Reflectivity Study of Sillenite Compounds $Bi_{12}MO_{20}$ (M= Si, Ge, Ti)

Dr. Ammar Sarem*
Dr. Talal Khalass**

☐ ABSTRACT ☐

Three sillenite compounds $Bi_{12}MO_{20}$ (M=Si, Ge, Ti) were synthesized, and the resulting single-phase crystals were then investigated in the energy range from 1.5 to 6eV at room temperature by reflectance method. A rich structure corresponding to the optical interband transitions were observed in the reflectivity spectra. The electronic band structure of modification of sillenite compounds resulting from the above data is analyzed and discussed. An analysis of the optical properties of the $Bi_{12}MO_{20}$ (M=Si, Ge, Ti) single crystals has been correlated with the structure of the bismuth-oxygen network of the sillenite crystals. The optical transitions occur at the saddle points on the Γ-P(Λ) line. The probability of transitions at the P and H points is low, because of the density of states is expected to be low there. The results contribute to the model of the electronic structure of these materials.

*Professor , Department of Physics, Faculty of Science, Tishreen University, Latakia, Syria.
** Assistant professor, Department of Physics, Faculty of Science, Tishreen University, Latakia, Syria.

دراسة انعكاسية مركبات السيلينيت من النوع Bi$_{12}$MO$_{20}$ (M= Si, Ge, Ti)

الدكتور عمّار صارم[*]

الدكتور طلال خلاص[**]

□ الملخّص □

تم تصنيع ثلاثة مركبات من النوع Bi$_{12}$MO$_{20}$ (M = Si, Ge, Ti)، ثم اختبرت البلورات الناتجة أحادية الطور في مجال الطاقة من 1.5 إلى 6 إلكترون فولت عند درجة حرارة الغرفة بوساطة طريقة الانعكاسية. لوحظت في أطياف الانعكاسية بنية غنية مطابقة إلى الانتقالات الضوئية ما بين الحزم. نوقشت وحللت من المعطيات السابقة تغيرات بنية الحزم الإلكترونية في مركبات السيلينيت. تم ربط تحليل الخواص الضوئية للبلورات الأحادية Bi$_{12}$MO$_{20}$ (M = Si, Ge, Ti) مع بنية الشبكة بزموث – أكسجين في بلورات السيلينيت. وإن الانتقالات الضوئية تحدث عند النقاط السرجية على المستقيم (Λ)P-Γ. واحتمال الانتقالات الضوئية عند النقطتين P و H منخفض، لأنـه يتوقع أن تكون كثافة الحالات عندهما منخفضة. وإن هذه النتائج ساهمت في نموذج البنية الالكترونية لهذه المواد.

الكلمات المفتاحية: السيلينيتات– أكسيد بزموث السيلكون– أكسيد بزموث الجرمانيوم– أكسيد بزموث التيتانيوم.

بحث تجريبي: أجريت القياسات في معهد الفيزياء بأكاديمية العلوم البولونية، وارسو– بولونيا

Introduction:

---

[*] أستاذ – قسم الفيزياء – كلية العلوم – جامعة تشرين– اللاذقية – سورية.

[**] مدرس – قسم الفيزياء – كلية العلوم – جامعة تشرين– اللاذقية – سورية.

At present, there is a strong need for sensitive fast nonlinear optical devices with potential applications in the areas of optical communications, optical storage, optical computing and optoelectronics. In the past, most of the fundamental and applied studies of materials have been concentrated on different semiconductors, but in recent years, increased attention has been given to sillenites crystals because of their significantly lower response time and high sensitivity in the near-IR region. They are very promising for future application [1-6].

$Bi_{12}SiO_{20}$ (BSO) and $Bi_{12}GeO_{20}$ (BGO) are the most known members of the sillenite family and are named as ideal sillenites. Bismuth titanium oxide crystal, $Bi_{12}TiO_{20}$ (BTO), have some practical advantages relative to its isomorphous $Bi_{12}SiO_{20}$ (BSO) and $Bi_{12}GeO_{20}$ (BGO), including lower optical activity, larger electro-optic coefficient and higher sensitivity to red light [4-6]. A very interesting class of photorefractive media is that of sillenite crystals have a faster response time as compared with, for example, perovskites $BaTiO_3$ and $LiNbO_3$, but they show lower gain owing to the low value of their electro-optic coefficient. The sillenite crystals are piezoelectric, optically active, and photoconductive and become, in addition, linearly birefringent in the presence of an electric field. Due to these properties, current applications of sillenites are mainly for electro-optical, elasto-optical and for many advanced and promising applications, such as a reversible recording medium for real-time holography or for image processing applications [7-9].

