Preparation of conducting In-based copper oxide by annealing under high pressure

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（平成18年９月15日受理）

Abstract

By annealing $InBa_2CuO_{4.44}$ in oxygen at a pressure of 60MPa, a new conducting cuprate $InBa_2CuO_{4.54}$ with having a- and c-axis lengths of 4.190Å and 8.363Å was formed. Its crystal structure was refined by the X-ray Rietveld analysis method. The factors R_{wp} , R_e, and S were 9.11%, 9.12%, and 1.0, respectively, indicating that the refined structure is an appropriate one. There were four distinct differences between $InBa_2CuO_{4.44}$ and $InBa_2CuO_{4.54}$. The first was an increase in the oxygen occupancy in the CuO_2 plane; the oxygen occupancy in the CuO_2 plane increased from 26.5% to 27%. The second was a drastic increase in the c-axis length from 8.09Å to 8.36Å. The third was the inter-substitution of In and Cu. About 35 % of In and Cu atoms were substituted each other in the $InBa_2CuO_{4.54}$. The fourth was a drastic decrease in the electrical resistivity; the resistivity at room temperature decreased from 28.8 MΩcm to 90.3 kΩcm. These differences are discussed in connection with the oxygen content in the $InBa_2CuO_y$.

PACS　74.72.Jt

Key words:
CuO_2 layer, Cu valence, high pressure synthesis, nBa_2CuO_y, oxygen content, tetragonal phase, orthorhombic phase,

Introduction

It has been revealed that Tc's of cuprate superconductors are very sensitive to their Cu-O-Cu length in the CuO_2 plane[1,2]. In Fig. 1, Tc's as a function of the Cu-O-Cu length are shown; the correlations are classified into Ln-, Sr-, and Ba-classes distinguished by the cations Ln^{3+}, Sr^{2+}, and Ba^{2+} occupying the 9-coordination sites. As the ion radius of the cation becomes larger, the maximum Tc of each class becomes higher. The highest Tc of each class is 38 K for $(La,Sr)_2CuO_4$ (Ln^{3+} class), 107 K for $(Bi,Pb)_2Sr_2Ca_2Cu_3O_y$ (Sr^{2+} class), and 132 K for $HgBa_2Ca_2Cu_3O_8$ (Ba^{2+} class), respectively. Comparing the three classes, the Ba-class has a larger Cu-O-Cu length than the

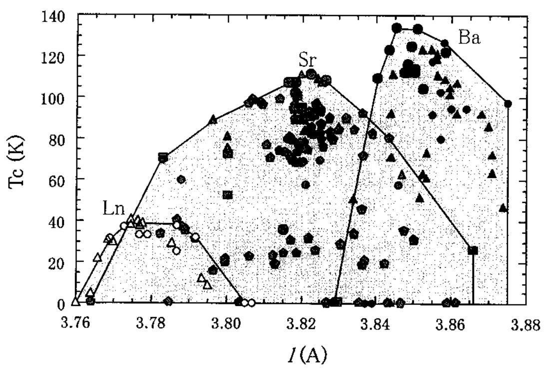

Fig.1 Tc's of the layered cuprates as a function of the Cu-O-Cu length. Three classes distinguished by the cations Ba^{2+}, Sr^{2+}, and Ln^{3+} occupying the 9-coordination are displayed in black, gray, and white points.

Sr-class, which has a larger Cu-O-Cu length than the Ln-class does. This is because the in-plane Cu-O-Cu length is primarily governed by the size of the 9-coordination site cation, which increases in the order $Ln^{3+} < Sr^{2+} < Ba^{2+}$.

It is to be noted that as the Cu-O-Cu length grows larger, Tc's of the cuprate superconductors become higher. We previously reported preparation of an In-based cuprate, $InBa_2CuO_{4.53}$[3], whose space group is *Pmmm* with lattice parameters a=4.18206 Å, b=4.18205 Å, and c=8.0889 Å (Fig. 2).

