Factors determining optical absorption of variously doped single crystals of Bi$_{12}$SiO$_{20}$

B Kostova$^1$ and L Konstantinov

Institute of Mineralogy and Crystallography “Acad. I. Kostov”, Bulgarian Academy of Sciences, 1113 Sofia, 107 Acad. G. Bonchev str. Bulgaria

E-mail: bilyana_k@abv.bg

Abstract. Bi$_{12}$SiO$_{20}$ are widely used in optical devices, spatial-time light modulators and as holographic media depending on their properties in a wide spectral range. This work deals with the optical absorption coefficient of pure and doped Bi$_{12}$SiO$_{20}$ (BSO) crystals measured in the energy region 1.5 – 3.2 eV and generalise our already published and new experimental data on crystals doped with Al, P, Cr, Mn, Fe, Co, Ni, Cu, Se, Ru. It is shown that such doping affects differently the optical absorption in both the near-fundamental-edge shoulder (3.2 – 2.2 eV) and on impurity levels in the band gap (2.2 – 1.5 eV). The main factors determining the absorption are concentration and segregation coefficient, electro-negativity of the doping ion and its difference from that of oxygen (DEN), the oxidation states, possible coordination and corresponding ionic radius. The role of some of these factors to the spectral dependence of the optical absorption of BSO is discussed from the view point of a suitable doping of BSO to obtain and modify the optical transparency.

1. Introduction

Sillenite-type Bi$_{12}$SiO$_{20}$ (BSO) pure and doped single crystals are widely used in optical devices, spatial-time light modulators and as holographic media [1,2]. BSO are cubic crystals, I23 space group symmetry, built up of Si-O$_4$ tetrahedrons and deformed Bi-On polyhedrons [3], defined by some authors as Bi-On (n = 7) - octahedrons [4] or as Bi-O-pseudo-octahedrons [5]. The chemical bonds Bi-O and Si-O in BSO are covalent [3]. In pure BSO the defects occur in the Si-O$_4$ tetrahedron, creating a spectral feature known as absorption shoulder, which result most probably due to energy levels from silicon vacancies [6] or holes from substitution of Si$^{4+}$ by Bi$^{3+}$ ions [7,8]. After reported literature data most of doping ions in BSO are placed at metal position in Si-O$_4$-tetrahedron [9]. For Ru, Cu and Mn - ions there are data for occupation of both metal position in tetrahedron (replacing Si) and in pseudo-octahedron (replacing Bi) [5,9,10].

Many studies on the optical absorption coefficient of pure BSO and doped with Al, P, Cr, Mn, Fe, Co, Ni, Cu, Se and Ru crystals in the UV-VIS spectral region have been reported so far and the effect of doping were discussed mainly in respect to: (i) absorption edge shifts [4,9-19], (ii) influence on the absorption shoulder region in 2.2-3.2 eV region [4,10-13,17,18] and (iii) possible oxidation states of doping ions, position of allowed electron transitions in the 1.5 – 2.2 eV region and the dependence of corresponding absorption coefficient on dopant concentration [5,10,16-24].

$^1$Corresponding author: bilyana_k@abv.bg
Nevertheless, until now there are no systematic complex investigations on doping effects in both the near-fundamental-edge absorption shoulder (3.2 – 2.2 eV) and on impurity levels in the band gap (2.2 – 1.5 eV). This work deal with the optical absorption coefficient of pure and doped BSO crystals measured in the energy region 1.5 – 3.2 eV, generalizing both our already published [25,26] and new experimental data on crystals doped with Al, P, Cr, Mn, Fe, Co, Ni, Cu, Se, Ru. We attempt to present the effect of doping as well as to specify some of main parameters controlling the observed effects, namely concentration and segregation coefficient, electrical-negativity of the doping ion and its difference from that of oxygen (DEN), the oxidation states, possible coordination and corresponding ionic radius. The role of some of these factors to the spectral dependence of the optical absorption of BSO is discussed from the view point of a suitable doping of BSO to obtain and modify the optical transparency of doped crystals.

2. Materials and methods

We investigated pure and doped BSO crystals with Al, P, Cr, Mn, Fe, Co, Ni, Cu, Se and Ru. All the crystals were grown from stoichiometric melts Bi$_2$O$_3$:SiO$_2$ = 6:1 using the Czochralski method under conditions described in detail elsewhere [12,14]. High purity Bi$_2$O$_3$, SiO$_2$, Al$_2$O$_3$, P$_2$O$_5$, Cr$_2$O$_3$, MnO$_2$, Fe$_2$O$_3$, Co$_3$O$_4$, Ni$_2$O$_3$, CuO, SeO$_2$ and RuO$_2$ were used for synthesis and doping. The concentration of doping was determined by flame (Zeeman 3030) and electrical-thermal atomic (Varian 240) absorption spectrometry as well as by inductively coupled plasma atomic emission spectrometry (Jobin Yvon, ULTIMA 2).