The optical properties of the sillenite are very important. The energy gap lies in the visible region and this is one reason why these materials are interesting [10].

Very little experimental information about the band structure of sillenite crystals is available. Futro [11] has measured the reflectivity of BGO ($Bi_{12}GeO_{20}$) from 1.5-8.5eV and the optical constants were derived by Kramers - Kroning (KK) method. Although the reflectivity of BSO ($Bi_{12}SiO_{20}$) was measured, no analysis of it was given [12]. Efendiev *et al.* [13] made measurements in the energy range of 1- 6eV for BTO ($Bi_{12}TiO_{20}$) and obtained optical constants.

Aim of the study:

The present paper is devoted to the investigation of the reflectivity spectra of three sillenite $Bi_{12}MO_{20}$ (M=Si, Ge, Ti) single crystal in the energy range from 1.5 to 6 eV, with the aim that some new data obtained allow us to construct band structure model for this material.

Description of the sillenite structure:

Stoichiometric sillenites are compounds with the general formula $Bi_{12}MO_{20}$ where M represents a tetravalent ion or a combination of ions which gives an average charge of 4+ (e.g., Ge^{4+}, Si^{4+} and Ti^{4+}). The sillenite structural family is isomorphic to the γ-Bi_2O_3 polymorph of Bi_2O_3, which is stabilized by the addition of small quantities of a variety of cations. The sillenites are a crystalline material group consisting of a stabilized body-centered cubic form of γ-Bi_2O_3 [14].

In 1937, Lars Gunar Sillen' [15] found several phases with the general formula $Bi_{24}Me_2O_{40}$ (Me=different cations) which also crystallize similar to $\square\square$-Bi_2O_3 in the non-centrosymmetrical space group I23. Abrahams *et al.* [16] did the first structural investigation of the sillenites.

All structurally known cubic sillenites with tri- and four valent cations (γ-Bi_2O_3, $Bi_{25}GaO_{39}$, $Bi_{25}FeO_{39}$, $Bi_{24}Ge_2O_{40}$, $Bi_{24}Ti_2O_{40}$, $Bi_{24}Si_2O_{40}$) were first solved with X-ray diffraction methods and later more precisely determined with neutron diffraction data (see table I) [17, 18]. They showed that the crystal structure is formed by a Bi–O polyhedra framework with only small differences, which connects to geometrically regular M–O tetrahedra. The Bi ions are coordinated with five oxygen ions which together with the stereo-chemically active $6s^2$ lone electron pair of Bi^{3+} form an octahedral arrangement. A Bi–O polyhedron network connects to the geometrically regular MO_4 tetrahedra. Each of the tetrahedra is formed by four oxygen anions while the M cation occupies the tetrahedral interstice Fig (1).
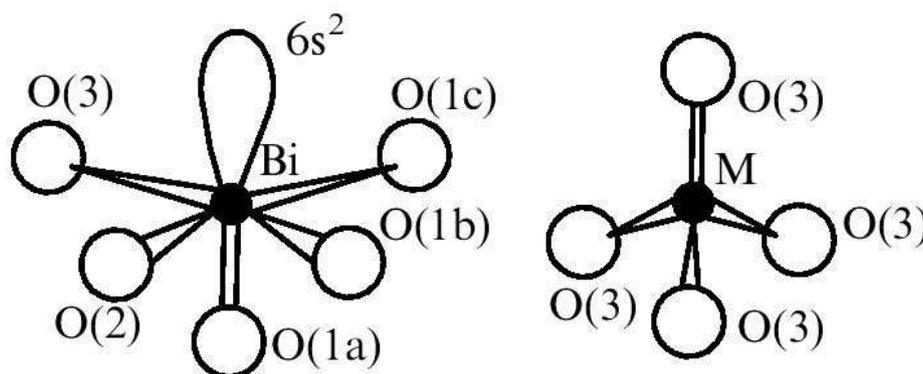
Fig. (1). Structure of stoichiometric sillenite $Bi_{12}MO_{20}$, (with M=Ge, Si and Ti) and the structures of [BiO_5] polyhedrons and [MO_4] tetrahedrons [after 17].

Table I. Bond length of first coordination sphere of Bi1 of all structural known sillenites with tri- and tetravalent M cations (with M = Ge, Si and Ti) [17, 18].

