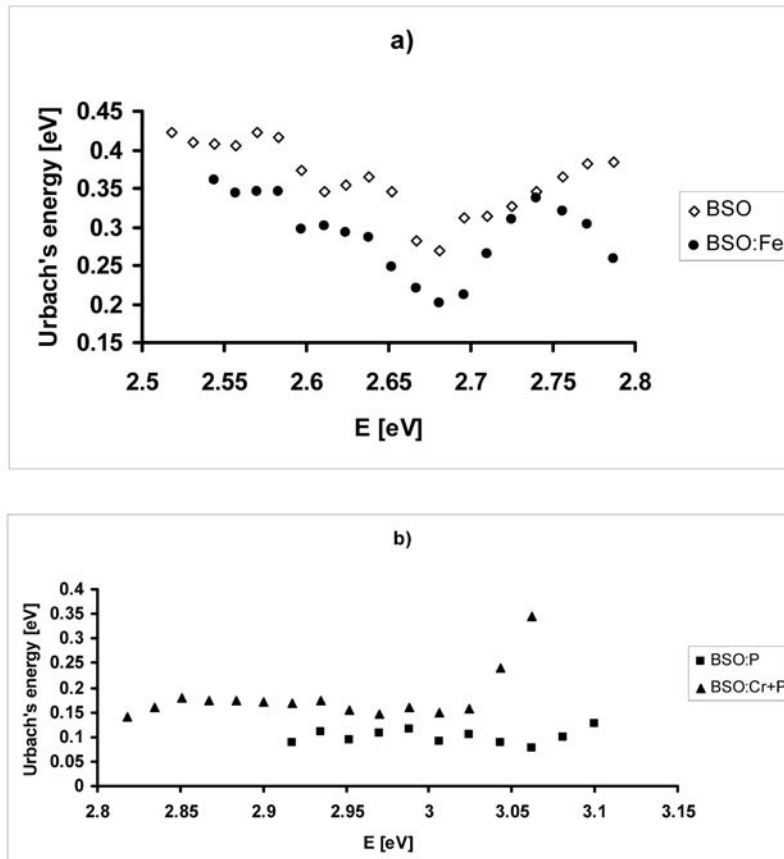

Fig. 3. Urbach's energy for the undoped and doped Bi$_{12}$SiO$_{20}$

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. For the investigated crystals here $E_1 = 2.5$ eV and $E_2 = 3.1$ eV. The cross-section σ_a can vary significantly from one absorption band to another. The value of σ_a is smallest for the crystal BSO:Fe and it is biggest for the co-doped BSO (Table1).

CONCLUSIONS

1. The parameter σ has the biggest value for BSO:P, but the electron-phonon interaction is the lowest in this case. The dynamic disorder in the crystal lattice is the smallest again in BSO:P. The value of the parameter E_0 is the smallest for the same crystal.

2. The acceptor P^{5+} has the greatest impact on the value of the cross-section σ_a.

3. The Urbach's energy for BSO:Fe in the spectral region 2.5–2.8 eV follows the shape of this energy for BSO. The shape of the Urbach's energy for BSO:Cr+P and BSO:P is the same.

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ЕЛЕКТРОН-ФОНОННО ВЗАИМОДЕЙСТВИЕ В $Bi_{12}SiO_{20}$, ЛЕГИРАН С ЙОНИТЕ Fe^{3+}, Cr^{3+} И P^{5+}

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(Резюме)

Измерен е коефициентът на поглъщане на единичните кристали $Bi_{12}SiO_{20}$:Fe, $Bi_{12}SiO_{20}$:P и $Bi_{12}SiO_{20}$:Cr+P в спектралния диапазон на правилото на Урбах (2,5–3,1 eV) при стайна температура. Изчислени са параметрите на електрон-фононното взаимодействие, енергията на Урбах и константите, участващи в правилото на Урбах. Установено е влиянието на донорите Fe^{3+} и Cr^{3+}, както и това на акцептора P^{5+} в областта на Урбах.