Oxygen Deficiency, Crystal System and Conduction Behavior of $BaPb_{0.75}Bi_{0.25}O_{3-\delta}$

Takuya Hashimoto and Ryo Hirasawa
Dept. of Chemistry, College of Arts and Sciences, University of Tokyo, 3-8-1 Komaba, Meguro-ku, Tokyo 153, Japan

Jun Komiya and Hidefumi Hirai
Dept. of Industrial Chemistry, Faculty of Engineering, Science University of Tokyo, Tokyo 162, Japan

Hideki Tanaka and Hiroaki Tagawa
Inst. of Environmental Science and Technology, Yokohama National University, Yokohama 240, Japan

Junichiro Mizusaki
Research Inst. of Scientific Measurements, Tohoku University, Sendai 980-77, Japan

The variation of crystal system and conduction behavior of perovskite superconductor, $BaPb_{0.75}Bi_{0.25}O_{3-\delta}$, with oxygen deficiency was studied. The crystal system of $BaPb_{0.75}Bi_{0.25}O_{3-\delta}$ changed from orthorhombic through tetragonal to pseudo-cubic as δ increases. The superconducting transition was observed in the specimens with the orthorhombic phase. Oxygen-deficient specimens with tetragonal or pseudo-cubic symmetry did not show a superconducting transition. The increase in electrical resistivity was also observed with an increase in δ, which suggested decrease of electron carrier mobility with the increase in δ. This effect of oxygen deficiency on conduction behavior of $BaPb_{0.75}Bi_{0.25}O_{3-\delta}$ showed contrast with those of the superconducting cuprates, in which carrier concentration is affected instead of carrier mobility. The difference in the effects of oxygen deficiency on conduction behavior could be attributed to the difference of crystal structure between $BaPb_{0.75}Bi_{0.25}O_{3-\delta}$ and superconducting cuprates.

Introduction

$BaPb_{0.75}Bi_{0.25}O_{3-\delta}$ (hereafter abbreviated as BPBO) is a superconductor with critical temperature T_c of 12 K (Sleight et al., 1975). Although extensive studies were carried out on the fundamental properties of BPBO (Tajima et al., 1985; Oda et al., 1985), controversy in the literature on the conduction mechanism and crystal system has remained. However, not much information on BPBO has been reported since the discovery of high-T_c cuprates (Bednortz and Müller, 1986) due to its low T_c compared to those of high-T_c cuprates. It is well known that the crystal structure of the high-T_c superconducting cuprates is in the perovskite-family (Tokura and Arima, 1990). The authors regard that BPBO can be regarded as a prototype for high-T_c cuprates since its crystal structure is a simple distorted perovskite. It is expected that the study to elucidate conduction mechanism of BPBO might give useful information for the study of conduction behavior of high-T_c cuprates.

Oxygen deficiency, which might be generated during the preparation, is one of the important elements which must be taken into consideration for the analysis of conduction property and crystal system of oxide material (Kröger, 1974). The effects of oxygen deficiency on the crystal structure, electrical conduction behavior and superconducting properties of high-T_c cuprates have been already reported (for example, Tokura et al., 1988). However, those of BPBO were not clear, because few studies concerning the oxygen deficiency were carried out except for our study (Hashimoto et al., 1995).

Correspondence concerning this article should be addressed to T. Hashimoto.

In the preceding work, the variation of crystal structure and conduction behavior of BPBO was examined using the specimens with four kinds of δ, which were prepared systematically using the oxygen-nonstoichiometry data (Hashimoto et al., 1995). It was concluded that crystal structure of BPBO varied from orthorhombic through tetragonal to pseudo-cubic. It was also suggested that the mobility of the electron carrier of BPBO drastically decreased with the increase in δ, resulting in an increase in electrical resistivity. The effect of oxygen deficiency on conduction mechanism of BPBO showed a difference from that of high-T_c superconducting cuprates, in which carrier concentration is affected instead of carrier mobility (Tokura et al., 1988; Suzuki et al., 1994). However, the boundary of the transition of the crystal symmetry was not clear due to a small number of the specimens employed in that study. There was no comment about the origin of decrease of mobility with the increase in δ of BPBO.

