PHOTOCONDUCTIVITY OF $Bi_{12}Ti_{1-x}Pb_xO_{20}$ SINGLE CRYSTAL

M.T. BOROWIEC[a]*, B. KOZANKIEWICZ[a], H. SZYMCZAK[a], J. ŻMIJA[b], A. MAJCHROWSKI[b], M. ZAŁĘSKI[a] AND T. ZAYARNYUK[a]

[a]Institute of Physics, Polish Academy of Sciences
Al. Lotników 32/46, 02-668 Warsaw, Poland
[b]Institute of Applied Physics, Military University of Technology
Kaliskiego 2, 00-908 Warsaw, Poland

(Received August 25, 1999; revised version November 8, 1999)

Single crystals of mixed sillenites $Bi_{12}Ti_{1-x}Pb_xO_{20}$ were grown using the top seeded solution growth method. The pulse illumination was used to study the phototransport properties of these crystals. It was evidenced that the illumination changed the photoconducting properties by 4–5 orders of magnitude comparing with previously studied $Bi_{12}MeO_{20}$, where Me = Ge, Si, Ti. The performed experiments indicate on the photogeneration of metallic grains in the insulating matrix of $Bi_{12}Ti_{1-x}Pb_xO_{20}$. Correlations between photochromism and photoconductivity was established.

PACS numbers: 72.40.+w, 78.20.Nv, 72.20.Jv

1. Introduction

Although the mechanism responsible for high-temperature superconductivity is still unclear, it is now well established that chemical doping of the parent oxide insulating cuprates may result in the appearance of metallic state and superconductivity. Apart from chemical doping there are also other techniques by which additional carriers may be introduced to the parent compound: charge transfer of carriers through application of hydrostatic pressure [1] and carriers generation by photodoping. The carriers induced by the photoexcitation can lead to the same results as chemical doping without changing the material composition and the crystal structure. This makes this kind of studies very interesting and opens possibility to observe photoinduced metallic state (or even superconductivity) in various insulating materials. Transient photoinduced changes of more than ten orders of magnitude in the surface resistivity of some parent compounds [2] have confirmed the possibility to induce metallic state in insulating oxides. The important point in

*Corresponding author: e-mail: borow@ifpan.edu.pl

transient photoconductivity experiments is to separate "true" and bolometric responses of the materials under studies. In Ref. [3] such separation for $YBa_2Cu_3O_x$ has been performed and the existence of "true" photoconductivity has been confirmed. In addition to the transient photoconductivity, the persistent photoconductivity has been observed in $YBa_2Cu_3O_x$ thin films near the metal–insulator transitions [3–5]. The photodoping creates in this case metastable states with a very long relaxation time [6]. Persistent photoconductivity has been observed in both insulating and superconducting $YBa_2Cu_3O_x$ thin films [7]. This experiment indicates that the existence of metal–insulator transition is not necessary condition for appearance of photoinduced effects in the parent compounds.

The idea of photoinduced 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.

2. Sillenites

Sillenites are well known group of non-centrosymmetric cubic crystals of $I23$ space group. The structure of metastable γ-Bi_2O_3 is stabilised 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. These crystals find many applications in such fields as data storage, optical signal processing, image amplification, and dynamic holography [9]. In the late 1970's some of the authors of this paper discovered very strong photochromic effect caused by doping of BSO and BGO crystals by a number of dopants, like Cr, Mn, Co, and Cu [10, 11]. The origin of photochromic effect is related to the photogeneration of polarons in doped sillenites. We have investigated photochromic effects in BSO and BGO single crystals doped with various transition metal ions [12, 13].

In this work we investigate photoconductive properties of BTO, where titanium atoms were 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.

3. 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 [14]. We have chosen the latter technique due to its similarity to the Czochralski growth which we 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. We 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.

4. 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 Oxford Instrument Cryostat CF 1104 (3.5–500 K). Samples placed in the cryostat were illuminated by 610 nm light pulses of 10 ns duration (20 mJ energy in a single pulse) by using the Lambda Physik FL3001 dye laser pumped by the LPX100 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 PAR 5209. 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.

5. Photoconductivity

Dark resistivity of sillenites was established to be higher than resistivity of the air (10^{15} Ω cm). However, the light illumination of sillenites provides excellent photoconductivity. Relatively high photoefficient 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 Ω cm.

In Fig. 1 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 220–260 K one can see distinct irregularities in the shape of photoconductivity curves. We assume that these irregularities are connected with transient photochromic processes [15]. In the figure inset, we present the (log–log) current–voltage (I–V) dependence.