Bond length	$Bi_{12}TiO_{20}$	$Bi_{12}GeO_{20}$	$Bi_{12}SiO_{20}$	γ -Bi_2O_3
Bi1 - O1^{i}	2.071	2.072	2.064	2.045
Bi1 - O1^{ii}	2.227	2.221	2.222	2.402
Bi1 - O1^{iii}	2.613	2.622	2.621	2.456
Bi1 - O2	2.220	2.215	2.201	2.278
Bi1 - O3^{iv}	2.612	2.624	2.647	2.561
M - O3	1.829	1.767	1.647	-

Several groups have already described the structural features of sillenite compounds. Radaev *et al.* [17] studied the γ-Bi_2O_3 and other sillenite crystals like BTO, 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%. In addition, the O atoms that form the tetrahedral environment of these Bi atoms occupy their sites with the same probability. Table II shows some physical parameters and structural data for sillenites $Bi_{12}TiO_{20}$, $Bi_{12}GeO_{20}$ and $Bi_{12}SiO_{20}$ [16-22]. The ionic radii of the Si^{4+} (0.42Å), Ge^{4+} (0.53Å) and Ti^{4+} (0.68Å) are distinctively shorter than that of Bi^{3+} (0.95Å) by 0.53Å, 0.42Å and 0.27Å, respectively. As seen from ionic radii difference, some of the tetrahedral sites are probably left vacant to

retain the charge balance in the grown crystals. This can make the reflectivity interpretation more complex.

Table II. Some physical parameters of sillenite $Bi_{12}MO_{20}$ (M = Ge, Si and Ti) [16-22].

Material	BSO	BGO	BTO
Chemical Formula	$Bi_{12}SiO_{20}$	$Bi_{12}GeO_{20}$	$Bi_{12}TiO_{20}$
Lattice Parameters, Å	10.104	10.145	10.175
Density, g/cm^3	9.14	9.2	9.2
Transparency Range, μm	0.4 - 6	0.4 - 7	0.5 - 6
Refractive Index at $\lambda = 0.63$ μm	2.54	2.55	2.56
Dielectric Constant	56	40	46

Crystal growth and measurements:

Pure BGO and BSO crystals belonging to the sillenite family were grown by Czochralski method and the BTO crystals were grown by the Top Seeded Solution Growth (TSSG) technique at the Institute of Physics, Military Academy of Technology, Warsaw-Poland [22-24]. High purity Bi_2O_3 and SiO_2, GeO_2 and TiO_2 were the starting materials for the host. All the crystals are transparent.

The samples were cut from pure BGO, BSO and BTO cubic single crystals. The measurements were performed on surfaces mechanically and chemically polished using progressively finer abrasives. For the final stage, the samples were polished with Al_2O_3 (0.05-micron grit). The surfaces were cleaned with ethyl alcohol just before the experiment.

We have measured the reflectivity of the pure BGO, BSO and BTO cubic single crystals for light energy between 1.5 and 6eV using unpolarized light. The measurements for light energy between 1.5 and 4eV were carried out on a quartz prism monochromator with a halogen lamp used as the light source. For higher energy range (from 4 to 6 eV) a vacuum ultraviolet monochromator based on the Seya-Namioka scheme was used. The source of the radiation was a hydrogen gas discharge lamp (pressure - 1.3Pa) connected with the monochromator. 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 a photomultiplier with a quartz window. The second part of the light went above the sample to another luminophor- photomultiplier set. For modulated signals from the two photomultipliers were measured with lock-in nanovoltmeters. X-type computer recorded the data. Other experimental details could be found in Ref. [25].

Experimental results and discussion:

Figure 2 shows the reflectivity spectra of Bi$_{12}$GeO$_{20}$, Bi$_{12}$SiO$_{20}$ and Bi$_{12}$TiO$_{20}$ sillenite crystals in the range of energy from 1.5 to 6eV at room temperature 300K. Considerable structure appears in all the curves, as expected; there is reasonably close correspondence in the positions and shapes of the peaks. The features in the spectra are indicated with capital letters. The main results of the study are summarized in the table III that show the energy positions of the structures observed in the R(hv) spectra.

The reflectivity spectra of Bi$_{12}$MO$_{20}$ (M=Si, Ge, Ti) seen by us were compared with that obtained previously [11-13, 26]. The observed transitions of the energy lower than the energy gap (the energy gap between the valence and conduction band for BGO, BSO and BTO was experimentally estimated, at about 3.2eV) are marked as A and B. There are two main maxima, each one having a doublet structure, in the low energy region of the reflectivity spectra (E=6eV). The corresponding peaks are D, E and F, G respectively.

Since the different chemical nature of the distribution atoms in the lattice of the crystals change distances between the nearest atoms neighbor in the crystals, this can lead to a considerable change in the bonding energy nuclei levels of anions, because of the ions Ge, Si, or Ti appear nearer to oxygen rather than bismuth (Table I). In addition, this disorder will affect the density of states distribution in valence band.

