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Optical Properties of $Bi_{40}Ga_2O_{63}$ Single Crystals

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□ ABSTRACT □

The normal-incidence reflectance spectrum of $Bi_{40}Ga_2O_{63}$ single crystal in the energy range from 1 to 12 eV at room temperature has been measured. Single crystals have been grown using Top Seeded Solution Growth (TSSG) technique. Several peaks found in the reflectivity spectrum have been assigned to interband transitions at □-P□□□□line. Others structures are also discussed and interpreted in the terms of transitions between O^{2-}(2p) states and conduction bands. The energy gap is indirect and lies between the top of the valence band at the Γ point and the bottom of the conduction band at the H point.

Keywords: Sillenite crystals, (BGaO) $Bi_{40}Ga_2O_{63}$ Single crystal, Top Seeded Solution Growth (TSSG) technique, Reflectivity spectrum, Optical interband transitions.

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الخواص الضوئية للبلورة الأحادية $Bi_{40}Ga_2O_{60}$

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□ الملخّص □

أنجز قياس معامل طيف الانعكاس للبلورة الأحادية $Bi_{40}Ga_2O_{63}$ في مجال الطاقة (1-12 eV) في غرفة ذات درجة حرارة. تمّت تنمية البلورات الأحادية باستخدام طريقة (TSSG). وقد لوحظ في طيف الانعكاس بنية غنية مطابقة للانتقالات الضوئية بين العصابات. وهي الحال التي فسرّت وجود قيم عدة في طيف الانعكاس بالانتقالات مابين العصابات على المستقيم Γ-P(Λ) . وفي ضوء ما تقدم فقد تمّت مناقشة بنى طيفية أخرى حيث فسرّت بدلالة الانتقالات مابين السويات (2p) O^{2-} وعصابات الناقلية حيث تمّ تحديد عصابة الطاقة المحظورة كعصابة غير مباشرة مابين أعلى عصابة التكافؤ عند النقطة Γ وأسفل عصابة الناقلية عند النقطة H .

كلمات مفتاحية : بلورات السيلينيت ، البلورة الأحادية $Bi_{40}Ga_2O_{63}$ (BGaO) ، تقنية (TSSG) لتنمية البلورة، طيف الانعكاسية ، الانتقالات الضوئية.

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1. Introduction

The term "sillenite" nowadays describes a fairly large group of ternary alloys formed between Bi_2O_3 and various others metal oxides such as Al_2O_3, PbO, TiO_2, Ga_2O_3, GeO_2 and SiO_2 [1,2,5]. The first group of these materials was synthesized and investigated by L. G. Silleń in 1937 [26] and the first single crystal to be obtained was grown by A.A.Balman in 1967 [3].

Considerable interest in the investigation of the different bismuth oxide compounds has been trigged by their unusual optical and electro- acoustic properties [20]. It shows characteristics that are interesting from the point of view of applications in optics (holography, optical memory cells), quantum electronics and in microwave acoustics [16,19,27]. New mixed sillenites $Bi_{12}Ti_{1-x}Me_xO_{20}$, where Me = Ga, V, Pb, with very high photoconductive efficiency were grown and investigated [7]. They are very promising from the point of view future applications.

The crystals BGaO ($Bi_{40}Ga_2O_{63}$), belonging to the body-centered cubic (b.c.c) class and described by the point group 23, have been found to be piezoelectric [3]. BGaO crystals exhibit strong optical activity [13]. Measurements of coefficients of the optical absorption in the region of fundamental absorption edge for BGaO crystals have been carried out by Borowiec et al. [8]. They estimated the band gap at 4.2 K, about 2.96 eV.

Very little experimental information about the band structure of sillenite crystals is available. Some reflection measurements in 1-8eV energy range for BGO ($Bi_{12}GeO_{20}$) [14] and BTO ($Bi_{12}TiO_{20}$) [11] and in 1-35eV for BSO ($Bi_{12}SiO_{20}$) [10] were pointed at in the literature. In this context, the present paper is devoted to the investigation of the reflectivity spectra of BGaO single crystals in the energy range from 1 to 12 eV, with the aim of obtaining some new data about their band structure.