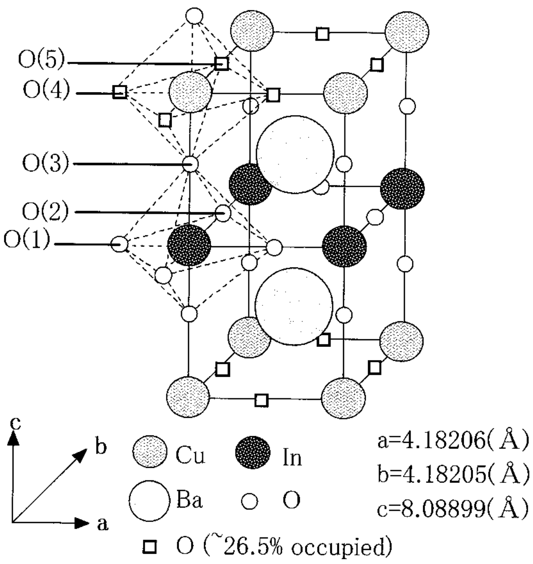

Fig.2 Crystal structure of $InBa_2CuO_y$. The occupancy of O(4) and O(5) sites is 26.5 %.

The fact that a- and b- axis lengths of the $InBa_2CuO_y$ are much longer than those of 3.9-4.0 Å for the other cuprate compounds is explained by the existence of about 74 % of oxygen vacancies in the CuO_2 layer. The resistivity of $InBa_2CuO_y$ at room temperature was as large as 28.8 MΩcm. The insulating property will also come from existence of the oxygen vacancies in the CuO_2 layer.

Since the structure of the $InBa_2CuOy$ belongs to the Ba^{2+} class, the Tc of a metallic $InBa_2CuO_y$ should be as high as 100 K. To realize the metallic $InBa_2CuO_y$, it is necessary to decrease the oxygen vacancies in the CuO_2 plane. If this oxygen vacancy is decreased, this compound should be conducting, or maybe superconducting. The objective of this study is to make the In-based cuprate conducting. For that, we tried annealing in oxygen at pressures of 20-60 MPa.

Since the weight of the samples prepared at pressures of 20-60MPa is as small as 50 mg, it is rather difficult to measure the oxygen content precisely by the conventional coulometric method. The second objective of this study is to realize to measure the oxygen content precisely with a sample of 50mg.

Experimental

An $InBa_2CuO_y$ sample was prepared by the solid reaction method. Fig.3 shows a flow chart of the sample preparation. The mixed powder of In_2O_3, BaO, and CuO was put into an aluminum crucible, and calcined at 900℃ in air for 10h, ground in the mortar, pressed into pellets at a pressure of $600 kgf/cm^2$. The pellets were put into an alumi-

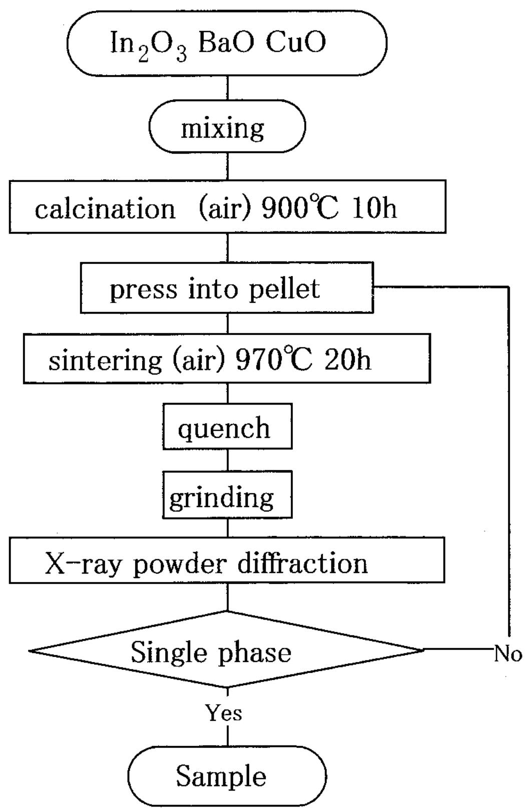

Fig.3 Preparation and measurement scheme of $InBa_2CuO_y$.

num crucible again, and sintered at 970℃ in air for 20h. After sintering, the pellets were quenched to room temperature. After grinding it to powder, the crystalline phases were examined by the powder X-ray diffraction method. Sintering was repeated until a single phase of $InBa_2CuO_y$ was prepared.

