Transactions of the Materials Research Society of Japan 24 [4] 671-674 (1999)

Optical properties of $Ba(Pb_{1-x}Bi_x)O_y$ films prepared by spin coating pyrolysis method

Katsuyoshi Kakinuma, Kazuo Fueki* and Hiroshi Yamamura

Department of Applied Chemistry, Faculty of Engineering, Kanagawa University

3-27-1, Rokkakubashi, Kanagawa-ku, Yokohama, Japan, 221-8686

Fax: +81-45-413-9770, e-mail: kaki@cc.kanagawa-u.ac.jp

*Department of Industrial Chemistry, Faculty of Science and Technology, Science University of Tokyo

2641, Yamazaki, Noda, Chiba, Japan, 278-8510

Fax: +81-471-23-9890

Highly *c*-axis oriented films of $Ba(Pb_{1-x}Bi_x)O_y$ were fabricated on a $SrTiO_3$ substrate by the spin-coating pyrolysis method. The transmittance and reflectivity of the films were determined and the absorption coefficient was calculated. The absorption spectra of $BaPbO_y$ revealed the existence of an energy gap between the Pb 6*s*-conduction band and the O 2*p*-valence band, though the electrical conduction was metal-like. This metal-like conduction was interpreted in terms of the formation of holes due to the overlapping of acceptor level originated from the excess oxygen with the O 2*p*-valence band. In the range $0.3<x<1.0$, the oxygen content was stoichiometric and the conduction was semiconducting. It was concluded that an energy gap existed from the valence band consisting of O2*p* and Bi(Ⅲ) energy levels to the conduction band originated from the Pb 6*s* and Bi(Ⅴ) levels.

Key words: Thin film, Transmittance, Reflectivity, Optical absorption spectra, Electronic structure

1. INTRODUCTION

Superconducting oxide of $Ba(Pb_{1-x}Bi_x)O_y$ is a perovskite type structure and its critical temperature is 12 K[1]. This material behaves metallic from x=0.0 to 0.3 and semiconductive from x=0.3 to x= 1.0 [2,3]. In order to clarify the conduction behavior, electronic structure has been studied by several researchers [4,5,6]. If $BaBiO_3$ has simple band model, where the electronic configuration of Bi was half-filled 6*s*, the conductivity behavior could be metallic. Actually, it is insulator. This result may be explained by several interpretations, such as the disproportionation of Bi and the formation of CDW [7,8], though the reason is in controversy.

Fueki et al. have found that the oxygen content was in excess of several percent in the compositional region where the superconduction appeared, and that the maximum Tc was observed at the highest excess oxygen content [9]. The authors have explained in the previous paper [10] that $Ba(Pb_{1-x}Bi_x)O_y$ is formed in compositions other than Ba: (Pb+Bi)=1:1 and the pseudo cubic structure region is equal to that of the superconducting state. Moreover, it was shown that superconduction appears in the composition domain where the amount of oxygen was in excess. This finding clearly indicates that excess oxygen will affect the electronic structure of $Ba(Pb_{1-x}Bi_x)O_y$. The electrical conductivity and the optical properties provide valuable information for clarification of the electronic structure. As for the measurement of the optical properties of $Ba(Pb_{1-x}Bi_x)O_y$, the reflectivity measurement connected with the Kramers-Kronig transformation has been widely used [5,6]. This method necessitates the assumption for the wavenumber range where the measurement is not possible. If absorption spectra were obtained from the two optical parameters, the accuracy of data improves better. The present authors have successfully measured both the reflectivity and the transmittance of $PrBa_2Cu_3O_y$ using highly oriented $PrBa_2Cu_3O_y$ films fabricated by the method of spin-coating pyrolysis and determined the absorption spectra without employing the Kramers-Kronig transformation[11]. The purpose of the present study is to directly determine the absorption spectra of $Ba(Pb_{1-x}Bi_x)O_y$ films with a well-controlled composition and to contribute to the elucidation of the electronic structure of $Ba(Pb_{1-x}Bi_x)O_y$.