In this study, a lot of specimens with various δ were prepared and relationship between δ and crystal system was presented more clearly. From the comparison of crystal structure of BPBO and high-T_c cuprates, the reason of the decrease of the mobility with increase of δ in BPBO is speculated.

Experimental Studies

BPBO ceramic samples were prepared by the solid state reaction of the mixtures of nominal composition of powdered $BaCO_3$ (99.9%), Bi_2O_3 (99.9%), and Pb_3O_4 (99.9%). The mixture was heated at 720°C for 12 h under an O_2 atmosphere. The calcined samples were ground, pressed into pellets, and subjected to sintering at 800°C for 12 h in an O_2 atmosphere. The sintered pellets were heated further at 850°C for 12 h in an Ar atmosphere to obtain the samples with high density, which was more than 85%, followed by heating at 800°C for 60 h in an O_2 atmosphere to remove oxygen vacancy. The oxygen content of the prepared samples was confirmed to be 3.00 by iodometric titration (Hashimoto et al., 1994). The cation content was confirmed to be Ba/Pb/Bi = 1.0/0.75/0.25 by inductively coupled plasma emission analysis.

For the control of the amount of oxygen deficiency δ, the specimens in Al_2O_3 crucible were annealed under the specified temperature and the oxygen partial pressure, which were determined by thermogravimetry, and successively quenched by using the furnace in which rapid quenching to water-cooled temperature was possible (Hashimoto et al., 1995). Prospected δ and annealing conditions determined from the data of thermogravimetry are summarized in Table 1. Iodometry was carried out for some specimens and the results are also listed in Table 1. Good agreement was observed between δ determined by thermogravimetry and iodometry.

X-ray diffraction data for δ-controlled samples were collected by a Rigaku RINT2400 (CuKα: 40 kV, 200 mA) at room temperature. The X-ray diffraction peaks in the range $76° < 2\theta < 78°$ and $90.5° < 2\theta < 93°$ were used to determine the crystal system. The lattice constants were calibrated by using the 422 or 600 diffraction peak of KCl as an internal standard. In addition, diffraction patterns in the range of $10° < 2\theta < 100°$ were collected to confirm the determined crystal system and absence of impurity. The electrical resistivity of the specimens was measured as a function of temperature, 4.2 K ~ room temperature, by a standard four probe method. Gold electrodes were sputtered on a rectangular specimen, and copper wires attached by silver paste on an electrode were employed as a lead.

Table 1. Prospected δ and Annealing Conditions for Their Control

Sample No.	1	2	3	4	5	6	7	8
δ	0.00	0.011	0.022	0.058	0.078	0.10	0.12	0.15
log (pO_2/bar)	0	−2	−3	−3	−4	−4	−4	−4
Temp. (°C)	600	820	800	840	800	810	830	840
δ_{io}	0.00			0.06		0.10		0.15

pO_2 = oxygen partial pressure
δ = the amount of oxygen deficiency prospected from nonstoichiometry data (Hashimoto et al., 1995)
δ_{io} = the amount of oxygen deficiency measured by iodometry

Results

Glazer (1972) reported that various polymorphs of perovskite structure would appear by rotations and tilts of octahedra composed of anion and so-called B-site cation. In the BPBO system, polymorphs which can be classified as orthorhombic and tetragonal were observed using powder neutron diffraction analysis by Asano et al. (1988). However, oxygen deficiency was not considered in their study. In this study, we observed that the crystal symmetry of above mentioned polymorphs of the perovskite structure of BPBO varied on oxygen deficiency δ.

Figure 1 shows X-ray diffraction peaks of BPBO with δ = 0.00, 0.10, and 0.15. If the crystal symmetry is orthorhombic ($a \neq b \neq c$), the diffraction peaks 404 and 044 are separate and appear in the range $76° < 2\theta < 78°$, and the 440 and 008 diffraction peaks must be observed in the range $90.5° < 2\theta < 93°$. In the case of tetragonal symmetry ($a = b$), the 404 and 044 peaks in the range $76° < 2\theta < 78°$ appear as a single peak.