3. Results and discussion

The optical absorption were measured at room temperature in the energy interval 1.5 – 3.2 eV on bi-side polished parallel plates using a Varian’s UV-VIS spectrophotometer Carry 100. Prior to measurement, the crystals were de-excited either by illumination for 20 min with a He-Ne laser Calr Zeiss Jena, HNA 188-S (the surface power of about 90mW/cm$^2$) or by annealing at 500°C in air for 20 min [10]. In order to attain better spectral resolution and accuracy we express some times the data on optical absorption coefficient in terms of its first and second derivatives with respect to photon energy. Three are the main spectral changes provoked in optical absorption of BSO by doping: (i) shift of the fundamental absorption edge, (ii) change of the shape position of the near-edge shoulder and (iii) appearance of impurity states and corresponding energy levels in the band-gap. In what follows we present representative dependencies illustrating the character of these three spectral changes.

There are numerous results published on the shift of the fundamental absorption edge [10-12,14,19] which coincide in principle with our experimental data, indicating that its position depends mainly on the type and concentration of doping ions. In sillenite-type Bi$_2$TiO$_5$ crystals doping with ions of lower electrical-negativity leads to an edge-shift towards longer wavelengths [18]. As electrical-negativity describes the ability of an atom to attract electrons/electron density towards itself and determines the type and strength of chemical bonds in a compound, we calculated the differences between electrical-negativity of the doping ions and that of oxygen (DEN) (Table 1) [29]. When DEN is between 1.7 and 2.0, the doping ion forms ionic bond with oxygen (this holds for Mn, Al and Cr), whereas for DEN between 0.5 and 1.7, the bond is polar covalent (Fe, Co, Cu, Ni, P, Ru, Se as well as for Si-O and Bi-O bonds). Respectively, the absorption edge upon doping with the first three elements shifts to higher, while with the other seven to lower energy. This behavior can be clearly seen from the spectra of the first derivative of absorption coefficient with respect to energy (Fig.1), where peak positions indicate the edge and their change describes the variation in its slope upon doping. Figure 1 have only illustrative character showing three typical cases of doping, namely very large low-energy edge-shift (Cu, reducing the edge position of pure BSO from 3.12 eV down to about 2.6 eV), no or very small edge-shift (Ru) and significant high-energy edge-shift (Mn, rising the edge position up to about 3.2 eV). These effects are of importance and have to be taken into account when model and modify the region of transparency of doped BSO crystals.
Figure 1. Energy dependence of first derivative of absorption coefficient for BSO, BSO:Mn, BSO:Ru and BSO:Cu in the absorption edge vicinity.

Figure 2. Energy dependence of absorption coefficient for BSO, BSO:Cr, BSO:Al and BSO:Se in the region of fundamental edge shoulder.

Figure 3. Energy dependence of absorption coefficient for BSO, BSO:Cr, BSO:Co and BSO:Se in the sub-band-gap optical range.

Table 1. Doping influence and parameters of dopants and major elements (Bi and Si) for BSO crystals.

| crystal  | Doping Influence | \( \chi \) | DEN | oxidation state \( ^b \) | electronic configuration | coordination type \( ^a \) | i. r. \( ^a \) [pm] |
|---------|-----------------|---|-----|-------------------|------------------------|-------------------|----------------|
| BSO:Mn  | strong weak     | 1.55 1.89 | 2\(^+\) [Ar]3d\(^5\) | Tetrahedral/Octahedral | 39/55 | 80/81 |
| BSO:Al  | strong strong   | 1.61 1.83 | 3\(^+\) [Ar]3d\(^3\) | Octahedral/Tetrahedral | 55/75 | 72 |
| BSO:Cr  | weak strong +   | 1.66 1.78 | 3\(^+\) [Ne] | Octahedral/Tetrahedral | 53/67.5 | 72 |
| BSO:Fe  | weak strong +   | 1.83 1.61 | 3\(^+\) [Ar]3d\(^5\) | Octahedral/Tetrahedral | 53/67 | 72 |
| BSO:Co  | strong weak     | 1.88 1.56 | 3\(^+\) [Ar]3d\(^5\) | Octahedral/Tetrahedral | 53/67 | 72 |
| BSO:Cu  | strong strong   | 1.90 1.54 | 1\(^+\) [Ar]3d\(^10\) | Octahedral/Tetrahedral | 74/91 | 72 |
| BSO:Ni  | weak weak      | 1.91 1.53 | 3\(^+\) [Ar]3d\(^4\) | Octahedral/Tetrahedral | 72/87 | 72 |
| BSO:P   | strong strong   | 2.19 1.25 | 5\(^+\) [Ne] | Octahedral/Tetrahedral | 53/67 | 72 |
| BSO:Ru  | weak weak      | 2.20 1.24 | 4\(^+\) [Kr]4d\(^6\) | Octahedral/Tetrahedral | 74/91 | 72 |
| BSO:Se  | weak weak      | 2.55 0.89 | 6\(^+\) [Ar]3d\(^10\) | Octahedral/Tetrahedral | 74/91 | 72 |