Figure 2 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. Inset in Fig. 2 presents frequency characteristics at $T = 287$ K. As one can see, the temperature dependences are complicated. In Fig. 2 very strong decrease in photoconductivity in the temperature range between 180 K and 220 K is observed. Such strong decrease in photocurrent is correlated with thermal stability curve of photochromism

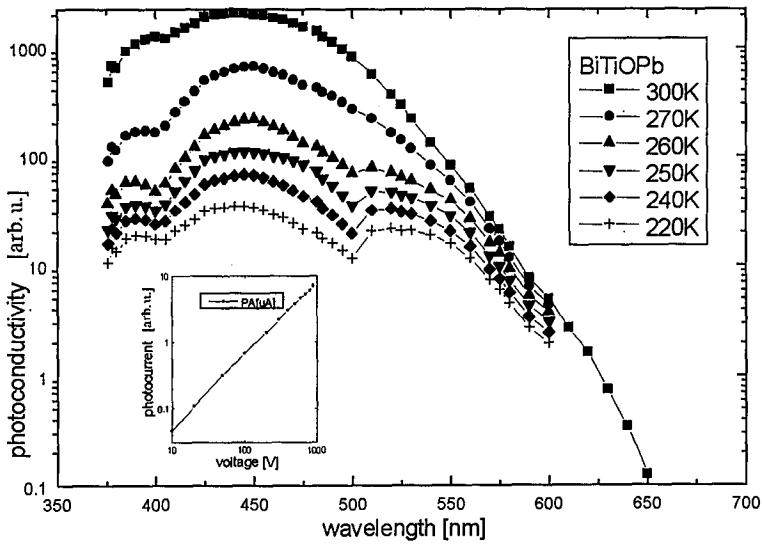

Fig. 1. The photoconductivity spectrum of BiTiPbO single crystal. In the inset the $I-V$ characteristics is shown.

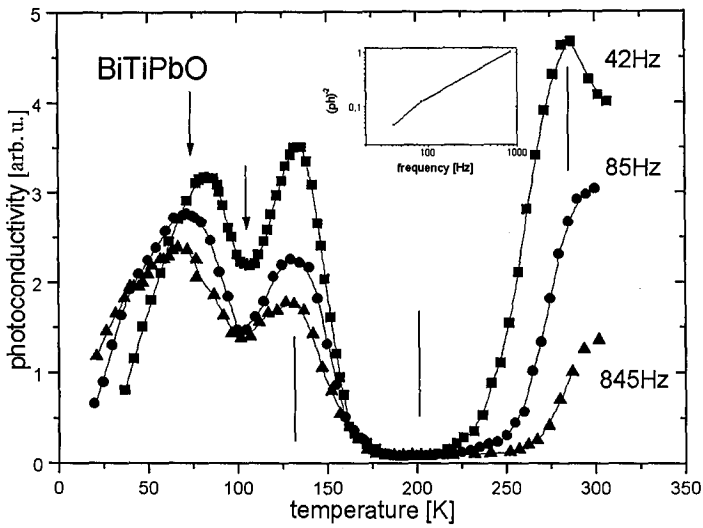

Fig. 2. The temperature dependence of photoconductivity for chopped light. In the inset the frequency dependence of photoconductivity is presented.

— Fig. 3. Not only this one feature is correlated — marked lines presented in both figures point to several common characteristic temperatures. Generally, photoconductivity curves presented in Figs. 2 can be separated into two temperature ranges: below 180 K — range A and above 220 K — range B.

In Fig. 4 results of transient photoconductivity obtained for sample illuminated by 10 ns laser light pulses (with repetition of 10 Hz) are presented. The

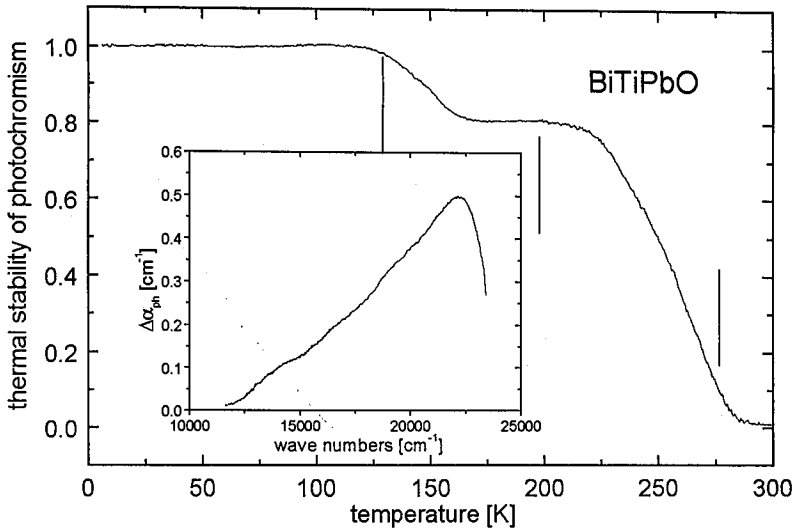

Fig. 3. Two-step thermal stability dependence of photochromic optical absorption. In the inset the photochromic spectrum is presented.