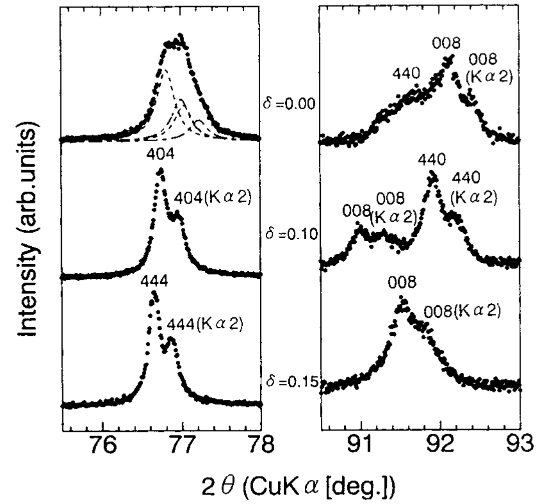

Figure 1. X-ray diffraction peaks of BPBO in the 2θ range of $76° < 2\theta < 78°$ and $90.5° < 2\theta < 93°$.

Peak of the specimen with $\delta = 0.00$ in the range $76° < 2\theta < 78°$ could be decomposed into two peaks. ——— 404, – – – 044.

Peaks of 440 and 008 should be two different peaks in the range $90.5° < 2\theta < 93°$ if crystal symmetry is tetragonal with $c \neq \sqrt{2}a$. Neither peak in the range $76° < 2\theta < 78°$ nor $90.5° < 2\theta < 93°$ should separate if the crystal symmetry is pseudo-cubic. (This explains why we refer to the phase as pseudo-cubic in the literature, rather than referring to it as cubic (Hashimoto et al., 1995).) The apparently broad peak of the specimen with $\delta = 0.00$ in the range $76° < 2\theta < 78°$ could be decomposed into two peaks, together with peaks from CuK$\alpha 2$ radiation, using a Lorentz function. Minute method for the peak decomposition was described in the literature (Hashimoto et al., 1994). The two diffraction peaks for $76° < 2\theta < 78°$, which could be indexed as 404 and 044, suggested that crystal symmetry for the specimen with $\delta = 0.00$ was orthorhombic. For the specimens with $\delta = 0.10$, a single 404 peak, together with peak by CuK$\alpha 2$ radiation, was observed in the range $76° < 2\theta < 78°$, and two peaks of 008 and 440 were observed in the range $90.5° < 2\theta < 93°$. This indicates tetragonal symmetry for the specimens with $\delta = 0.10$. In the case of the sample with $\delta = 0.15$, neither splitting was observed in the range $76° < 2\theta < 78°$ nor in $90.5° < 2\theta < 93°$. Thus, crystal symmetry of the sample with $\delta = 0.15$ is pseudo-cubic.

Figure 2 shows X-ray diffraction peaks of BPBO with various δ. The peaks in the range $76° < 2\theta < 78°$ of the specimens with $0.00 \leq \delta \leq 0.058$ could be decomposed into two peaks indicating that orthorhombic phase existed in these specimens. (There is a possibility that these specimens are mixtures of orthorhombic and tetragonal phases as Marx et al. (1992) suggested. However, it could not be distinguished if the specimens were composed of single phase or mixture due to the resolution of X-ray diffraction employed in this study. A minute study of crystal structure with high resolution using syncrotron X-ray diffraction is now in progress.) The single peak in the range $76° < 2\theta < 78°$ and two peaks in the range $90.5° < 2\theta < 93°$ indicate that crystal symmetry is tetragonal for the specimens with $0.078 \leq \delta \leq 0.12$. Pseudo-cubic symmetry can be determined for the specimen with $\delta = 0.15$. X-ray diffraction patterns for the range $10° < 2\theta < 100°$ for each specimen could be indexed according to thus determined crystal symmetry, and no peak identified as impurities was observed. It was concluded that the crystal system of BPBO is nearly isotropic perovskite although δ-dependent variation of crystal system was observed in this system.