2. The Crystal Growth and Measurements

The BGaO crystals belonging to the sillenite family were grown by Top Seeded Solution Growth (TSSG) technique at the Institute of Physics, Military Academy of Technology in Warsaw, Poland [21]. High purity $Bi_2O_3$and Ga_2O_3 was the starting materials for the host. All the crystals are transparent. The structure of these materials is similar to that of γ-Bi_2O_3 and Ga ion tetrahedrally surrounded by oxygen ions [2].

Several groups have already described the structural features of sillenite compounds previously [1-3,5,20,26]. *Radaev et al.* [24] studied the γ- $Bi_2O_3$and other sillenite crystals like BGaO, BFeO and BZnO. They found that the tetrahedral sites in the γ- Bi_2O_3 structure are populated by Bi^{3+} ions with probability of 80%. Also, the O atoms that form the tetrahedral environment of these Bi atoms occupy their sites with the same probability. Table 1 shows some structural data for sillenite [24]. The ionic radius of the Ga^{3+} (0.62Å) is distinctively less than that of Bi^{3+} (0.95 Å) (by 0.33 Å). As seen from ionic radii difference, some of the tetrahedral sites are probably left vacant to retain the charge balance in the grown crystals.

Table 1. The crystal structures of sillenites and the ionic radii of the atoms.

Crystal	Structure	Space group	Ion-radius (inÅ)	Lattice a (Å)	Constant c (Å)
$Bi_{40}Ga_2O_{63}$	Cubic- b.c.c	T^3 –I23	O^{2-}: 1.40	-	-
□γ-Bi_2O_3	Cubic- b.c.c	T^3 –I23	Bi^{3+} : 0.95	10.245	-
Ga_2O_3	Corundum	D^6_{3d} – R 3m	Ga^{3+}: 0.62	4.98	13.46

We have measured the reflectivity of the BGaO crystals for light energy between 1 and 12eV using unpolarized light at the Institute of Physics, Polish Academy of Sciences, Warsaw-Poland. The measurements for light energy between 1 and 4 eV were carried out on quartz prism monochromator with a halogen lamp used as the light source. At higher energy (from 4 to 12eV) a vacuum ultraviolet monochromator based on the Seya-Namioka scheme was used. The source of the radiation was a hydrogen gas discharge lamp (pressure 10^{-2}Torr) connected with the monochromator. Both systems worked at the similar conditions. Rotating modulator modulated the beam exiting from the monochromator. The part of the light transmitted through the modulator was reflected by the sample towards a prism coated with luminophor (sodium salicylate) and then measured by means of photomultiplier with a quartz window. The second part of the light went above the sample to another luminophor- photomultiplier set. Modulated signals from the two photomultipliers were measured with lock-in nanovoltmeters. IBM-XT computer recorded the data. Other experimental details could be found in Ref. [25].

The samples were cut from BGaO cubic single crystals. The measurements were performed on mechanically and chemically polished surfaces using progressively finer abrasives. For the final stage the samples were polished with Al_2O_3 (0.05-micron grit). The etched surfaces were omitted because of the difficulties in finding a chemical etch giving sufficiently good optical surface quality. The surfaces were, therefore, cleaned with ethyl alcohol just before the experiment and hence the spectra obtained may be somewhat smeared out.

3. Results and Discussion

In the measured reflectivity spectra of $Bi_{40}Ga_2O_{63}$ crystals, the shapes and positions of the characteristic maxima are the impression of relating the spectra to the electronic band structures of the compounds. In ternary alloys, crystalline disorder appears as a result of the local structure (the Bi-O distance is different from the Ga-O) as well as chemical disorder in the lattice of the BGaO crystals. An analysis of the reflectivity spectra of the compounds BGaO is quite difficult because the theoretical explanation of the observed features would require a calculation of the band structures of these materials, which are unknown at present. Therefore, the spectra were explained on the basis of the compound band structures related to them, which are available in the literature. The structures shown in the spectrum are indicated by capital letters.