2. Experimental

The fabrication of highly *c*-axis oriented films was made by the spin-coating pyrolysis method[12, 13]. Toluene solutions of naphtenic salts of Ba, Pb and Bi were used as starting materials. The concentration of these solutions was determined as follows. About one gram of undiluted toluene solutions of Pb and Bi was weighted and heated to 500 °C to convert into oxide. Similarly, the undiluted solution of Ba was converted to carbonate at 800 °C. The resulted oxides and carbonate were dissolved with diluted nitric acid and the amounts of metals were determined by the ICP method. From the result, the concentration of undiluted solutions was calculated. Then, the undiluted solutions were mixed in the desired ratio and diluted with toluene twice. One or two drops of the diluted solution was applied to the $SrTiO_3$(001) substrate, 10 mm × 10 mm × 0.5 mm , and the substrate was spun at 4000 r.p.m. for 5 seconds. It was pyrolyzed at 500 °C for 10 minutes to convert to oxides. The spin coating and pyrolysis process was repeated 5 times when the sample for transmission measurement was presented and was repeated 15 times when the sample for reflectivity measurement was prepared. The heat treatment for the formation of $Ba(Pb_{1-x}Bi_x)O_y$ was performed at 750 °C for the samples with the composition of x=0.0, 0.25 and 0.5, and at 700 °C for x=1.0. Then, the samples were annealed in oxygen at 300 °C for 24 hours. The film thickness was determined by vibrating needle galvanometer. In order to check the surface roughness, the surface of films was observed by SEM. The sample orientation and homogeneity were checked by X-ray diffraction. This study revealed that the samples consisted of a single phase. The metal composition was determined by the ICP method after the film was dissolved with diluted nitric acid.

The transmittance and reflectivity of films were then measured in the photon energy range of 0.2 to 3.5 eV. The multiple reflection effect within a film is negligible in the wavenumber region employed, and the absorption coefficient was calculated using the following equation:

$$\alpha = \frac{1}{d}\{2\ln(1-R)-\ln T\} \qquad (1)$$

where R is the reflectivity, T is the transmittance and d is the film thickness.

3. Results and discussion

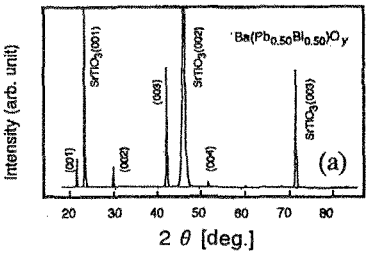
3.1 Characterization of film

The chemical composition was showed in Table Ⅰ. The results would denote the composition was well controlled.

Table Ⅰ Chemical composition of $Ba(Pb_{1-x}Bi_x)O_y$ film

x	Desired composition			Final composition		
	Ba	Pb	Bi	Ba	Pb	Bi
0	1.00	1.00	0.0	1.00	1.00	0.0
0.25	1.00	0.75	0.25	1.00	0.74	0.26
0.50	1.00	0.50	0.50	1.00	0.52	0.48
1.0	1.00	0.0	1.00	1.02	0.0	0.98

The X-ray diffraction pattern of Fig. 1 (a) indicates that the film is a single phase and highly orients in the *c*-axis direction. The SEM photograph of Fig. 1 (b) represents that surface of film is flat. The surface roughness for 0.4 μm thick film was 0.05 μm by vibrating needle galvanometer. This result suggests that the surface of the film was flat and reflectivity had no effect on diffuse reflection.