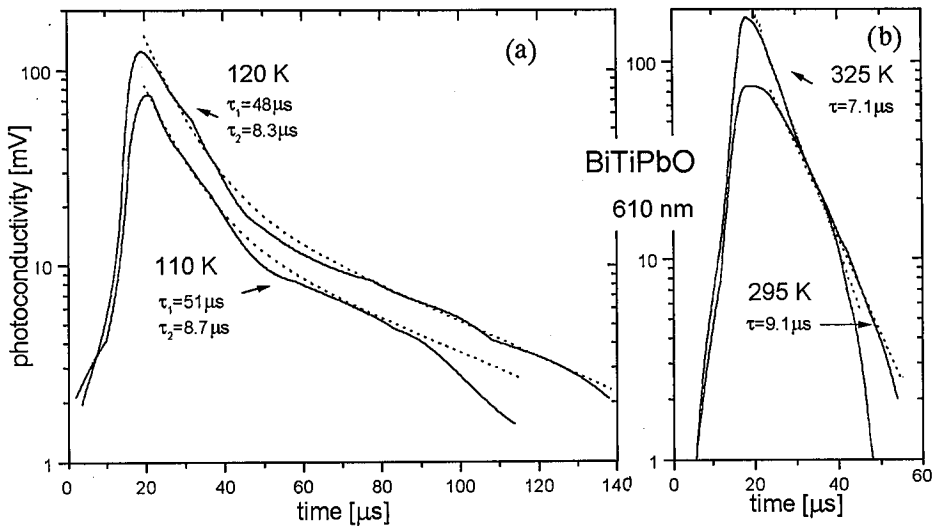

Fig. 4. Transient photoconductivity in different temperature ranges: (a) in range A, (b) in range B. The dotted lines correspond to the indicated parameters of the decays.

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. 4a. In the temperature range B this long decay component is absent (see Fig. 4b).

6. Discussion

Recently, we have performed detailed studies of the photoconductivity of single crystalline sillenites with various energy band gap [16]. It has been shown that the observed shift of the fundamental absorption edge towards lower energy is due to the decrease in electronegativity of ions located in tetrahedral positions. The absorption edge shifts in the following order: $Ti^{4+} < Ga^{3+} < V^{5+} < Pb^{2+}$ [16]. 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.

It has been observed that BiTiPbO single crystals are characterized by relatively high photoefficiency [17]. In the case of white light illumination by a 250 W halogen lamp resistivity decreases to about 10^5 Ω 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 behaviour 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. [18] and Yu et al. [19] 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 photoresponse of $YBa_2Cu_3O_x$ thin film microstructures [20].

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 retrapping on shallow electron traps as presented in [18]. This result indicates also on the correlations between photochromism and photoconductivity (indicated by marked lines in Figs. 2 and 3), because of the shape of thermal stability curves of photochromism is clearly explained as due to the electron shallow traps [12, 13]. The behaviour at temperatures below 70 K (indicated by arrow in Fig. 2) may be connected with the presence of shallow hole traps [21].

Another relation between photochromism and photoconductivity results from the analysis of the dependences presented in Fig. 1. For wavelength of light of 500 nm we observed unusual decrease in photoconductivity with the temperature decrease. This behaviour can be correlated with maximum of the most in-

tense optical absorption band in the photochromic spectrum (presented in the inset of Fig. 3) [15].

7. Conclusion

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

Electron phototransport 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 $BiTi_{0.8}Me_{0.2}O$, where Me = Ga^{3+}, V^{5+}, Pb^{2+}.

The measured temperature dependences of photoconductivity are complicated. Despite this, from the analysis of photoconductivity in the case of chopped light or laser pulse illumination some characteristic temperatures can be found (see Fig. 2). The temperature dependence of photoconductivity can be connected with the presence of shallow traps. The same traps are involved in temperature stabilisation of photochromic effect in sillenites (Fig. 3).

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.

The results presented in this paper can be shortly summarised by the following sentence: conductivity of sillenites can vary as much as 15 orders of magnitude (from the metallic to dark resistivity) when changing their illumination.

Acknowledgments

Investigations reported in this paper were partly supported by the Committee for Scientific Research grant No. 7 T08A 009 11.