Figure 1 presents the measured room-temperature reflectivity in $Bi_{40}Ga_2O_{63}$ crystals in the energy range from 1 to 12 eV. The positions of the experimental reflectivity peaks are summarized in table 2.

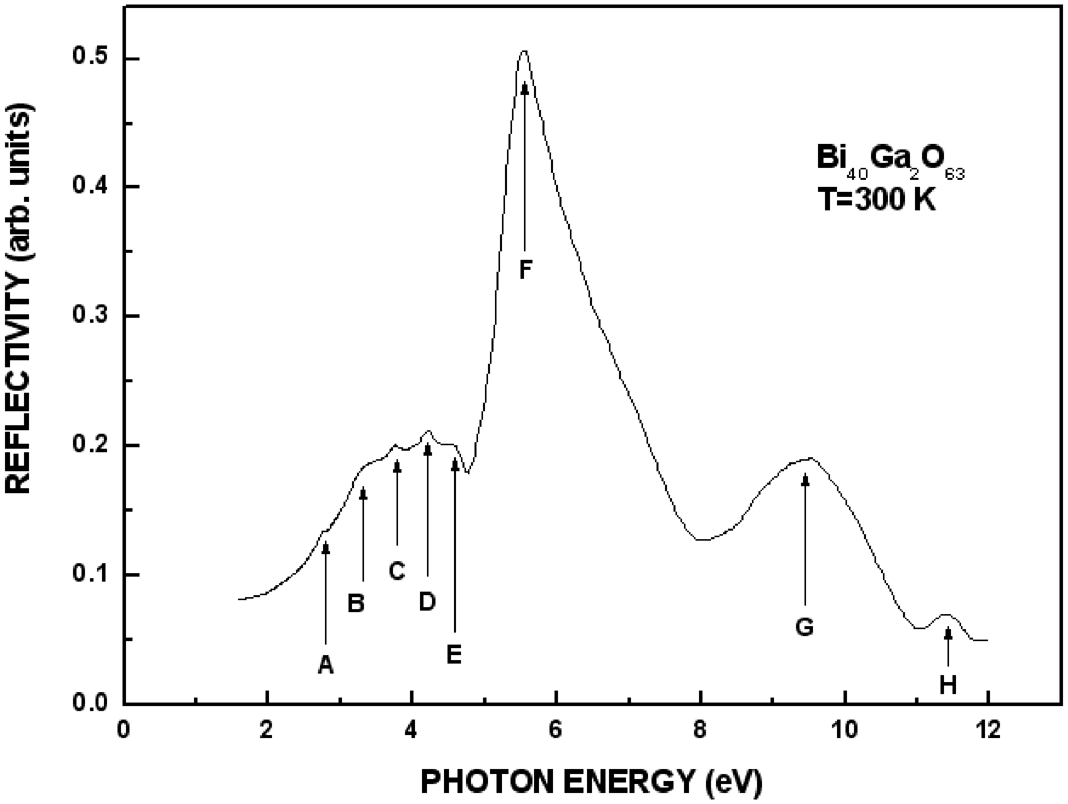

Fig.1. Fundamental reflectivity spectrum of $Bi_{40}Ga_2O_{63}$ crystals at room temperature.

Table 2. Energies of the position peaks and shoulders discerned in the reflectivity spectra of the $Bi_{40}Ga_2O_{63}$ at room temperature (in eV).