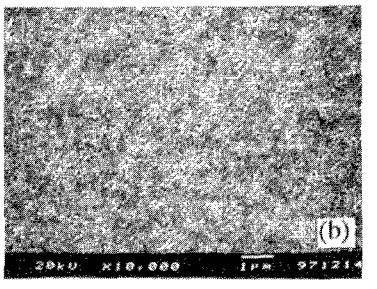


Fig. 1 XRD pattern (a) and SEM photograph (b) for $Ba(Pb_{0.50}Bi_{0.50})O_y$

3.2 Transmittance, reflectivity and absorption coefficient

In Fig. 2, we showed the transmittance spectra of $BaPbO_y$, $Ba(Pb_{0.75}Bi_{0.25})O_y$, $Ba(Pb_{0.5}Bi_{0.5})O_y$ and $BaBiO_y$, respectively. In spite of the existence of band gap around 1.5 eV, sharply decreasing transmittance appears in low energy for $BaPbO_y$. The result indicates that electronic structure of $BaPbO_y$ will not represent simple metal band model. As for the electronic structure in high temperature superconducting oxide, mid gap state originated from excess oxygen overlaps with valence band in metallic phase[16].

The reason why $BaPbO_y$ indicates metallic behavior will be explained that the level of excess oxygen overlaps with valence band. Moreover, the transmittance of $Ba(Pb_{0.75}Bi_{0.25})O_y$ around 0.2 eV is much smaller than that of any other sample. The amount of excess oxygen in $Ba(Pb_{0.75}Bi_{0.25})O_y$ is larger than any other $Ba(Pb_{1-x}Bi_x)O_y$ system[9]. It is supposed that the acceptor level originated from excess oxygen is overlapped with valence band deeply. $Ba(Pb_{0.5}Bi_{0.5})O_y$ and $BaBiO_y$ were semiconducting behavior, so these transmittance decreased sharply.

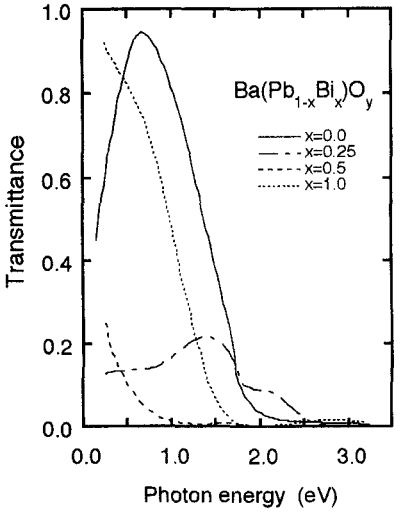


Fig. 2 Transmittance spectra of $Ba(Pb_{1-x}Bi_x)O_y$

The reflectivity showed in Fig. 3 was similar to that obtained by Tajima et al. using single crystals[5,6]. According to the Hall effect measurements by Tanh, the carrier density is maximum when x=0.25, meaning that carrier density corresponds to the reflectivity. Disappearance of phonon peak in our result is attribute to measurement up to 0.2 eV[14].

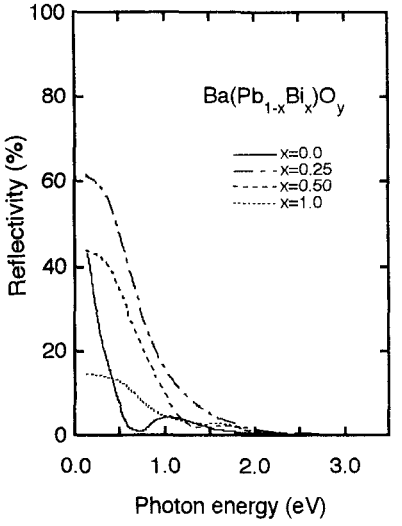


Fig. 3 Reflectivity spectra of $Ba(Pb_{1-x}Bi_x)O_y$

Absorption spectra were shown in Fig. 4. In $BaPbO_y$, the intraband transition associated with the metallic behavior was in low energy region. Fueki et al. found that the conductivity of $Ba(Pb_{1-x}Bi_x)O_y$ ($0 \leqq x \leqq 0.3$) increased with the content of excess oxygen [9,10], suggesting that the absorption originates from the excess oxygen. On the other hand, absorption edge associated with an interband gap appeared around 0.8 eV. On the basis of the XPS study of $Ba(Pb_{1-x}Bi_x)O_y$, Lin et al. have concluded that the valence band of $Ba(Pb_{1-x}Bi_x)O_y$ originated from the O2*p* level [15]. Namatame et al. have performed the XPS and UPS studies of $BaPbO_y$ and have reported that the valence and conduction bands originates from the O2*p* and Pb6*s* levels[4]. Therefore, it is supposed that the edge around 0.8 eV corresponds to the gap from the top of the O2*p* valence band to the bottom of the Pb6*s* conduction band. This result supports the fact that the metallic behavior of $Ba(Pb_{1-x}Bi_x)O_y$ is not caused by overlapping between O2*p* and Pb6*s*. The absorption spectra of x=0.25 has two peaks which have maximums at 1 eV and 3 eV, respectively. These spectral features resemble to that of x=0.5 and 1.0.

