مجلة جامعة تشرين للدراسات و البحوث العلمية _ سلسلة العلوم الأساسية المجلد (24) العدد (12)2002
Tishreen University Journal for Studies and Scientific Research- Basic Science Series Vol (24) No (12) 2002

Study the Photoconductivity of $Bi_{12}Ti_{0.80}Pb_{0.20}O_{20}$ Single Crystal at Range Temperatures (3.5-500 K)

Dr. Ammar Sarem *
Dr. Hani M. Shaaban *

(Accepted 19/8/2002)

□ ABSTRACT □

Single crystals of mixed sillenites $Bi_{12}Ti_{0.80}Pb_{0.20}O_{20}$ were grown using the top seeded solution growth method. The laser light was used to study the photo-transport properties of these crystals. The measurements were made at temperature range (3.5-500K). Electron photo-transport properties have been shown to be strongly dependent on electronegativity of ions, located in the tetrahedral positions of sillenites. It was evidenced that the illumination changed the photo-conducting properties by 4-5 orders of magnitude comparing with previously studied $Bi_{12}MeO_{20}$, where Me=Ge, Si, Ti. The maximum of transient photoconductivity observed under a laser light excitation is delayed in respect of the light pulse. It found that the temperature dependence of photoconductivity can be connected with the presence of shallow traps. An attempt to find a correlation between photochrmatic and photoconductivity effect is made.

The experimental measurements were carried out on Institute of Physics, Polish Academy of Sciences, Warsaw, Poland, 2001.

* **Associate professor, Department of Physics, Faculty of Sciences, Tishreen University, Lattakia, Syria.**
* **Associate professor, Department of Physics, Faculty of Sciences, Tishreen University, Lattakia, Syria.**

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دراسة الناقلية الضوئية للبلورة الأحادية $Bi_{12}Ti_{0.80}Pb_{0.20}O_{20}$ في مجال درجات الحرارة (3.5 - 500 K)

الدكتور عمار صارم *
الدكتور هاني شعبان*

(قبل للنشر في 2002/8/19)

□ الملخّص □

تمت تنمية بلورات السيلينيت الأحادية $Bi_{12}Ti_{0.80}Pb_{0.20}O_{20}$ باستخدام طريقة (top seeded solution) . استخدم ضوء الليزر لدراسة خواص النقل الضوئي لهذه البلورات. أجريت القياسات في مجال درجة الحرارة (3.5-500K). وقد تبين أن خواص إلكترون النقل الضوئي يمكن أن تكون بشدة متعلقة بقدرة على الجذب للأيونات المتوضعة في مواقع رباعي السطوح لبلورات السيلينيت. تبين أن الإضاءة غيرت خواص الناقلية الضوئية بمقدار 5−4 مراتب في القيمة بالمقارنة مع البلورات المدروسة سابقاً $Bi_{12}MeO_{20}$ حيث Me=Ge, Si, Ti. إن الناقلية الضوئية الانتقالية الملاحظة تحت إثارة ضوء الليزر متأخرة بالنسبة إلى نبض الضوء. وجد أن علاقة الناقلية الضوئية بدرجة الحرارة يمكن أن ترتبط مع المصائد السطحية. تمت المحاولة لإيجاد رابط بين مفعول اللونية الضوئية ومفعول الناقلية الضوئية.

أجريت القياسات التجريبية في معهد الفيزياء في أكاديمية العلوم البولونية – وارسو–بولونيا عام 2001.

* أستاذ مساعد في قسم الفيزياء من كلية العلوم في جامعة تشرين– اللاذقية – سورية.
* أستاذ مساعد في قسم الفيزياء من كلية العلوم في جامعة تشرين– اللاذقية – سورية.

1. Introduction

Sillenites are well known group of cubic crystals with space group symmetry I23 T^3, containing two molecular units per unit cell. Some of the properties making these materials of technological interest include low ultrasonic velocity, small acoustic damping up to 1 GHz, data storage, optical signal processing, image amplification, and dynamic holography [1-5]. The structure of metastable g-Bi_2O_3 is stabilized by the addition of many oxides, mainly in the molar ratio of 6:1. The best-known sillenites $Bi_{12}SiO_{20}$ (BSO) and $Bi_{12}GeO_{20}$ (BGO) melt congruently while $Bi_{12}TiO_{20}$ (BTO) melts incongruently. In the late 1970's was discovered very strong photochrmatic effect caused by doping of BSO and BGO crystals by a number of dopants, like Cr, Mn, Co, and Cu [6, 7]. The origin of photochrmatic effect is related to the photogeneration of polarons in doped sillenites.