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. However, the valence band structure is constructed prevalently from the anion p-like orbitals only very near to the Γ point [27]. 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. [28]. 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. Also, they 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. On the other hand, Kalinkin et al. [27] have reported an electronic structure calculation for Bi$_{12}$GeO$_{20}$. They used an X$_\alpha$-Relativistic Self-Consistent Method to calculate the density of electronic states. These authors arrived at the conclusion that O(2p) and Bi(6p) states form the maximum of the valence band. The upper valence band close to Γ point stem mostly from the O(2p) states, while in the next parts of the valence band, there was a participation of the p-like states to the Bi and O atoms. Also, Medvedeva et al. [29] calculated the electronic structure of the δ-Bi$_2$O$_3$ compound using LMTO method. They showed that the both valence and conduction bands consist of Bi(6p) and O(2p) states. The topmost valence bands are the oxygen 2p states, while the upper and the lowest part valence bands are formed fundamentally 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.

Table III. Energies of the position peaks and shoulders discerned in the reflectivity spectra observed of the Bi$_{12}$GeO$_{20}$, Bi$_{12}$SiO$_{20}$ and Bi$_{12}$TiO$_{20}$ crystals at room temperature (in eV).

Peaks	Bi$_{12}$GeO$_{20}$	Bi$_{12}$SiO$_{20}$	Bi$_{12}$TiO$_{20}$
A	2.51	2.51	2.45
B	2.85	2.83	2.98
C	3.41	3.40	3.44
D	3.88	3.91	3.90
E	4.31	4.31	4.30
F	5.31	5.32	5.31
G	5.76	5.75	5.75
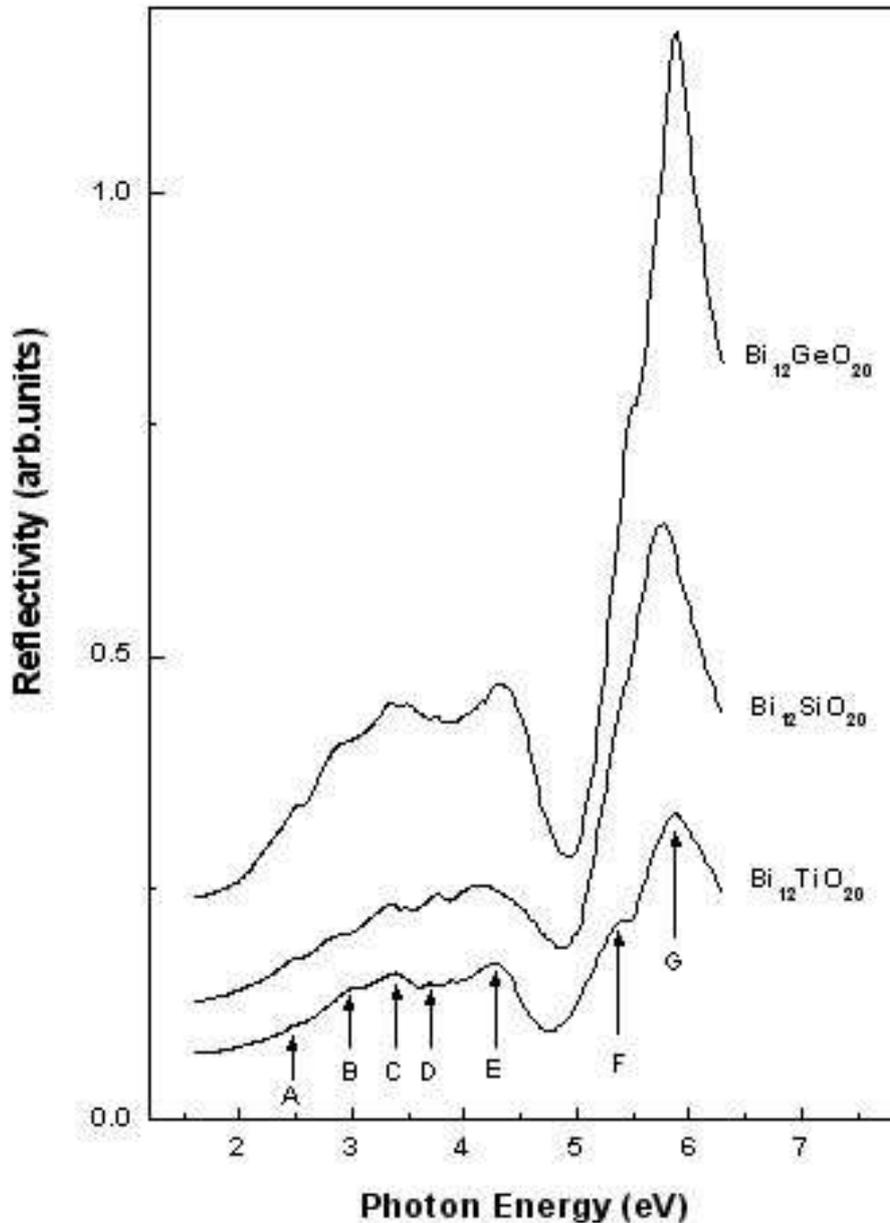
Fig.2. Fundamental reflectivity spectra of the Bi$_{12}$SiO$_{20}$, Bi$_{12}$GeO$_{20}$ and Bi$_{12}$TiO$_{20}$ crystals at room temperature for unpolarized light.

