

## Optical Properties of $\text{Bi}_{12}\text{Ti}_{0.8}\text{Ga}_{0.2}\text{O}_{20}$ Single Crystal

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### □ ABSTRACT □

We have measured the reflectivity of  $\text{Bi}_{12}\text{Ti}_{0.8}\text{Ga}_{0.2}\text{O}_{20}$  single crystal at room temperature using energy range from 1.5 to 6eV. Top Seeded Solution Growth (TSSG) technique has been used to produce mixed  $\text{Bi}_{12}\text{Ti}_{0.8}\text{Me}_{0.2}\text{O}_{20}$  single crystals in which Ti was substituted with gallium Ga ions. The results are qualitatively interpreted in terms of the presence of gallium. These structures have been assigned to transitions from energy bands derived mainly from the O2p states and the Bi-O bonding states. As a result, two main effects associated with Ga states have been observed in the spectra. The first is a significant energy shifting of the critical points with respect to  $\text{Bi}_{12}\text{TiO}_{20}$  single crystal. The second is a broadening of the characteristic reflectivity maxima. These results reveal a stronger interaction between O2p and Ga4p states close to the top of the valence band maximum (VBM).

**Keywords:** Sillenites,  $\text{Bi}_{12}\text{TiO}_{20}$ ,  $\text{Bi}_{12}\text{Ti}_{0.8}\text{Ga}_{0.2}\text{O}_{20}$ .

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## الخواص الضوئية للبلورة الأحادية $\text{Bi}_{12}\text{Ti}_{0.8}\text{Ga}_{0.2}\text{O}_{20}$

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### □ الملخص □

تم قياس الانعكاسية للبلورة الأحادية  $\text{Bi}_{12}\text{Ti}_{0.8}\text{Ga}_{0.2}\text{O}_{20}$  عند درجة حرارة الغرفة باستخدام مجال الطاقة من 1.5 إلى 6 eV. استخدمت تقنية التمية العلوية من خلال بذرة المحلول (Top Seeded Solution Growth) (TSSG) لإنتاج بلورات أحادية مختلطة من النوع  $\text{Bi}_{12}\text{Ti}_{0.8}\text{Me}_{0.2}\text{O}_{20}$ ، حيث حلت أيونات الغاليوم Ga محل أيونات التيتانيوم Ti. فسرت النتائج نوعياً بوجود ذرات الغاليوم. أسندت البنى الطيفية الملاحظة في القياس إلى الانتقالات من عصابات الطاقة الناتجة من السويات O2p بشكل رئيسي وسويات الارتباط Bi-O. نتيجة لذلك، لوحظ في أطراف القياس أثرين رئيسيين مرتبطين مع سويات الغاليوم. الأول هو انزياح كبير لطاقة النقاط الحرجة نسبة إلى البلورة الأحادية  $\text{Bi}_{12}\text{TiO}_{20}$ .

والثاني هو تعرض نطاق قمم الانعكاسية المميزة .

تكشف هذه النتائج عن تفاعل قوي بين السويات O2p والسويات Ga4p بقرب أعلى عصابة التكافؤ

(VBM).

الكلمات المفتاحية: السيلينيدات،  $\text{Bi}_{12}\text{TiO}_{20}$ ،  $\text{Bi}_{12}\text{Ti}_{0.8}\text{Ga}_{0.2}\text{O}_{20}$ .

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## Introduction:

Bismuth oxide ( $\text{Bi}_2\text{O}_3$ ) is an interesting dielectric material with potential applications such as optical coatings, metal/insulator/semiconductor (MIS), capacitors and integrated microwave circuits [1]. The Bi-O system is rather complicated and can have four different main crystalline phases, usually indicated by the letters  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$ . The  $\alpha$ -phase bismuth oxide is a very important material for optical applications, when stabilized at room temperature. The  $\alpha$ -phase can be stabilized by adding some ions to its crystalline structure [2].