The idea of photo-induced enhancement of the conductivity in insulating or semiconducting oxides is used in this paper. Since the photoexcitations have been shown [8] to be relatively long-lived polarons (or bipolarons) we have chosen for our studies materials in which such polarons are relatively easily created by the light. Such materials are the sillenites.

In this work we investigate photoconductive properties of BTO, where titanium atoms are replaced by lead ions. The ratio of titanium to lead atoms was 4:1 and therefore we call this crystals mixed sillenites instead of doped ones.

2. Crystal growth

Bismuth titanium oxide melts incongruently, so one cannot obtain BTO single crystals from stoichiometric mixture of Bi_2O_3 and TiO_2 having the molar ratio (6:1). BTO crystals can be grown from aqueous solutions by hydrothermal method or from high-temperature solutions in Bi_2O_3 acting as a self-flux [8]. Therefore, it was chosen the latter technique due to its similarity to the Czochralski growth, which was used earlier to produce BGO and BSO single crystals (top seeded solution growth, TSSG). A two-zone resistance furnace with precise temperature regulation (Eurotherm 906S regulator/programmer) was used. The starting molar composition of Bi_2O_3: TiO_2 (or TiO_2 + lead oxide) was 9:1. Lead oxide was added to form mixed BTO crystals in the TiO_2:PbO molar ratio 4:1. Crystals were grown from platinum crucibles on [110] BSO seeds. During the growth procedure crystals were rotated at the rate of 30 rpm and pulled up 0,3 mm/h. Two-zone construction of the furnaces allowed to shape the temperature gradients, and in this way influence the growth conditions. It found temperature conditions under which BTO crystals interface was the totally flat (110) plane. This shape of the bottom of crystals made the growth procedure stable, and as-grown BTO crystals were uniform. Figure 1 shows a BTO picture taken with an optical microscope.

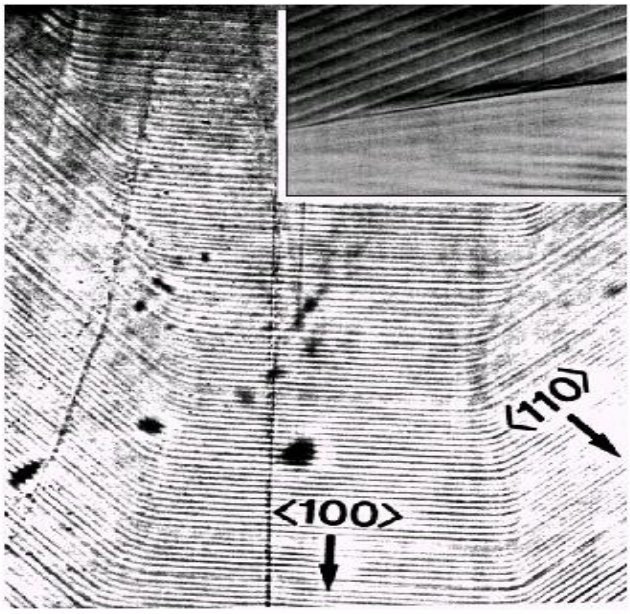

Fig.1 Shows a BTO picture taken with an optical microscope with low intensity polarized light.

3. Experimental

In this paper we report results of photoconductivity investigations of mixed $Bi_{12}Ti_{1-x}Pb_xO_{20}$ (BiTiPbO) single crystals, with x = 0.2. The experiments were performed over the temperature range 3.5-500 K by using two cryostats of different construction (operating with different experimental systems).

Temporal investigations were carried out by using the Cryostat (3.5-500 K). Samples placed in the cryostat were illuminated by 610 nm light pulses of 10 ns duration (20 m J energy in a single pulse) by using the dye laser pumped by the excimer laser. The frequency of pulses was 10 Hz, The transient photoconductivity was monitored directly by oscilloscope.

Frequency characteristics were made by phase sensitive technique with the use of the Lock-In Amplifier. In this case, the samples were placed in the two-step Cryodyne Refrigerator 22C/350C. A 250 W halogen lamp was the source of the probing light. All experiments were done under the electric field of the order of 10^4 V/cm.

4. Results

Dark resistivity of sillenites was established to be higher than resistivity of the air (10^{15} W cm). However, the light illumination of sillenites provides excellent photoconductivity. Relatively high photo-efficient materials are BiTiPbO single crystals. In the case of white light illumination by a 250 W halogen lamp the crystal resistivity decreases to about 10^5 Wcm.