The Brillouin zones of sillenites-type are body cubic centered, but the 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.

The feature A beginning at 2.51 for BGO, 2.51 for BSO and 2.45 for BTO is believed to correspond to transitions within the band gap (3.2eV), since the energy of this structure is less than the energy gap; about 0.69 eV for BGO, 0.69 eV for BSO and 0.75 eV for BTO, respectively. Montenegro *et al.* [30] studied the photoactive centers in the BTO material by photoconductivity measurements. They showed a very sharp steep at 2.2eV in the band gap and attributed it to the presence of a photoactive center. Marqute *et al.* [31] 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 to the conduction band because of the n-type photoconductivity of these crystals. Also, Bloom and McKeever [32] studying $Bi_{12}GeO_{20}$ and $Bi_{12}SiO_{20}$ crystals, arrive at the conclusion that, the absorption which gives the specimen a yellow coloration, is believed to be caused by the optical excitation of electrons from deep donor states located below the Fermi level to the conduction band. Following Montenegro *et al.* [30], Marqute *et al.* [31] and Bloom & McKeever [32], we attribute this peak to the transition from deep donor states lying in energy gap to the minimum of the conduction band. In addition, photoconductivity, optical absorption and photocurrent excitation have been reported in $Bi_{12}GeO_{20}$, $Bi_{12}SiO_{20}$ and $Bi_{12}TiO_{20}$ by several groups [2, 12 and 13]. They found a shoulder (about 2.6 eV) in the spectra and attribute this feature to the presence of a Ge, Si or Ti vacancy complex below the conduction band edge.

The features B and C, which occur at energy 2.85 and 3.41eV for BGO, 2.83 and 3.40eV for BSO and 2.98 and 3.44eV for BTO respectively, seem to be connected with the indirect optical transitions from valence band to the conduction band. This is consistent with the results reported by Efendiev et al. [12, 13 and 33]. These workers 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. Also, 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, B and C peaks correspond to the indirect optical transitions. The first one correspond to transition from states located below the Fermi level in the band gap to the conduction band (the transition B→Γ(CB)), in agreement with the assignment reported by Efendiev *et al.* [33], who ascribes it to the transition from centres in the band gap to conduction band at Γ. The second transition C occurs from the topmost valence band to the minimum of conduction band; that is from O(2p) states to minimum of the conduction band; probably the transition at the point H(Δ). Thus, based on the discussion above-mentioned 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.

The reflectivity peaks D and E occurring at 3.97 and 4.31 eV for BGO, 3.95 and 4.30 eV for BSO and 3.96 and 4.31 eV for BTO respectively, are connected with direct "allowed" optical transition. Our assignment agrees well with that reported previously [12, 13 and 33]. Hence, we expect that the direct optical transitions occur from valence band to conduction band; that is from Bi (6p)-O (2p) states to minimum of the conduction band. On the other hand, the separation between peaks D and E is 0.34eV for BGO, 0.35 eV for BSO and 0.35 eV for BTO. Therefore, we can attribute the value 0.34-0.35eV to spin-orbit □$_{so}$ valence band splitting at □ point occurring below the top of the valence band. These

transitions, as we expect, have the same final states. Also, the values of the energy difference between the fundamental absorption edge E_g and the peaks D and E are 0.75 and 1.11eV, respectively. Hence, we expect that the first transition D occurs from the state lying about ~0.75 eV below the top of valence band, whereas the second from the state lying about ~1.11 eV below the one. Probably these transitions occur at Γ in the direction Λ.

The peak G exhibits a fine structure consisting of an additional shoulder F. These peaks (G and F) occur at energies of 5.31 and 5.76 eV for BGO, 5.32 and 5.76 eV for BSO and 5.31 and 5.75 eV for BTO. The energy of peak F is in agreements with that shown in the pure Bi reflectivity spectrum [34]. Cardona and Greenway [34] interpreted this peak as the optical transition occurring at □ point of the Brillouin zone. One can notice also that the separation between the two energy components G-F is 0.45 eV for BGO, 0.44eV for BSO and 0.44eV for BTO. This value □□≈□0.44 eV is in good agreement with the corresponding value reported by Efendiev *et al.* [12]; about 0.5eV. Therefore, we attributed this value to the spin-orbit valence band splitting at □ point. Although, we expect that the transitions G and F, correspond the transitions from Bi (6p) - O (2p) valence band to conduction band.