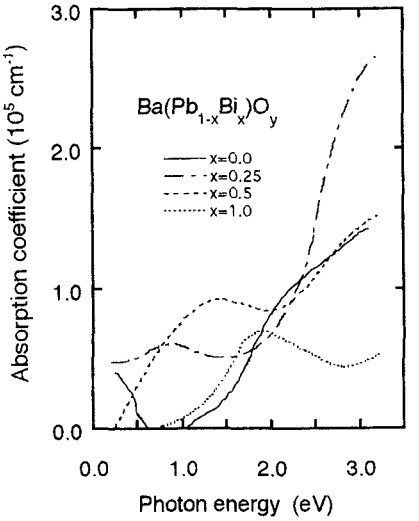


Fig. 4 Absorption spectra of $Ba(Pb_{1-x}Bi_x)O_y$

If the simple band model is applied for $BaBiO_y$, the band originating from the Bi 6*s*[1] should be half-filled. However, it has been found that $BaBiO_y$ is semiconducting. Several interpretations have been proposed so far about the existence of an energy gap. One interpretation is that the disproportionation of Bi^{4+} into Bi^{3+} and Bi^{5+} would produce two subbands of Bi(III) and Bi(V)[4]. According to another interpretation, the strain of the oxygen octahedron causes the alternating array of Bi^{3+} and Bi^{5+}, and the charge density wave produces the band gap[3,6].

The origin of the gap is not clearly defined at the present time. If the disproportionation of Bi^{4+} produces Bi(V) $6s^0$ and Bi(Ⅲ) $6s^2$, the valence band would be formed by the hybridization of the O2*p* and Bi(Ⅲ) $6s^2$, while the conduction band would be formed by the hybridization of the Pb6s^0 and Bi(V) bands, as mentioned by Namatame et al[4]. From the point of view, the electronic structure of $Ba(Pb_{1-x}Bi_x)O_y$ in three regions is schematically shown in Fig. 5. In metallic region, there is a band gap and the excess oxygen acts as acceptor to produce holes in the valence band and the metal-like conduction is observed. In semiconducting region, there is an energy gap without acceptor level orginated from excess oxygen.