Crystals with a nominal chemical formula of  $\text{Bi}_{12}\text{MO}_{20}$ , where M = Ge, Si or Ti (hereafter BGO, BSO and BTO, respectively), known as sillenites, crystallize in the cubic system with a I23 space group. They display a fast photorefractive effect, which renders them suitable as a reversible recording medium for real-time holography and image processing applications [2, 3]. In comparison to BSO and BGO, BTO presents some practical advantages for holographic applications, including higher sensitivity to red light, a higher electro-optic coefficient and smaller optical activity [4]. However, intrinsic defects such as core, striations and inclusions appear during the preparation of single crystals, degrading their optical quality and, thus, requiring a means for its elimination.

In recent years, many articles have been published about the influence of impurities added to these crystals in the attempts that have been made to improve their optical properties [5]. Gallium doped BTO crystals (BTO:Ga), in particular, have lately been prepared but few reports discuss the synthesis, growth process and properties of these crystals [6].

Considerable interest in the investigation of the different bismuth oxide compounds has been triggered by their unusual optical and electro-acoustic properties. It shows characteristics that is interesting from the point of view of applications in optics (holography, optical memory cells), quantum electronics and in microwave acoustics [7]. A mixed sillenites  $\text{Bi}_{12}\text{Ti}_{1-x}\text{Me}_x\text{O}_{20}$ , where Me = Ga, with very high photoconductive efficiency were grown and investigated [8]. It is very promising from future application point of view.

Measurements of coefficients of the optical absorption in the region of fundamental absorption edge for the  $\text{Bi}_{12}\text{TiO}_{20}$   $\text{Bi}_{12}\text{Ti}_{0.8}\text{Ga}_{0.2}\text{O}_{20}$  crystals have been carried out by Borowiec *et al.* [9]. They showed that the fundamental absorption edges of all investigated crystals shift towards lower energies due to decreasing electronegativity of the ions placed in tetrahedral positions ( $\text{Ti}^{4+} > \text{Ga}^{3+}$ ).

## Aim of Study:

Fundamental reflectivity is a direct method of investigating the electronic band structure of materials, in this context, the present paper is devoted to the investigation of the reflectivity spectrum of  $\text{Bi}_{12}\text{Ti}_{0.8}\text{Ga}_{0.2}\text{O}_{20}$  single crystal in the energy range 1.5 to 6eV, as well as to the effect of gallium on the reflectivity spectrum of  $\text{Bi}_{12}\text{TiO}_{20}$  with the aim of obtaining some new data about their band structure.

## Methodes and Materials:

$\text{Bi}_{12}\text{TiO}_{20}$  single crystals doped with Ga were grown by Top Seeded Solution Growth (TSSG) technique at the Institute of Physics, Military Academy of Technology [10]. The purity of the starting products  $\text{Bi}_2\text{O}_3$  and  $\text{TiO}_2$  was 99.999% and their proportion was 11:1. The dopant was introduced into the melt solution in the form of oxides  $\text{Ga}_2\text{O}_3$ . In this work pure BTO sample and sample with a Ga concentration in the melt of 80% were used

[10, 11]. All the crystals are transparent. The structure of this material is similar to that of  $\gamma\text{-Bi}_2\text{O}_3$  [3]. The ionic radius of the  $\text{Ga}^{3+}$  (0.62 Å) is less than that of  $\text{Ti}^{4+}$  (0.68 Å) by 0.06 Å, and distinctively less than  $\text{Bi}^{3+}$  (0.95 Å) (by 0.33 Å) [11].

The sample was cut from mixed  $\text{BiTiGaO}$  cubic single crystals. The reflectivity measurements were performed on mechanically and chemically polished surfaces 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 quartz prism monochromator with a halogen lamp used as the light source. At higher energy (from 4 to 6eV) 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. Both systems worked at the similar conditions. Rotating modulator modulated the beam exiting from the monochromator. Other experimental details could be found in Ref. [12].