In Fig. 2 the temperature dependent photoconductivity spectrum of BiTiPbO is presented. The measurements were carried out with the use of the phase sensitive technique. Region of photoconductivity related to the energy gap is clearly seen. Usually, at low energies, sillenites show photoconductivity connected with local states located inside the energy gap. For BiTiPbO crystals, this region of photoconductivity spectrum is absent. In the range of temperatures 220-260K, one can see distinct irregularities in the shape of photoconductivity curves. We assume that these irregularities are connected with transient photochrmatic processes [9].

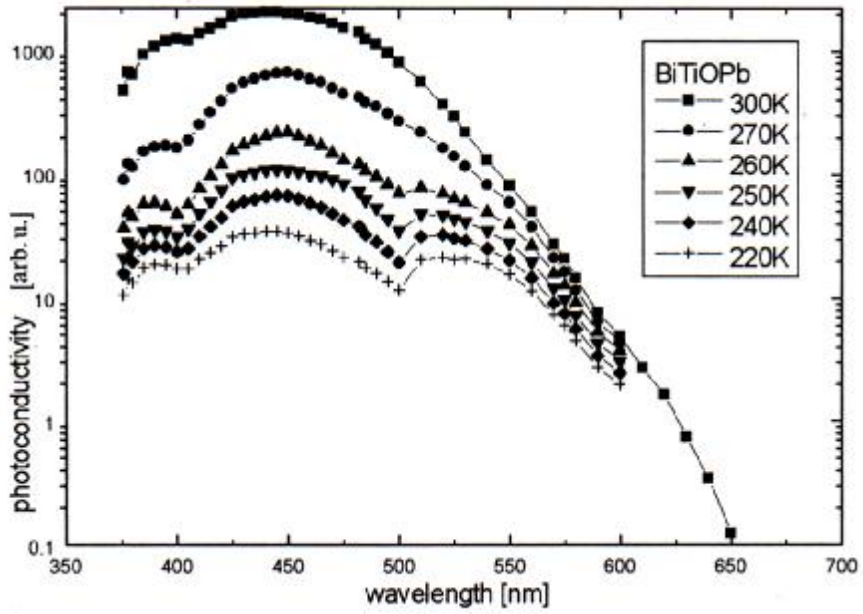

Fig. 2. The photoconductivity spectrum of BiTiPbO single crystal for different temperatures.

Figure 3 shows temperature dependence of the photoconductivity in the temperature range from 4 up to 300 K. In this figure conductivity observed under chopped light condition, for some, indicated chopping, is presented. As one can see, very strong decrease in photoconductivity in the temperature range between 180 K and 220 K.. Such strong decrease in photocurrent is correlated with thermal stability curve of photochromism - Fig. 4. Not only is this one feature correlated - marked lines presented in both figures point to several common characteristic temperatures. Generally, photoconductivity curves presented in Figs. 3 can be separated into two temperature ranges: below 180 K-range A and above 220 K -range B.

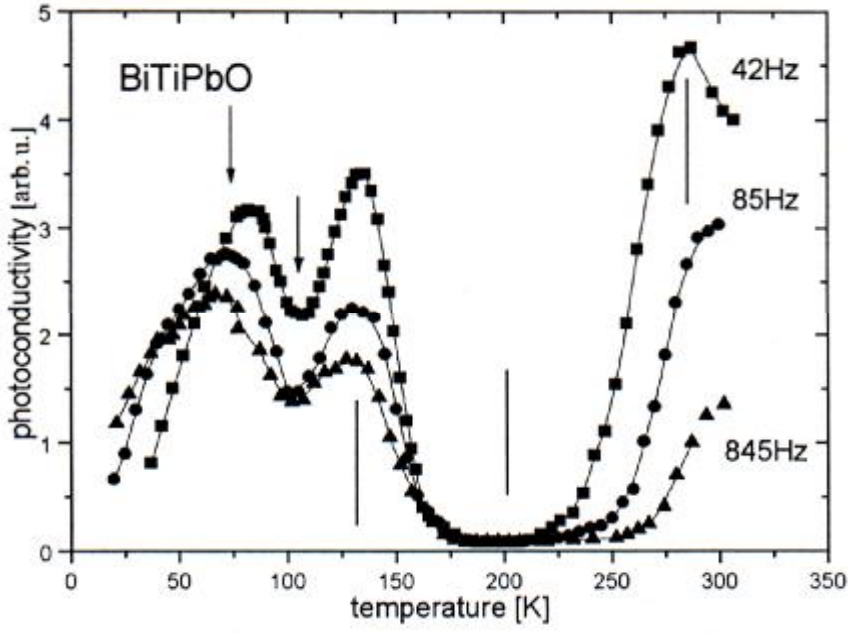

Fig. 3. The temperature dependence of photoconductivity for chopped light.