Crystal	A	B	C	D	E	F	G	H
BGaO	2.72	3.28	3.74	4.20	4.60	5.54	9.46	11.41

The reflectivity spectrum of $Bi_{40}Ga_2O_{63}$ seen by us was compared with that obtained previously for $Bi_{12}MO_{20}$ (M= Si, Ge, Ti) [10,11,14]. The observed transition of the energy lower than the energy gap (the energy gap between the valence and conduction band was experimentally estimated, at about 2.96eV) is marked as A. For low energy region less than E=6eV, there is one maximum having a doublet structure, in the reflectivity spectrum. The corresponding peaks are C and D. We observe also two peaks G and H in the region of photon energy higher than 6eV. These peaks should correspond to higher energy transitions, i.e. from lower valence bands to higher conduction bands with high densities of states.

To understand the experimental data, we should note that, for instance, in $A^{II}B^{VI}$ crystals the valence bands are created from the anion p-like orbitals and by substitutional contribution of cation s and p-like orbitals [4]. Also, as it is well known, the valence band structure is constructed prevalently from the anion p-like orbitals only close to the Γ point. The band structure calculations for Ga_2O_3 [15] show that the lowest lying conduction band consists 64% Ga 4s contribution. On the other hand, the higher part of the valence band consists entirely of weakly interacting O 2p orbital while the lower energy band contains the Ga 4s–O 2p bonding state. *Medvedeva et al.* [23] calculated the electronic structure of the δ-Bi_2O_3 compound using LMTO method. They showed that the energy gap (3.96eV) and valence band structure close to Γ point stem fundamentally from O 2p states. The topmost valence bands are the oxygen 2p states, while the upper and the lowest part valence bands are formed from hybridized Bi(6p) and O(2p) electronic states and there are in the Γ-X(Δ) direction bands resulting from Bi (6p) states. They indicate also that the bottom of conduction bands at Γ-point steam mainly from Bi (6p) states; whereas, *Kalinkin et al.* [17] have reported an electronic structure calculation for $Bi_{12}GeO_{20}$. They used an X_α-Relativistic Self-Consistent Method to calculate the density of electronic states. These authors arrive at the conclusion that the maximum of the valence band is formed by Ge 4p and O 2p and Bi 6p states. The upper valence band close to Γ point originates mostly from the O 2p states, while in the next parts of the valence band, there was a participation of the p-like states of the Bi atom and the p-like states of the O(1) atom. They also showed strong hybridization in the sublattice Bi-O(1), which is responsible for optical properties. Moreover, the energy band structure of the $Bi_{12}GeO_{20}$ and $Bi_{12}SiO_{20}$ single crystals were calculated using a local pseudo-potential method by *Kityk et al.* [18]. They showed that the valence bands originate from Bi (6p), O (2p) and Bi (6s) states, and the band dispersion increases in the vicinity of Γ and P points of the first Brillouin zone. They also indicate that the valence bands are distributed between 0 eV and 19 eV, and such a wide bands of relatively high density of states reflects a dominant covalent bond nature between bismuth and oxygen atoms.

The Brillouin zones of sillenites-type are body cubic centered, but examination of particular points and lines, based on the above-mentioned facts, reveals that the Γ-P (Λ) and Γ-H(Δ) directions are the most interesting ones. The Λ-line lies along [111] axis and the Δ-line along the [100] axis. Hence, it is reasonable to search for an explanation for the spectral features in the electronic structure in the crystals in terms of the above picture.

On account of the relatively large energy gap of sillenite, localized transitions with energies smaller than energy gap can be easily observed. The feature *A* beginning at 2.72 is believed to correspond to transitions within the band gap (2.96eV), since the energy of this structure is less than the energy gap; about 0.24 eV. Photoconductivity, optical absorption and photocurrent excitation have been reported in $Bi_{12}GeO_{20}$, $Bi_{12}SiO_{20}$, $Bi_{12}TiO_{20}$ and Ga-doped $Bi_{12}GeO_{20}$ crystals by Bloom and McKeever [6]. They showed that the band-edge absorption is observed in the energy range from 2 to 3.10eV in the spectra, and they arrive at the conclusion that, the absorption in this region is believed to be caused by the optical excitation of electrons from deep donor states about 2.6 eV located below the Fermi level to the conduction band. *Marqute et al.* [22] also studied the role of some shallow-trap centres in the photochromism of $Bi_{12}GeO_{20}$. They found that the absorption spectrum at 300K shows strong step at 3.2eV, corresponding to band-to-band transitions, and a weaker band at 2.5eV. They attributed the latter band to transitions from deep donor centres (Bi in place of Ge) to the conduction band because of the n-type photoconductivity of these crystals. Following Marqute et al. [22] and Bloom and McKeever [6], we attribute this peak, to the transition from deep donor states lying in energy gap to the minimum of the conduction band at Γ point.