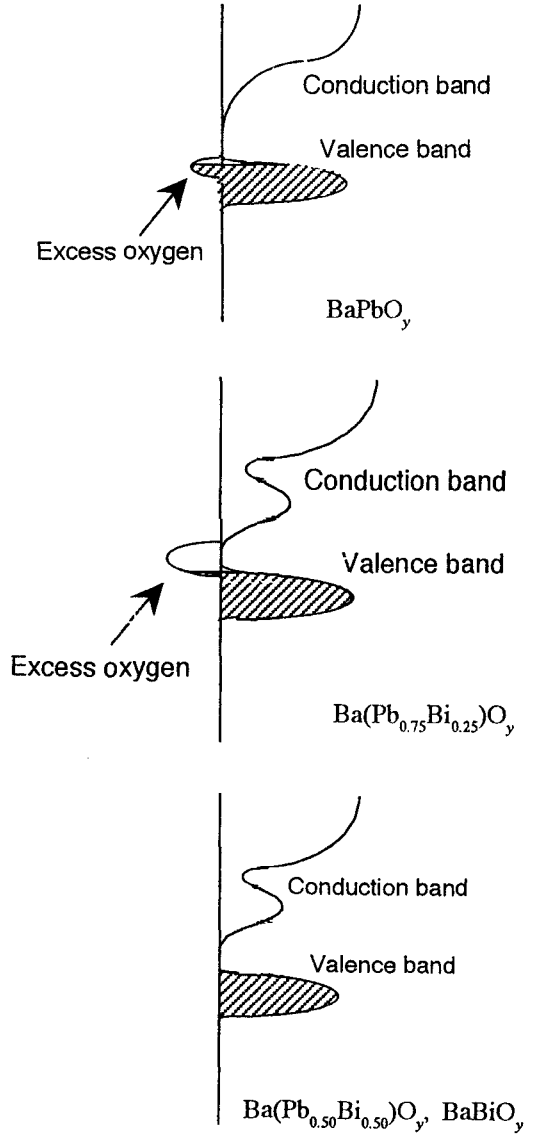


Fig. 5 Shematic drawing of electronic structure for $Ba(Pb_{1-x}Bi_x)O_y$

4. Conclusion

High *c*-axis oriented films of $Ba(Pb_{1-x}Bi_x)O_y$ were grown on a $SrTiO_3$ substrate by the spin coating-pyrolysis method. From the transmittance and reflectivity spectra, the absorption coefficient was calculated. In x=0.0 and 0.25, there are the O2*p* valence band and the Pb6*s* conduction band where the acceptor originated from excess oxygen overlapped. In x=0.50 and 1.0, the band gap exists without intraband absorption. Two absorption peaks at photon energies of 1.3 ~ 1.8 eV and 3.0 eV or higher were attributed to the transition from the (O2*p*+Bi(Ⅲ)) band to the (Pb6*s*+Bi(V)) band and from the valence band to the Pb6*s* one.

References

1. A.W. Sleight and J.L. Gillson and P.E. Bierstedt *Solid State Commun.*,17, 27 (1975).
2. D.E. Cox and A.W. Sleight *Acta. Cryst.*, B35, 1 (1979).
3. T. Itoh, K. Kitazawa and S. Tanaka *J. Phys. Soc. Jpn.*, 53, 2668 (1984).
4. H. Namatame, A. Fujimori, H. Takagi, S. Uchida, F.M.F de Groot and J.C. Fuggle *Phys. Rev. B* , 48, 16917 (1993).
5. S. Tajima, S. Uchida, A. Masaki, H. Takagi, K. Kitazawa S. Tanaka and A.Katsui *Phys. Rev. B* , 32, 6302 (1985).
6. S. Tajima, S. Uchida, A. Masaki, H. Takagi, K. Kitazawa and S. Tanaka *Phys. Rev. B* , 35, 696 (1987).
7. M. Suzuki and T. Murakami *Solid State Commun..*, 53, 691 (1985).
8. T.M. Rice and L. Sneddon *Phys. Rev. Lett.*, 47, 689 (1981).
9. K. Fueki, Y. Idemoto and T. Yamauchi *Physica C* ,190, 6 (1991).
10. K. Kakinuma and K. Fueki *Solid State Commun..*, 105,173 (1997).
11. K. Kakinuma, K. Fueki, H. Takahashi, R. Pittini, N. Sata, M. Ishigame and M. Ikezawa *J. Appl. Phys.*, 83, 4436 (1998).
12. T. Manabe, W. Kondo, S. Mizuta and T. Kumagai *J. Mater. Res.*, 9, 858 (1994).
13. T. Manabe, I. Yamaguchi, S. Nakamura, W. Kondo, S. Mizuta and T. Kumagai *Physica C* , 276, 160 (1997).
14. T.D. Thanh, A. Koma and S. Tanaka *Appl. Phys.*, 22, 215 (1980).
15. C.L. Lin, S.L. Qiu, J. Chen, M. Strongin, G. Cao, Chan-Soo Jee and J.E. Crow *Phys. Rev. B* , 39, 9607 (1989).
16. K. Kakinuma and K. Fueki *Phys. Rev. B* , 56, 3494 (1997).

(Received December 10, 1998; accepted April 14, 1999)