A model of sillenite-type crystals:

Spectra of such sillenites are assumed to cover different regions of a major part of the Brillouin zone. As usual we shall assume that the M_1 an M_2 saddle point are the dominant critical points in the interband spectra, and the structure in the reflection spectra is due to transitions at high symmetry points or lines in Brillouin zone, at which $\nabla_k E_c(k) = \nabla_k E_v(k) \neq 0$.

The optical properties of $Bi_{12}MO_{20}$ (M=Si, Ge, Ti) type sillenites are mainly connected with the Bi-O net structures with respect to the valence and conduction bands. Our interpretation of the optical properties of these materials suggests that the feature in the vicinity of the top of valence band originate from the transition from the O(2p) electron states to the empty electron states dominating the bottom of the conduction bands. Also, the fundamental absorption edge starts from 3.2 eV which correspond to the indirect □□□□ transition. On the other hand, we showed that there is a feature A in the energy gap region resulting from Si, Ge or Ti vacancy complex in the lattice of BGO, BSO and BTO crystals.

The twenty O^{-2} ions per unit cell produce many degenerate levels at Γ in k=0 separated by small energies. This splitting is produced by the crystal field and the electrostatic interaction between O^{-2}(2p) ionic orbitals from one hand and between O(2p) and Bi(6p) ionic orbitals on other hand. This splitting is quite close to the D-E and G-F transitions.

Based on the discussion above-mentioned, we can arrive at the conclusion that the O(2p) contributions are the largest in the higher part of the valence band. Also the presence of strongest covalent bonding between bismuth and oxygen atoms is localized at the bottom of the upper valence bands and consists of hybridized Bi(6p) - O(2p) states.

Figure 3 presents the proposed optical transition model for an explanation of the reflectivity spectra in sillenite type crystals, where the conduction band CB is shown as the band with its minimum not in the centre of the Brillouin zone k=0. The model to explain the reflectivity spectra assumes the existence of an indirect and direct band structure for sillenites common to different crystals, and to determine the energy difference between the

band extrema (special points of the density of states) from the shape of spectra according to the energy distance between the band thresholds.
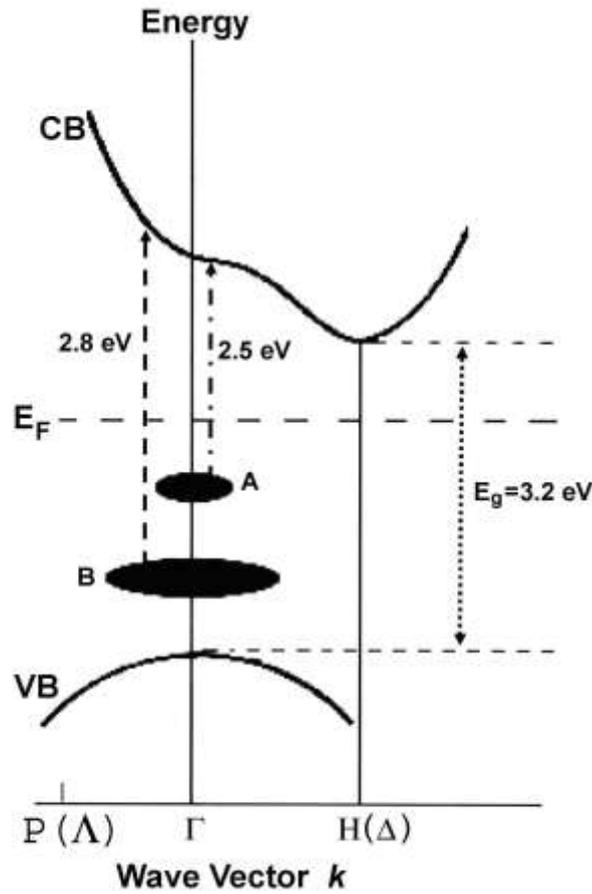
Fig. 3. Model of sillenite-type $Bi_{12}MO_{20}$ (M=Ge, Si, Ti) crystals

Conclusion:

In this paper, we presented results of a study of the optical properties of representative three sillenite $Bi_{12}MO_{20}$ (M=Si, Ge, Ti) single crystals in the energy range from 1.5 to 6 eV at room temperature. The observed optical structures in the spectra were interpreted in terms of transitions between $O^{2-}(2p)$ levels and the various conduction bands. The energy band scheme of $Bi_{12}MO_{20}$ (M=Ge, Si, Ti) is determined mainly by the bismuth and oxygen net structure. The optical transitions occur at the saddle points on the Γ-P (Λ) line.