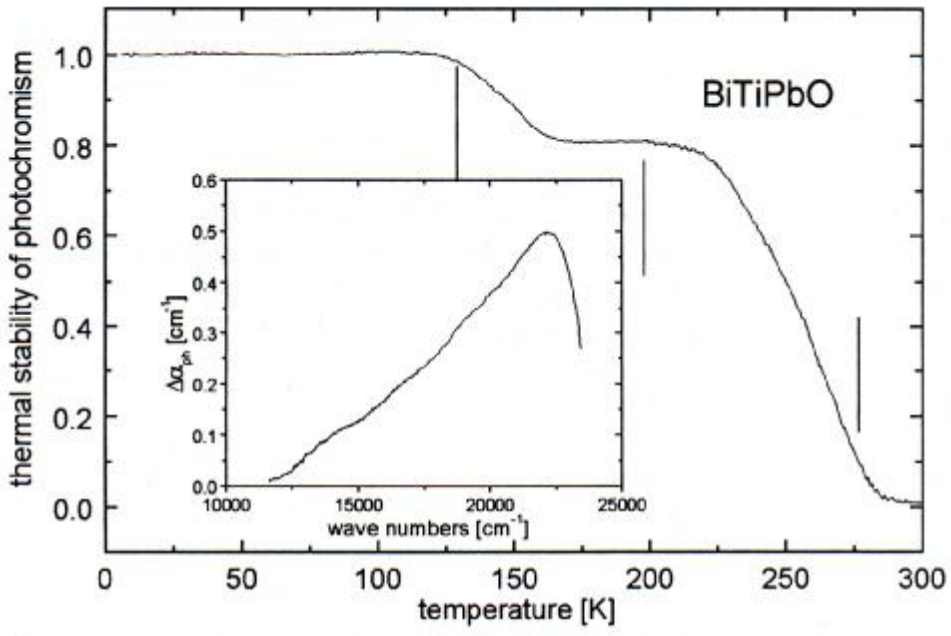

Fig.4. Thermal stability dependence of photochrmatic optical absorption. In the inset, the photochrmatic spectrum is presented.

In Fig. 5 results of transient photoconductivity obtained for sample illuminated by 10 ns laser light pulses (with repetition of 10 Hz) are presented. The maximum of the photoconductivity curve was reached with some delay in respect of a laser light pulse and this delay was dependent on temperature. In the low temperature range, below 180 K, we observe a long-time photoconductivity decay component-see Fig. 5a. In the temperature range B this long decay component is absent (see Fig. 5b).

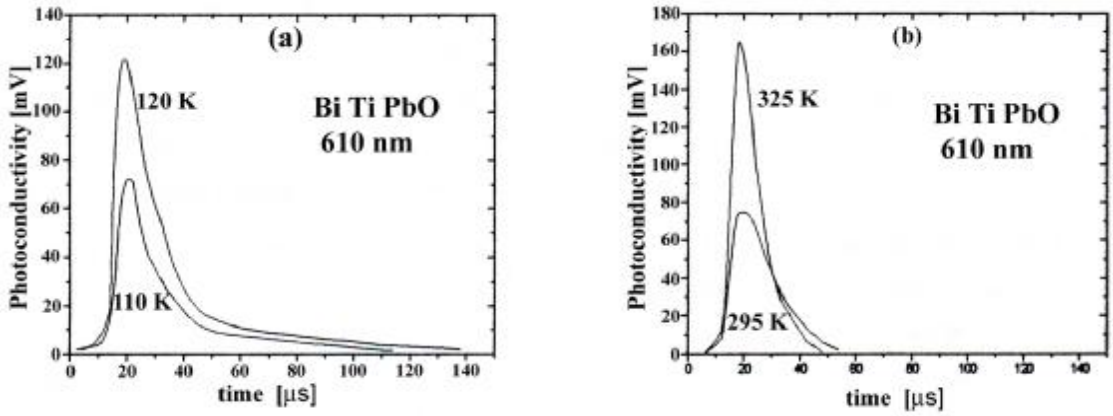

Fig. 5. Transient photoconductivity in different temperature ranges:(a) in range A, (b) in range B.