To increase the oxygen content in the oxygen vacancies in the CuO_2 layer, we annealed the specimens under pressures of 20-60MPa oxygen at a temperature of 500℃ for 10 hours.

The crystal structure was determined with a powder X-ray diffractometer at room temperature using Cu-Kα radiation. Its crystal structure was refined by a Rietveld refinement program RIETAN[4).] Oxygen contents and average Cu valences were determined by a newly developed coulometric method[5)]. Coulometry was carried out in a cell under a stream of Ar to remove dissolved oxygen at room temperature. Five miligrams of copper (I) chloride (High Purity Chemicals, 99.99 %) was dissolved in 0.5 mol/l aq. HCl. A specimen whose weight was 50mg was dissolved in the solution, where Cu^{3+} in the specimen reacts with Cu^{+} in the solution and makes two Cu^{2+} ions;

$$Cu^{3+} + Cu^{+} \rightarrow 2Cu^{2+}. \quad (1)$$

The rest of Cu^{+} in the solution is oxidized on a cathode (Fig.4);

$$Cu^{+} \rightarrow Cu^{+} + e^{-}. \quad (2)$$

From the amount of the electric quantity, we determined the amount of Cu^{3+} and estimated the Cu valence.

Resistivity as a function of temperature was measured by the conventional four-probe method.

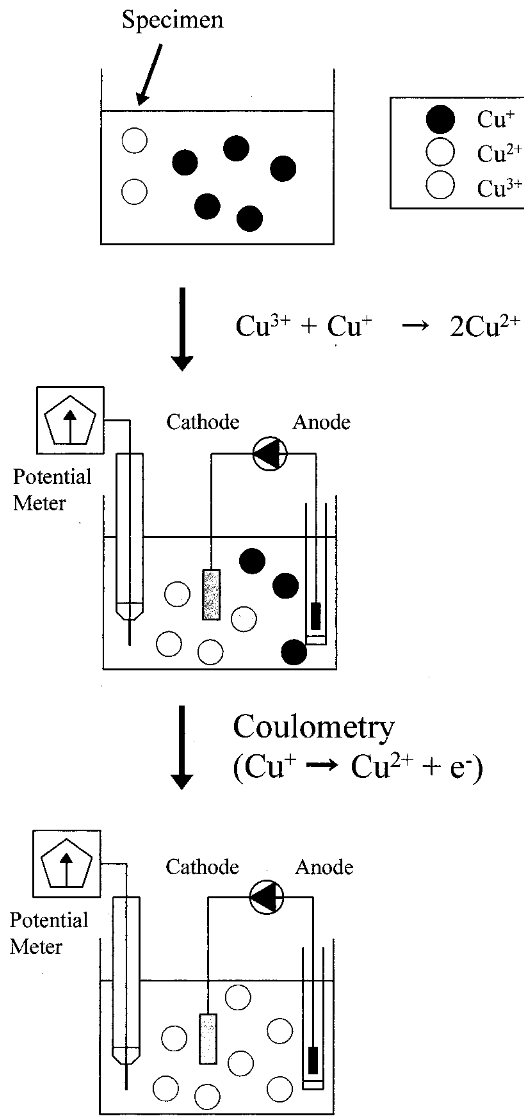

Fig.4 Scheme of coulometry. Cu^{3+} in the specimen reacts with Cu^{+} in the solution and makes two Cu^{2+}. The rest of Cu^{+} is oxidized to Cu^{2+} on the cathode.

Results and discussion

As shown in Fig.5, the oxygen content increased drastically from 4.45 to 4.54 with an increase in pressure from 40 MPa to 60 MPa. The Cu valence increased from 1.90 to 2.08. The error of measurement was ± 0.02, revealing that precise measurement on the oxygen content was done for the high-pressure annealed specimens.

In Fig.6, powder X-ray diffraction patterns of the $InBa_2CuO_y$ from y=4.44 to 4.54 are shown. Two peaks in the vicinity of 30° changed into one peak at y=4.54 (60MPa), indicating that the crystal structure is changed. To investigate it in more detail, we measured the lattice parameters by the least square method.