References:

1. MARINOVA, V. *Optical properties of photorefractive $Bi_{12}TiO_{20}$ single crystals doped with Al, P, Ag, Cu, Co and Al + P.* Vacuum, Vol. 58, 2000, 408-414.

2. HOU, S. L.; LAUER, R. B.; ALDRICH, R. E. *Transport processes of photoinduced carriers in $Bi_{12}SiO_{20}$.* J. Applied Physics, Vol. 44, 1973, 2652-2658; ALDRICH, R. E.; HOU, S. L.; HARWILL, M. L. *Electrical and Optical properties of $Bi_{12}SiO_{20}$.* J. App. Phys., Vol. 42, 1971, 493-494.

3. BURIANEK, M.; MUHLBERG, P. *Improved single crystal growth of the boron sillenite "$Bi_{24}B_2O_{39}$" and investigation of the crystal structure*, Crystal Research Technology, Vol. 37, 2002, 785-796.

4. MARINOVA, V.; SAINOV, V.; LIN, S.; HSU, K. *DC and AC conductivity measurements of $Bi_{12}TiO_{20}$ photorefractive crystals doped with Ag, P, Cu and Cd.* Jap. J. App.Phys., Vol. 41, 2002, 1860-1863.

5. NECHITAILOV, A.; KRASINKOVA, M.; MOKRUSHINA, E.; PETROV, A.; KARTENKO, N.; PROKOFIEV, V. *Correlation between the impurity content, the average charge state of chromium cations and optical absorption in sillenite crystals doped by chromium in wide range of concentrations.* Crystal Research Technology, Vol. 2, 2001, 147- 156.

6. VALANT, M.; SUVOROV, D. *Processing and dielectric properties of sillenite compounds $Bi_{12}MO_{20-\delta}$ (M = Si, Ge, Ti, Pb, Mn, $B_{1/2}P_{1/2}$).* J. Am. Ceram. So., Vol. 84, 2001, 2900-2904.

7. SIMONOV, V. I 1997 *Structural investigation of single crystals and the structure - properties correlation*, Uspekhi, Vol. 40. 964-974.

8. VALANT, M.; SUVOROV, D. *Synthesis and characterization of a new sillenite compound - $Bi_{12}(B_{0.5}P_{0.5})O_{20}$.* J. Am. Ceram. Soc., Vol. 85, 2002, 355-358.

9. GUDAEV, O.; SEDELNIKOV, A. P. Soviet Phys. Solid State, Vol. 29, 1987, 946 -949.

10. MAJCHROWSKI, A.; BOROWIEC, M. T.; ZMIJA, J.; SZYMCZAK, H.; MICHALSKI, E; BARANSKI, M *Crystal growth of mixed titanium sillenites*, Crystal Research Technology, Vol. 37, 2002, 797–802.

11. FUTRO, A. *Analysis of reflectivity spectrum and band structure of $Bi_{12}GeO_{20}$*, J. Phys. Chem. Solids, Vol. 40, 1979, 201-207

12. EFENDIEV, SH.; BAGIEV, V. Soviet Solid. Stat. Phys., Vol. 22, 1980, 3705-3708.

13. EFENDIEV, SH.; BAGIEV, V.; ZEINALLY, A.; ABALASZOV, V.; LOMONOV, V.; MAJER, A. *Optical properties of $Bi_{12}TiO_{20}$ single crystals.* Physica Status Solidi (a), Vol. 63, 1981, K19 – K22; EFENDIEV, SH.; BAGIEV, V.; ZEINALLY, A; SKORIKOV, V. *Optical transitions of $Bi_{12}SiO_{20}$.* Physica Status Solidi (a), Vol. 50, 1978, K141-K143.

14. RADAEV, Sh.; SIMONOV, V. Sov. Phys Kristallografiya, Vol. 37, 1992, 914 -919.

15. SILLEN', L. G. Ark. Kemi, Mineral. Geol., Vol. 12A. 1937, 1-3.

16. ABRAHAMS, S.; JAMIESON, P.; BERNASTIEN, J. *Crystal structure of piezoelectric bismuth germanium oxide $Bi_{12}GeO_{20}$.* J. Chem. Phys., Vol. 47, 1967, 4034- 4041.

17. RADAEV, Sh.; SIMONOV, V.; KARGIN, YU. *Structural features of γ-phase Bi_2O_3 and its place in the sillenite family.* Acta Cryst., Vol. B 48, 1992, 604 – 609.