\(^a\) literature data [12-14,28,29]
\(^b\) possible oxidation states of dopants, proven by other with different experimental methods [5,9,10,13,14,17,18,21-24]

The edge of fundamental absorption is the high-energy end of the so-called optical absorption shoulder which for doped BSO crystals covers the spectral range 3.2-2.2 eV where the absorption takes place on energy levels from both intrinsic and more or less shallow electron states as result of
doping. Figure 2 shows the spectra of absorption coefficient of pure BSO and crystals doped with Cr, Se, and Al. Again, the spectra illustrate the general observed peculiarities of the effect of doping. The doping with Se does not change seriously the absorption of pure BSO, while that with Al modifies the shapes of absorption shoulder making it almost stepwise due to compensation of intrinsic states (most probably structural defects) of the pure material. Totally different is the spectrum of BSO:Cr revealing the presence of a very intense wide band in the spectral range 2.5 – 3.1 eV, which is typical for this ion only. Such a strong and unusual effect of doping of BSO with Cr can be expected due to the suitable oxidation states in tetrahedral coordination with electronic configuration allowing crystal-field electron transitions. Table 1 presents schematically the significance of doping for the three spectral regions, the electrical-negativity X, DEN, oxidation state, electronic configuration, coordination type and ion radius for the ten doping elements as well as for Bi and Si. Thus, among the four possible oxidation states of chromium, most appropriate for forming optical absorption levels would be 4+ and 5+ with tetrahedral coordination.

The doping of BSO with elements, involving oxygen in ionic bonds, shifts as a rule the absorption edge of doped crystal to higher energies, while for these forming polar covalent bonds the edge shifts to lower energies. On the other hand, elements that affect strongly the absorption shoulder (Mn, Fe, Cu, P and Al in our case) probably substitute Bi3+ in tetrahedral position and in oxidation states forbidden for electron transitions. Contrary, doping elements not affecting this spectral range most probably substitute Si4+ in tetrahedral position as their oxidation state and corresponding electronic configuration allow crystal-field transitions. For instance, ions Al3+ and P5+ are with noble-gas electronic configurations, Cu1+ with d10-configuration (filled 3d-electronic shell), Fe3+ and Mn2+ with d5-configuration (half-filled shell), and for all these elements the electron transitions are forbidden or with lower probability and low intensity.

In the spectral range 2.2 – 1.5 eV, optical absorption takes place on deep impurity levels formed upon doping, which in some cases, particularly at high values of segregation coefficient for a given doping ions assuring high density of states and concentration of doping, may lead to very intense absorption. Figure 3 shows as typical illustrations the spectra of optical absorption coefficient of BSO, BSO:Cr, BSO:Co, and BSO:Se in this range.

The spectra of pure BSO and of BSO:Se (continuous lines) seem quite alike in shape, being structureless. This holds also for other investigated doped samples except for BSO:Cr and BSO:Co (dotted lines). The latter two exhibit intense spectral bands in the optical absorption coefficient at about 1.56, 1.65, 1.74 eV for BSO:Cr and at 1.78, 1.95 and 2.10 eV for BSO:Co. These peak positions are determined either via decomposition of the spectrum using Gauss functions [10] or, to enhance the spectral resolution, by calculating its second derivative, both methods giving results in a good agreement with published data [11-14,23,26]. In addition, careful inspection of the spectra of BSO and BSO:Se reveal the presence of very weak absorption peaks near 1.51, 1.70, 1.88 and 2.18 eV which could be due to undesirable doping of the crystals with Fe and Mn [9,26,27]. Practically, except Cr and Co, doping with all other elements under study do not affect the optical transparency of BSO.