References

[1] V.P. Dyakonov, I. Fita, N. Doroshenko, M. Baran, S. Piechota, H. Szymczak, *Physica C* **276**, 245 (1997).

[2] G. Nieva, E. Osquiguil, J. Guimpel, M. Maenhoudt, B. Wuyts, Y. Bruynseraede, M.P. Maple, J.K. Schuller, *Phys. Rev. B* **46**, 14249 (1992).

[3] V.I. Kudinov, I.L. Chaplygin, A.I. Kirylyuk, N.M. Kreines, R. Laiko, E. Lähderanta, C. Ayache, *Phys. Rev. B* **47**, 9017 (1993).

[4] A.I. Kirylyuk, N.M. Kreines, V.I. Kudinov, *Pis'ma Zh. Eksp. Teor. Fiz.* **52**, 695 (1990) [*JETP Lett.* **52**, 49 (1990)].

[5] S.L. Gnatchenko, A.M. Ratner, M. Baran, R. Szymczak, H. Szymczak, *Phys. Rev. B* **55**, 3876 (1997).

[6] C. Stockinger, W. Markowitsch, W. Lang, W. Kula, R. Sobolewski, *Phys. Rev. B* **57**, 8702 (1998).

[7] S.L. Budko, H.H. Feng, M.F. Davis, J.C. Wolfe, P.H. Hor, *Phys. Rev. B* **48**, 16707 (1993).

[8] Y.H. Kim, C.M. Foster, A.J. Heeger, S. Cox, L. Acedo, G. Stucky, *Phys. Scr. Vol. T* **27**, 19 (1989).

[9] S.I. Stepanov, M.P. Petrov, in: *Topics in Applied Physics*, Vol. 61, Eds. P. Günter, J.P. Huignard, Springer-Verlag, Berlin 1988, p. 263.

[10] W. Wardzyński, T. Łukasiewicz, J. Żmija, *Opt. Commun.* **30**, 203 (1979); M.T. Borowiec, W. Wardzyński, T. Łukasiewicz, J. Żmija, in: *Proc. X Int. Conf. Phys. Semicond. Comp., Jaszowiec (Poland) 1980*, Ed. J.M. Langer, Ossolineum, Wrocław 1980, p. 132.

[11] W. Wardzyński, H. Szymczak, M.T. Borowiec, K. Pataj, T. Łukasiewicz, J. Żmija, *J. Phys. Chem. Solids* **46**, 1117 (1985); M.T. Borowiec, *Physica B* **132**, 223 (1985).

[12] T.N. Nguyen, M.T. Borowiec, *J. Phys. Chem. Solids* **49**, 1379 (1988); M.T. Borowiec, B. Kozankiewicz, T. Łukasiewicz, J. Żmija, *J. Phys. Chem. Solids* **54**, 955 (1993).

[13] M.T. Borowiec, *Proc. SPIE* **1845**, 110 (1993); *Proc. SPIE* **3178**, 173 (1997); M. Załęski, M.T. Borowiec, H. Szymczak, K. Przegiętka, H.L. Oczkowski, *Opt. Commun.* **151**, 46 (1998).

[14] T.M. Bruton, J.C. Brice, O.F. Hill, P.A.C. Whiffin, *J. Cryst. Growth* **23**, 21 (1974); S. Miyazawa, *Opt. Mater.* **4**, 92 (1995); M.L. Barsukova, V.A. Kuznetsov, A.N. Lobachev, Yu. Shaldin, *J. Cryst. Growth* **13/14**, 530 (1972).

[15] M.T. Borowiec, A. Majchrowski, H. Szymczak, J. Żmija, M. Załęski, *Proc. SPIE* **3724**, 260 (1999).

[16] A. Majchrowski, M.T. Borowiec, J. Żmija, H. Szymczak, E. Michalski, M. Załęski, *J. Mater. Sci.*, in press.

[17] J. Żmija, M.T. Borowiec, A. Majchrowski, H. Szymczak, M. Załęski, *Proc. E-MRS'99 Spring Meeting, Strasbourg 1999*, in press.

[18] R. Boyn, K. Lube, H.-U. Habermeier, N. Pruss, *Physica C* **181**, 75 (1991).

[19] G. Yu, A.J. Heeger, G. Stucky, N. Herron, E.M. Carron, *Solid State Commun.* **72**, 345 (1989).

[20] J. Demsar, M. Zavratnik, B. Podobnik, V.I. Dediu, D. Mihailovic, *J. Supercond.* **10**, 455 (1997).

[21] M. Załęski, M.T. Borowiec, H. Szymczak, A. Majchrowski, J. Żmija, *Proc. SPIE* **3724**, 264 (1999); M. Załęski, *J. Appl. Phys.*, 1999, in press.