## Results and Discussion:

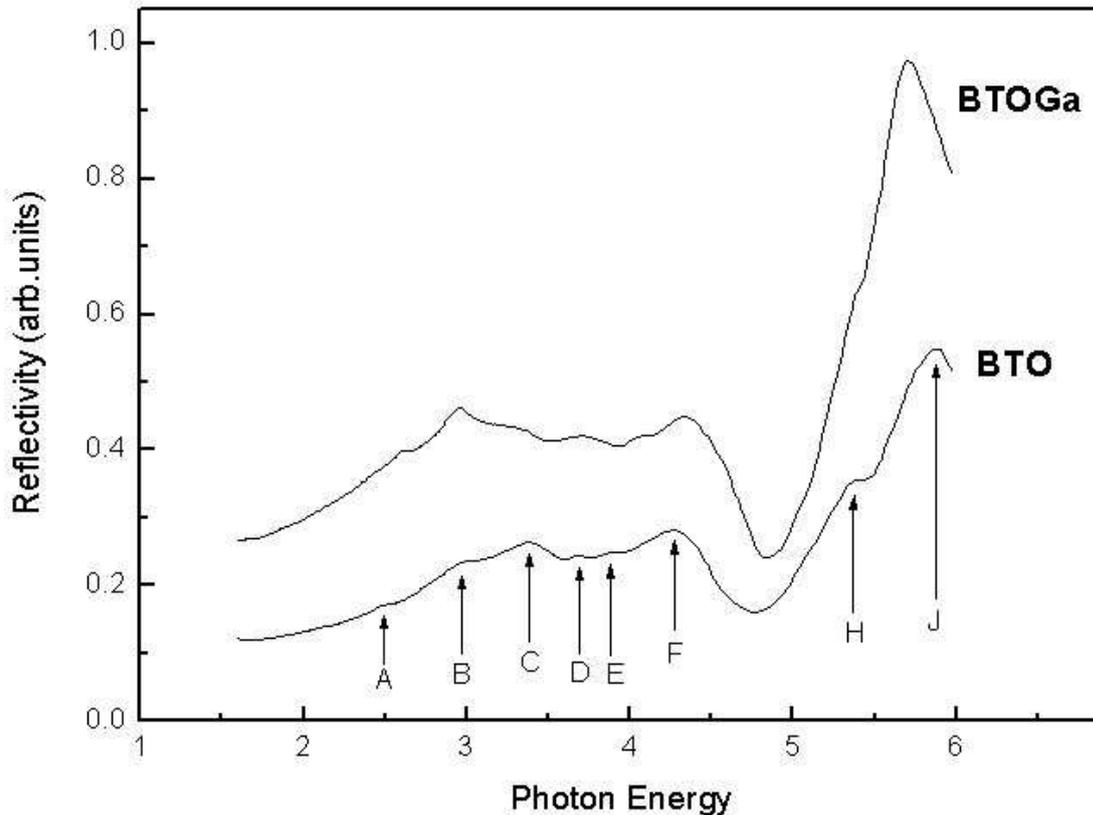
In ternary alloys, the crystalline disorder appears as a result of the local structure (the Bi-O distance is different from the Ga-O or Ti-O) as well as chemical disorder in the lattice of the  $\text{BiTiGaO}$  crystals. This can lead to a considerable broadening and some shift of the reflectivity structures and makes their interpretation more complex. In the measured reflectivity spectrum of  $\text{Bi}_{12}\text{Ti}_{0.8}\text{Ga}_{0.2}\text{O}_{20}$  crystal, the shape and position of the characteristic maxima are relating the spectra to the electronic band structures of the compounds.

Figure 1 presents the measured room temperature reflectivity of  $\text{Bi}_{12}\text{TiO}_{20}$  and  $\text{Bi}_{12}\text{Ti}_{0.8}\text{Ga}_{0.2}\text{O}_{20}$  single crystals in the range of energy from 1.5 to 6eV. The structures are indicated by capital letters. The  $\text{BiTiGaO}$  spectrum is significantly modified with Ga content with respect to  $\text{Bi}_{12}\text{TiO}_{20}$  spectrum. Also, it is clear that there are some peaks, which are independent of Ga composition. The positions of the experimental reflectivity peaks are summarized in table 1.