18. ABRAHAMS, S.; BERNASTIEN, SVENSSON, J. C. J. Chem. Phys., Vol. 71, 1979, 788 -792.

19. FOX, A. J.; BRUTON, T. M. *Electro-optic effects in the optically active compounds $Bi_{12}TiO_{20}$ and $Bi_{40}Ga_2O_{63}$.* Appl. Phys.Letters, Vol. 27, 1975, 360 – 362.

20. OBERSCHMID, R. *Absorption centers of $Bi_{12}GeO_{20}$ and $Bi_{12}SiO_{20}$ crystals*. Phys. Stat. Solidi (a), Vol. 89, 1985, 263-270

21. GRABMAIER, B. C.; OBERSCHMID, R. *Properties of pure and doped $Bi_{12}GeO_{20}$ and $Bi_{12}SiO_{20}$ crystals*. Phys. Stat. Solidi (a), Vol. 96, 1986, 199-210.

22. WARDZYNSKI,W.; SZYMCZAK, H.; BOROWIEC, M.; PATAJ, K.; LUKASIEWICZ, T.; ZMIJA, J. *Light- induced charge transfer processes in Mn-doped $Bi_{12}GeO_{20}$ and $Bi_{12}SiO_{20}$ single crystals*. J. Phys. Chem. Solids, Vol.46, 1985, 1117-1129.

23. MAJCHROWSKI, A.; ZMIJA, J. *Czochralski growth of oxide single crystals under conditions of forced convection in the melt. Material Science and Enegineering,*Vol. A173, 1993, 19-22.

24. WARDZYNSKI,W.; SZYMCZAK, H. *The center of orthorhombic symmetry in Cr-doped $Bi_{12}GeO_{20}$ and $Bi_{12}SiO_{20}$ single crystals.* J. Phys. Chem. Solids, Vol. 45, 1984, 887-896.

25. SAREM, A. KOWALSKI, B. J.; ORLOWSKI, B. A. *Optical properties of Fe-based semimagnetic semiconductors*, J. Phys.: Condens. Matter, Vol. 2, 1990, 8173 – 8187.

26. CARDONA, M.; GREENAWAY, D. L. *Optical properties and band structure of group IV-VI and group V materials*, Phys. Rev., Vol. 133 A, 1964, A1685 - A1697.

27. KALINKIN, A.; SCORICOV, V.; SOLDATOV, A. *Electronic structure of $Bi_{12}GeO_{20}$ crystals*, Inorganic Materials, Vol. 28, 1992, 558 – 562.

28. KITYK, I.; ZAMORSKII, M.; KASPERCZYK, J. *Energy band structure of $Bi_{12}GeO_{20}$ and $Bi_{12}SiO_{20}$ single crystals*. Physica B, Vol. 226, 1996, 381-384.

29. MEDVEDEVA, N. I.; ZHUKOV, V. P.; GUBANOV, V. A.; NOVIKOV, D. L.; KLEIN, B. M J. *Electronic structure and chemical bonding in δ-Bi_2O_3.* Phys. Chem. Solids, Vol. 57, 1996, 1243-1250

30. MONTENEGRO, R.; INOCENTE, N.; FREJLICH, J. *Photoactive centers in photorefractive sillenite crystals.* Annals of Optics, Vol. XXIX, 2006, 193-195.

31. MARQUET, H; GIES, J. G.; MERLE, J. C. *The role of some shallow – trap centers in the photochromism of $Bi_{12}GeO_{20}$.* Europhysics Letters, Vol. 46, 1999, 389 – 394.

32. BLOOM, D.; MCKEEVER, S. W. S. *Trapping of photocarriers in Ga-doped $Bi_{12}GeO_{20}$ at 80K*. J. Appl. Phys., Vol. 77, 1995, 6511- 6520; BLOOM, D; MCKEEVER, S. W. S. *Trap level spectroscopy of undoped and Ga-doped $Bi_{12}GeO_{20}$ using thermally stimulated conductivity*. J. Appl. Phys., Vol. 77, 1995, 6521 – 6533.

33. EFENDIEV, SH.; GAVRYUSHIN, V.; RACIUKAITIS, G.; BAGIEV, V.; KAZLAUSKAS, V.; PUZONAS, G.; ALIEV, R.; USTAFAEV, E. *Induced absorption spectroscopy by lattice defects in sillenite -type crystals*, Physica Status Solidi (b), Vol. 162, 1990, 281- 288.

34. CARDONA, M.; GREENAWAY, D.L. Phys. Rev. 133A, 1964, 1685-1693.