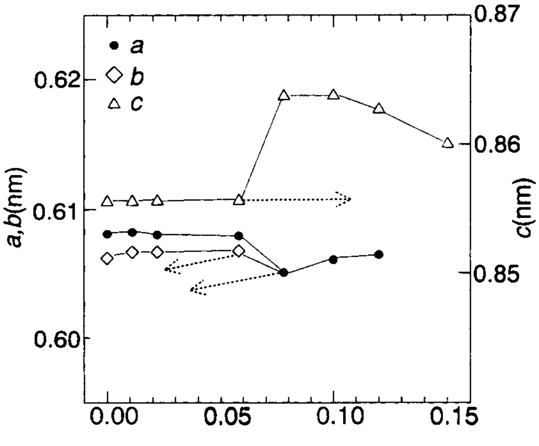

Figure 3. Variation of lattice constants of BPBO on δ.

Figures 3 and 4 shows variation of lattice constants and molar volumes on δ, respectively. In the orthorhombic phase, the lattice constant and molar volume were almost constant regardless of δ. An abrupt expansion of c-axis and shrinkage of a-axis was observed in the transition region from orthorhombic to tetragonal. It was also observed that volume expansion with δ was far smaller in the orthorhombic phase than that in the tetragonal and the pseudo-cubic one.

Temperature dependence of electrical resistivity was measured for each BPBO and showed same tendency with the results of the preceding article (Hashimoto et al., 1995). As δ increased, the electrical resistivity of the samples at a normal state increased in the order and T_c decreased and finally dis-

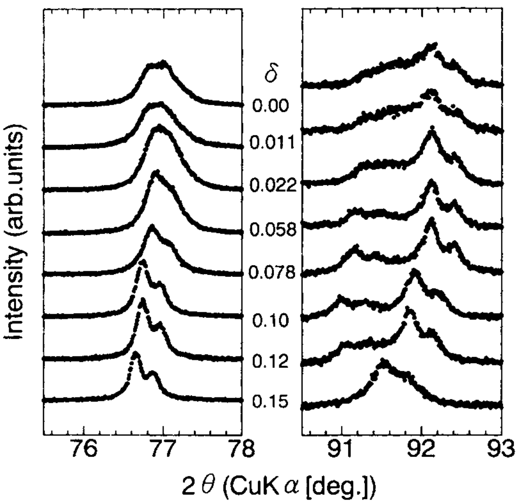

Figure 2. X-ray diffraction peaks of BPBO with various δ in the 2θ range of $76° < 2\theta < 78°$ and $90.5° < 2\theta < 93°$.

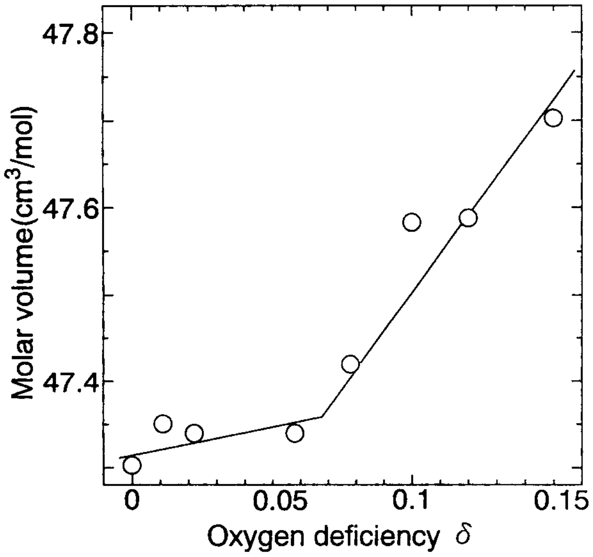

Figure 4. Variation of molar volumes of BPBO on δ calculated from the data depicted in Figure 3.

appeared. The superconducting transition was observed only for the specimens with orthorhombic phase. For the specimens of tetragonal and pseudo-cubic phase, a superconducting transition was not observed.