The structure labeled *A* (see fig.1) for BTO, which occurs at photon energy of 2.50eV, is influenced by presence of the gallium ions, shifting strongly towards higher energies (0.11eV). One of the main structure *B* at 2.97 eV is nearly constant in position with presence of Ga ions, at the same time, its height strongly increase. With presence of Ga ions, the feature *C*, at 3.38 eV also is nearly constant, and simultaneously its height rapidly decreases. Introducing Ga ions shift slightly the maximum labeled *D*, which occurs at photon energy at 3.68 eV (0.04eV). A peculiar feature of the spectrum is the peak *E* at energy 3.90 eV which, in the presence of Ga atoms, shifts towards higher energy (0.16 eV), simultaneously its height slightly increases. The structure *F* is influenced by presence of Ga ions. This feature shifts slightly to higher energy (0.04 eV) and at the same time its height increases (see Fig.1). As seen in Fig. 1, the shoulder *H* at 5.38eV is constant in position with presence of Ga ions. Finally, the energy at which the *J* structure occurs is strongly sensitive to the presence of the Ga ions where its height increases and becoming sharp as shown in Fig. 1. This structure shifts towards lower energy (0.17eV).

**Table 1. Energies of the position peaks and shoulders discerned in the reflectivity spectra of the  $\text{Bi}_{12}\text{TiO}_{20}$  and  $\text{Bi}_{12}\text{Ti}_{0.8}\text{Ga}_{0.2}\text{O}_{20}$  at room temperature (in eV).**

Crystal	A	B	C	D	E	F	H	J
$\text{Bi}_{12}\text{TiO}_{20}$	2.50	2.97	3.38	3.68	3.90	4.28	5.38	5.87
$\text{Bi}_{12}\text{Ti}_{0.8}\text{Ga}_{0.2}\text{O}_{20}$	2.61	2.96	3.37	3.72	4.06	4.32	5.38	5.70



**Fig.1. Fundamental reflectivity spectra of pure  $\text{Bi}_{12}\text{TiO}_{20}$  (BTO) and  $\text{Bi}_{12}\text{Ti}_{0.8}\text{Ga}_{0.2}\text{O}_{20}$  (BTOGa) crystals at room temperature.**

We should note that, the electronic structure of  $\text{Bi}_{12}\text{TiO}_{20}$  was studied by Zhou *et al.* [13] using the plane-wave density functional theory method. They showed that the band structure of  $\text{Bi}_{12}\text{TiO}_{20}$  is determined by Ti3d and the hybridized band of Bi 6s and O2p. This hybridization shifted the VB upward so that the band gap of  $\text{Bi}_{12}\text{TiO}_{20}$  was narrowed. Also, they showed that, the spectra of the prepared BTO samples possessed steep absorption edges, indicating that the absorption in the visible light region may be not due to the transition from the impurity level but due to an intrinsic band transition.

With presence of Ga, the shift of A maximum with respect to  $\text{Bi}_{12}\text{TiO}_{20}$  spectrum was found to be 0.11eV, while the peak B is constant in spite of this one affected by Ga ions. This suggests that the minimum of the conduction band rise and the next conduction band still constant. We should notice that the separation between A and B peaks in the presence of Ga ions being about 0.35eV (see table 1). Also, as is shown (see figure 1), the constant value of the feature B suggest that, the Ga states as well as the increasing heights dominate this region. This effect may be explained as a result of the large admixture of the