6. Discussion

Recently, we have performed detailed studies of the photoconductivity of single crystalline sillenites with various energy band gap [10]. We observed shift of the fundamental absorption edge towards lower energy, and this attributed to the decrease in electronegativity of ions located in tetrahedral positions. The absorption edge shifts in the following order: $Ti^{4+} < Ga^{3+} < V^{5+} < Pb^{2+}$. As a rule the photoconductivity, caused by band-to-band transitions, is shifted towards lower energies in the same way as the fundamental absorption edge, see table 1.

Table 1. Values of energy gap at temperature 4.2 K for various single crystalline sillenites [10].

Crystals	Energy gap (in eV) at temperature 4.2 K
$Bi_{12}TiO_{20}$	3.08
$Bi_{12}Ti_{0.80}Ga_{0.20}O_{20}$	3.00
$Bi_{12}Ti_{0.80}V_{0.20}O_{20}$	2.82
$Bi_{12}Ti_{0.80}Pb_{0.20}O_{20}$	2.80

It has been observed that BiTiPbO single crystals are characterized by relatively high photoefficiency [11]. In the case of white light illumination by a 250 W halogen lamp resistivity decreases to about 10^5 W.cm. It means that we managed to improve the photoconducting properties of this material by more than 4-5 orders of magnitude as compared with previously studied sillenites (BGO, BSO, BTO). It is clear that further decrease in resistivity is still possible because no saturation of photoconductivity as a function of light intensity is observed.

New experimental results presented in this paper are consistent with the assumption that one can generate metal grains in sillenites. The most significant argument for this behavior provided photoconductivity obtained with the laser illumination. The transient photoconductivity observed under such conditions is delayed in respect of laser light pulse. The observed signal is composed of two, at least, decay components - Fig.4a. The long-time decay component is similar to that observed by Boyn et al. [12] and Yu et al. [13] for non-metallic samples of $YBa_2Cu_3O_x$. The effect of illumination was identified in this case as arising due to the generation of metallic grains. Since in both $YBa_2Cu_3O_x$ and BiTiPbO polarons were shown to exist, we should assume that the light illumination creates the metallic grains, which are responsible for long-time decay of photoconductivity. Microsecond timescale of transient photoconductivity in BiTiPbO is connected with the characteristic relaxation time of traps contributing to the photochromism in these crystals. This result indicates on the correlations between photochromism and photoconductivity. The same very long timescale phenomenon was presented earlier for photo-response of $YBa_2Cu_3O_x$ thin film microstructures [14].

Temperature dependence of photoconductivity for the different frequency of illuminating light is very interesting although still not clear. Mechanism of frequency dependent photoconductivity is probably related to the same mechanism of trapping and re-trapping on shallow electron traps as presented in [12]. This result indicates also on the correlations between photochromism and photoconductivity (indicated by marked lines in Figs. 3 and 4), because of the shape of thermal stability curves of photochromism is clearly explained as due to the electron shallow traps [15, 16]. The behavior at temperatures below 70 K (indicated by arrow in Fig. 3) may be connected with the presence of shallow hole traps [17].

Another relation between photochromism and photoconductivity results from the analysis of the dependences presented in Fig.2. For wavelength of light of 500 nm we observed unusual decrease in photoconductivity with the temperature decrease. This behavior can be correlated with maximum of the most intense optical absorption band in the photochrmatic spectrum (presented in the inset of Fig. 4) [9].

7. Conclusion

In this paper, we have optimized TSSG technique to obtain uniform mixed BiTiPbO single crystals.

Electron photo-transport properties have been shown to be strongly dependent on electronegativity of ions, located in the tetrahedral positions of sillenites. Shift of photoconductivity spectra to lower energy was directly related to the energy gap between the valence and conduction bands. The energy gap in BiTiPbO single crystals is smaller than that in other sillenites like BTO and $Bi_{12}Ti_{0.8}Me_{0.2}O_{20}$, where Me = Ga^{3+}, V^{5+}, Pb^{2+} (table1)

From the analysis of photoconductivity in the case of chopped light or laser pulse illumination some characteristic temperatures can be found (see Fig. 3). The temperature dependence of photoconductivity can be connected with the presence of shallow traps. The same traps are involved in temperature stabilization of photochrmatic effect in sillenites (Fig. 4).

The maximum of transient photoconductivity observed under a laser light excitation is delayed in respect of the light pulse. In the low temperature range it is composed of two, at least, time components. We suggest that the long-time decay tail is connected with metallic conductivity in light-induced metal grains.

Acknowledgments

Investigations reported in this paper were supported by Tishreen University, Lattakia, Syria.

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