Discussion

The increase of normal state resistivity of BPBO with δ is not due to a decrease of electron carrier concentration, but rather to a decrease in the mobility of electrons. Conventionally, oxygen deficiency produces electrons according to the defect equilibrium formula described below

$$O_o^x \leftrightarrow V_o^{\cdot\cdot} + 1/2\,O_2 + 2e^-$$

Here, the Kröger-Vink-type notation for defects (Kröger, 1974) was used. Since the major carrier of BPBO was confirmed to be electrons from Hall measurement (Thanh et al., 1980) and Seebeck measurement (Tani et al., 1980), the concentration of conduction carrier would increase and resistivity would decrease if the electron mobility was constant regardless of δ. The observed increase in the resistivity with δ, however, suggests that oxygen deficiency decreased the mobility of electron carriers.

The effect of oxygen deficiency on the conduction mechanism of BPBO contrasts those of high-T_c cuprates. In high-T_c cuprates, oxygen deficiency affects carrier concentration rather than carrier mobility (Tokura et al., 1988). Tokura and Arima reported that the structure of all the high-T_c cuprates is composed of [CuO_2] layer and a layer other than the [CuO_2] layer, which they regarded as electronic conduction layer and charge reservoir, respectively (Tokura and Arima, 1990). Their proposal was supported by a photoelectron spectroscopy (Takahashi et al., 1989) and scanning tunneling microscopy (Oda et al., 1996).

Figures 5a and 5b depict crystal structure of BPBO and $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ (hereafter abbreviated as NCCO), which is a representative of high-T_c cuprates. It was confirmed that the major carrier of NCCO is electrons as in the case of BPBO and that oxygen deficiency decreased electrical resistivity and was necessary for superconducting transition (Takagi et al., 1989). From Hall measurement of NCCO thin film, it was revealed that oxygen deficiency increased electron carrier concentration (Suzuki et al., 1994).

Partitioning of the crystal structure of BPBO into a conduction layer and a charge reservoir layer is not possible since BPBO is nearly isotropic with only a slight deviation of perovskite structure, as revealed by X-ray diffraction. Therefore, an oxygen vacancy in BPBO directly changes the dispersion of the conduction band composed of Pb(Bi)6s and O2p orbitals, which was confirmed by electronic band calculation (Mattheiss and Hamann, 1982), thus resulting in decrease in electron mobility.

On the contrary, the crystal structure of NCCO is anisotropic which is composed of a [CuO_2] layer and the so-called fluorite layer. There has been no conclusive research on the site of oxygen vacancy due to its small δ in NCCO. However, we speculate that oxygen vacancies are generated mainly in the fluorite layer and not in the [CuO_2] layer. It is suggested that oxygen vacancies in NCCO scarcely affect the dispersion of the conduction band composed of Cu3d and O2p orbitals in the [CuO_2] layer and that a vacancy generated in the fluorite layer, which is charge reservoir, and works as electron generation center. As a result, carrier concentration and not carrier mobility is supposed to be affected by oxygen deficiency for NCCO. This speculation agrees well with the neutron diffraction study by Izumi et al. (1989).

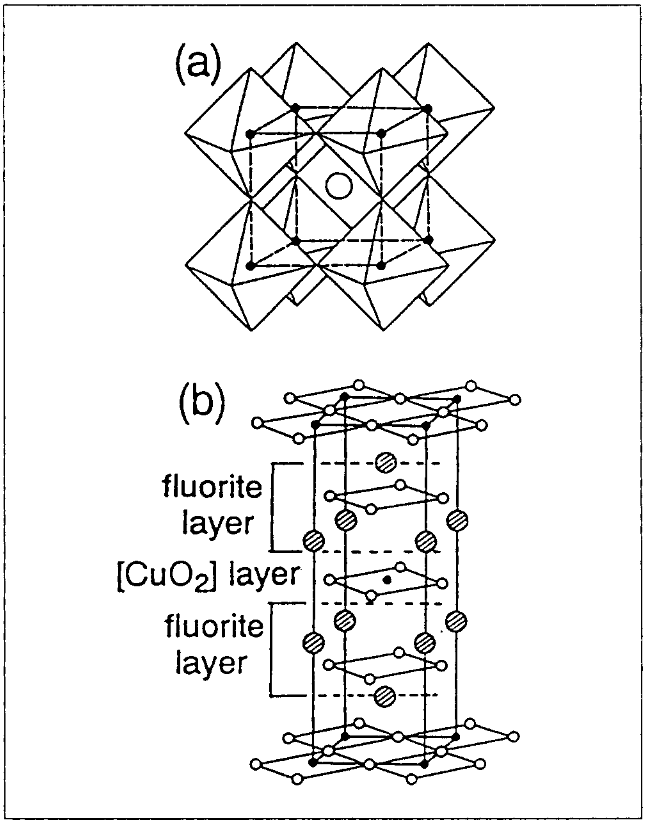

Figure 5. Crystal structure of (a) BPBO and (b) NCCO.