4. Conclusions

On the basis of experimentally measured optical absorption spectra and of literature data for ionic electrical-negativity, oxidation states, electronic configuration, coordination type and ionic radii, we were able to draw some general conclusions and prognosis about the effect of doping on the optical absorption of variously doped crystal of BSO:

(i) The doping of BSO with elements, involving oxygen in ionic bonds, shifts the absorption edge of doped crystal to higher energies, while for such forming polar covalent bonds the edge shifts to lower energies.

(ii) Elements that upon doping of BSO affect strongly the absorption shoulder probably substitute Bi3+ in tetrahedral position and in oxidation states forbidden for electron transitions. Contrary, doping elements not affecting this spectral range
most probably substitute Si\textsuperscript{4+} in tetrahedral position as their oxidation state and corresponding electronic configuration allow crystal-field transitions.

(iii) Only doping of BSO with Cr and Co forms absorbing states in the sub-band-gap spectral range.

Acknowledgments
Authors gratefully acknowledge the financial support of the Bulgarian National Scientific Research Fund by contract TK-X-1715/2007.

References
[1] Gunter P and Huignard J 2006 Photorefractive materials and their applications. Part 1, New York, Springer Science+Buisness Media
[2] Gunter P and Huignard J 2007 Photorefractive materials and their applications. Part 2 and 3, New York, Springer Science+Buisness Media
[3] Mihailova B, Gospodinov M and Konstantinov L 1999 J. Phys. Chem. Solids 60 1821
[4] Marinova V, Velea M and Petrova D 2001 JAP 89 2686
[5] Ramaz F, Rakitina L, Gospodinov M and Briat B 2005 Opt. Mat. 27 1547
[6] Burkov V, Kargin Y, Kivel V, Sitinkova V and Skorikov A 1983 JETP Let. 38 390
[7] Reyher H, Hewlwing U and Thiemann O 1993 Phys. Rev. B 47 5638-5646
[8] Ahmad I, Marinova V and Goovaerts E 2009 Phys. Rev. B 79 033107
[9] Kargin Y, Burkov V, Maryin A and Egorysheva A 2005 Alphabet, Moscow 180 (in Russian)
[10] Marquet H, Tapiero M, Merle J, Zielinger J and Launay J 1998 Opt. Mater. 11 53
[11] Gospodinov M, Doshkova D, Sampil A and Aneva Z 1993 Comp. Rend. Acad. Bulg. Sci. 46 45
[12] Gospodinov M and Doshkova D 1994 Cryst. Res. Technol. 29 603
[13] Gospodinov M and Doshkova D 1994 Mat. Res. Bull. 29 681
[14] Petrova D, Gospodinov M and Sveshtarov P 1995 Mat. Res. Bull. 30 1201
[15] Petrova D and Gospodinov M 1996 Cer. Intern. 22 45
[16] Nechitailov A, Krasinkova M, Mokrashina E, Petrov A, Kartenko N and Prokofiev V 2000 JNORG 36 820
[17] Egorysheva A, Burkov V, Kargin Y, Vasiliev A, Volkov V and Skorikov V 2001 JNORG 37 817
[18] Egorysheva A 2005 JNORG 50 407
[19] Marinova V, Lin S, Hsieh M, Liu R and Hsu K 2009 Photorefractive Matt, Effects, and Devices PR’09 P1-39
[20] Egorysheva A, Volkov V, Coya C and Zaldo C 1998 Phys. Stat. Sol. B 207 283
[21] Potera P and Pircuch A 2007 Physica B 387 392
[22] Kovacs L, Capelli R and Gospodinov M 2008 Vib. Spec. 46 69
[23] Zmija J and Malchowski M 2008 Arh. Mat. Sci. Eng. 33 101
[24] Ahmad I, Marinova V and Goovaerts E 2009 Photorefractive Matt, Effects, and Devices PR’09 P1-38
[25] Kostova B, Milenov T, Rafailov P, Egorysheva A, Yankova L, Velea M, Dobreva S and Skorikov V 2009 AIP Conf. Proc. 1203 188
[26] Kostova B, Gospodinov M and Konstantinov L 2009 AIP Conf. Proc. 1203 193
[27] Leonite L, Caraman M, Delibas M and Rusu G 2001 Mat. Res. Bull. 36 1629
[28] Skorikov V, Milenov T, Egorysheva A, Rafailov P, Dudkina T, Velea M, Vasiliev A and Gospodinov M 2003 Phys. Stat. Sol. B 235 3292
[29] http://www.webelements.com