4s states Ga compared with Ti 4s. From the photoconductivity and optical absorption measurements on Ga-doped  $\text{Bi}_{12}\text{GeO}_{20}$  crystals, Bloom and McKeever [14] showed that the band-edge absorption is observed in the energy range from 2 to 3.10eV and close to the intrinsic band edge when estimated this at room temperature (about 3.10eV). Also, they arrive at the conclusion that, for undoped sample, the absorption in this region is believed to be caused by the optical excitation of electrons from deep donor states located below the Fermi level to the conduction band, and the addition of the Ga states causes a lowering of the Fermi level. This creates a  $\text{Ga}^{3+M}$  acceptor center, residing approximately 0.8eV above the top of valence band [14, 15, 16]. This supports our suggestion that there is an interaction of the electrons in the valence band close to the  $\Gamma$  point of the Brillouin zone with the 4p electrons of Ga. So, as we see, the A and B peaks are connected with the fundamental energy gap. On the other extreme, we expect that the transitions A and B occur from state lying in the forbidden gap to the minimum of the conduction band. On account of the relatively large energy gap of sillenite, localized transitions with energies smaller than energy gap can be easily observed. The band gap is about 3.20eV at room temperature as was estimated by Oberschmid [15] for  $\text{Bi}_{12}\text{TiO}_{20}$  crystals, whereas the one was about 3.0eV for  $\text{Bi}_{12}\text{Ti}_{0.8}\text{Ga}_{0.2}\text{O}_{20}$  at 4.2 K [8]. If we consider the above picture, we expected the transitions A and B for  $\text{Bi}_{12}\text{Ti}_{0.8}\text{Ga}_{0.2}\text{O}_{20}$  occur from the existence of acceptor state  $\text{Ga}^{3+M}$  in the band gap lying above the top of valence band to conduction band. This consistent with the results reported previously [14, 15, 16]. As a consequence, this enables us to attribute carefully the above modification to strong hybridization of the top of valence band O2p with the 4p states of Ga. Thus, these transitions, as we expect, have the same initial states. In this instance, the transitions A, B should be occurred from acceptor state  $\text{Ga}^{3+M}$  lying in the band gap. This effect suggests that the lowest conduction bands are pushed apart from each other by the empty Ga 4p states, which should be placed between them.

Another problem is that, the C feature is strongly connected with the Ga 4p states in spite of no change observed in position in the spectrum. Moreover, we interpret a stronger decreasing its height as the result of the contribution of several transitions occurring in the large parts of the Brillouin zone. Therefore, deformation of the bands due to the blurring of the Van Hove critical points can cause the strong decrease in height of the C peak. The shift of D seems to be an evidence for the existence and influence of the Ga empty states on the conduction band. Although, the initial valences band states that contribute to the transitions should be repelled to higher energies or remains nearly the same. This, however, remains unexplained. The situation for E and F structures is different. These structures are likely to be affected by the presence of the Ga ions. The maxima identify the transitions close to the  $\Gamma$  point of the Brillouin zone due to of the strong hybridization between O 2p and 4p Ga.

The peak J for pure BTO exhibits a fine structure consisting of an additional shoulder and H, in the neighborhood of the main peak. This splitting of J and H features is small. Although, one can notice that the separation between the two energy components have the same value for J-H doublet; about 0.47eV. The value 0.47eV for J-H doublet is in agreement with the results reported by Efendiev *et al.* [17] for BTO; about 0.5eV. With presence of Ga ions, the separation for J-H doublet decreases (~0.32eV). Our assignment agrees well with that reported by Futro [18] for BGO and by Efendiev *et al.* [17] for BTO, whose assumed that the doublet structure in the reflectivity spectrum is caused by spin-orbit valence band splitting. Therefore, we attributed this value to the spin-orbit valence band splitting and the optical transitions J and H occur at the saddle points on

$\Gamma$  line and not in the high symmetry points of the Brillouin zone. Although, we expect the transitions J and H have the different final states and different initial states close to maximum of the valence band.

### Suggestion and Recommendation:

In this paper, we presented results of the study of the optical properties of representative  $\text{Bi}_{12}\text{TiO}_{20}$  and  $\text{Bi}_{12}\text{Ti}_{0.8}\text{Ga}_{0.2}\text{O}_{20}$  single crystals in the energy range from 1.5 to 6eV at room temperature. It follows from our results that there exists discernible change in the shapes of the valence and conduction bands, caused by the disorder occurring in the lattice. The presence of Ga ions gives (i) almost no change in position of some of the peaks (B, C and H), (ii) a remarkable broadening and shifting of the reflectivity peaks observed in the  $h\nu$  energy range between 3 and 5eV. The results reveal a stronger interaction between O2p and Ga4p states close to the top of the valence band maximum.

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