Open circle and closed one in (a) represent Ba and Pb (or Bi), respectively. Oxygen ions are located at the corner of the octahedra. Hatched circle, closed one and open one in (b) represent Nd (or Ce), copper and oxygen, respectively. Oxygen ions of NCCO can be classified into two kinds, one in the [CuO_2] layer, and the other in the fluorite layer.

For the superconducting cuprates with a hole carrier, it is clearly concluded that oxygen vacancies are generated in the layer other than a [CuO_2] layer and that they affect carrier concentration rather than carrier mobility. For example, the crystal structure of $Ba_2YCu_3O_{7-\delta}$ is depicted in Figure 6. $Ba_2YCu_3O_{7-\delta}$ is a hole type superconductor with a critical temperature of 90 K at most. It has an anisotropic crystal structure composed of a [$BaCuO_{1+z}$] layer and a [CuO_2] layer. From the neutron diffraction measurement, it was revealed that oxygen vacancies are generated mainly in the [$BaCuO_{1+z}$] layer and not in the [CuO_2] layer (Jorgensen et al., 1987). Therefore, we know that oxygen vacancies affect carrier concentration and not carrier mobility. It was confirmed by Hall measurement that the oxygen vacancy in this system decreases hole carrier concentration by the recombination of hole and electron which is generated from oxygen vacancy, resulting in an increase of electrical resistivity and a disappearance of superconductivity (Wang et al., 1987).

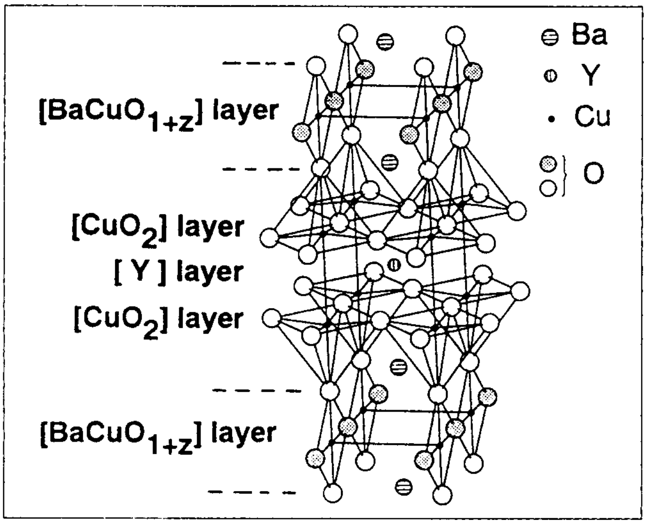

Figure 6. Crystal structure of $Ba_2YCu_3O_{7-\delta}$.

This structure can be divided into [$BaCuO_{1+z}$], [CuO_2] and [Y] layers. Oxygen ions can be classified into two kinds, one in the [$BaCuO_{1+z}$] layer, and the other in the [CuO_2] layer. Oxygen vacancy is observed in [$BaCuO_{1+z}$] layer, which is represented by hatched circle (Jorgensen et al., 1987).

Conclusion

The crystal structure of BPBO varied from orthorhombic through tetragonal to pseudo-cubic with increasing oxygen deficiency δ. Only orthorhombic phase showed superconducting transition. The results suggested that the mobility of electron carriers in BPBO drastically decreased with an increase of δ, resulting in an increase in electrical resistivity. The effect of oxygen deficiency on the conduction mechanism in BPBO showed a difference from that of high-T_c superconducting cuprates, in which carrier concentration is affected instead of carrier mobility. The origin of the difference on the behavior of oxygen deficiency could be regarded to be due to the difference of crystal structure between BPBO and high-T_c cuprates.

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