The structure *C* that occurs at energy 3.74 eV seem to be connected with the feature *D* observed at energy 4.20eV. It seems to be a dominating peak between them and split into two components *B* and *C*. This splitting is about 0.46 eV and is in agreement with the photon energy of $Bi_{12}TiO_{20}$ [11]. Therefore, we can attribute the value *B-C*= 0.46 eV to spin-orbit □$_{so}$ valence band splitting at □ point occurring below the top of valence band. On other hand, *Efendiev et al.* [10 - 12] showed that there are direct and indirect optical transitions in BGO, BSO and BTO single crystals within the energy range (2.8-4.5eV) at room temperature. They indicate that the indirect transitions are observed in the energy range (2.8-3.5eV), whereas in the energy range (3.5-4.5eV) the direct transitions are observed. As we see, *C* and *D* peaks correspond to the direct optical transitions, in agreement with the assignment reported by *Efendiev et al.* [11, 12], who ascribes it to the transition from topmost valence band to the minimum of conduction band; that is from O(2p) states to minimum of the conduction band; i.e. to the transition at the point H (Δ).

The reflectivity peak *E* occurring at 4.60 eV is connected with direct optical transition. Our assignment agrees well with that reported previously [10 - 12]. Hence, we expect that the direct optical transition occurs from valence band to conduction band; that is from Bi (6p)-O (2p) states to minimum of the conduction band; probably this transition occurs at saddle point on the Γ - P(Λ) line.

The peak *F* occurring at energy 5.54 eV is in agreement with that shown in the pure Bi reflectivity spectrum [9]. *Cardona and Greenway* [27] interpreted this peak as the optical transition occurring at □ point of the Brillouin zone. Therefore, we expect that the peak *F* corresponds to the transition from Bi (6p)-O (2p) valence band to conduction band.

The reflectance peak *G*, which occur at photon energy of 9.46 eV corresponds to optical transition from valence band to conduction band and is in agreements with the results reported by *Cardona and Greenway* [9] for pure Bi. They interpreted this peak and optical transition occurs at □□and X points of the Brillouin zone. We expect that the feature *G* corresponds to the transition from Bi (6p)-O (2p) states valence band to conduction band, i.e. to the transition at Γ point, and some contribution of the states from the □ [100]□direction of the Brillouin zone.

Another problem is that, at even high energy, we observe peak *H* around 11.41eV. It has to be pointed out that observed peak is probably due to transitions from the p-like states of the Bi atom and the p-like states of the O atom to the conduction band, as it was suggested by *Kalinkin et al.* [17]. Thus, we attribute tentatively this peak to transition from Bi (6p)-O (2p) states to the conduction band. However, the precise nature of those transition remains unexplained at present.

Conclusion

In this paper, we presented results of the study of the optical properties of representative $Bi_{40}Ga_2O_{63}$ single crystals in the energy range from 1 to 12eV at room temperature. The observed optical structures in the spectrum were interpreted in terms of transitions between O (2p) levels and the various conduction bands. The energy band scheme of $Bi_{40}Ga_2O_{63}$ is determined mainly by the bismuth and oxygen net structure. The optical transitions occur at the saddle points on the Γ-P (Λ) line. Based on the discussion, one can conclude that the energy gap is indirect and lies between the top of the valence band at the Γ point and the bottom of the conduction band at the H point and is in good agreement with the model proposed reported by *Efendiev et all* [12].

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