In Fig.7, a- and c-axis lengths of the $InBa_2CuO_y$ as a function of the oxygen pressure during annealing are shown. As the oxygen pressure during

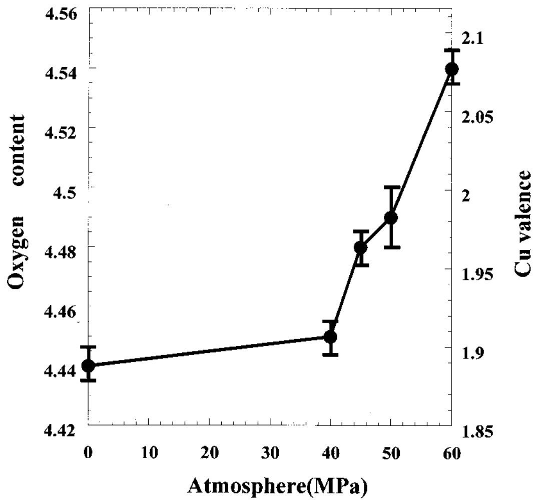

Fig.5 Changes of the Cu valence and oxygen content of $InBa_2CuO_y$ prepared by O_2 HIP at a pressure from 0.1 to 60 MPa. Over 40 MPa, the oxygen content drastically increased from 4.44 to 4.54.

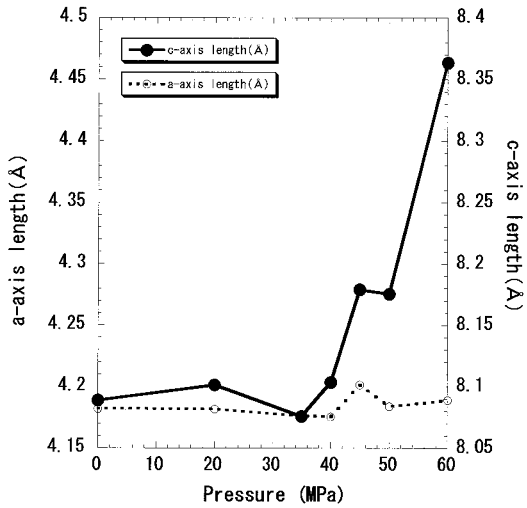

Fig.7 Lengths of a- and c-axes of $InBa_2CuO_y$ as a function of oxygen pressure during annealing. As the oxygen pressure during annealing was increased, the c-axis lengths became larger.

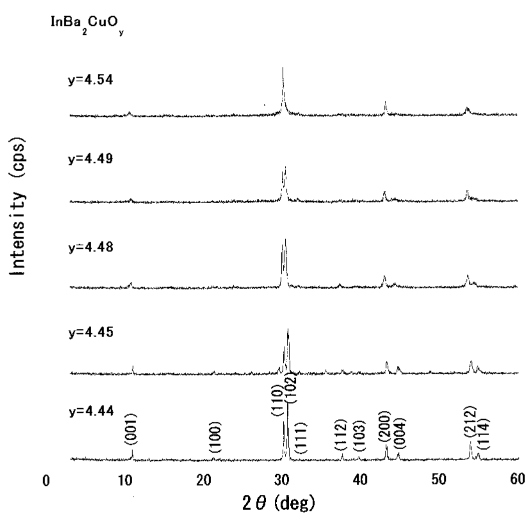

Fig.6 XRD patterns of $InBa_2CuO_y$ (0.44≦y≦0.54) samples annealed under pressures of 20-60 MPa at a temperature of 500℃ for 10 hours.

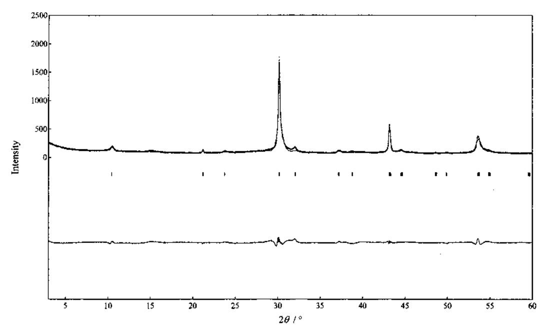

Fig.8 The observed and refined XRD patterns by the Rietveld analysis. The observed XRD pattern coincided well with the one calculated by the Rietveld analysis.

annealing was increased, the c-axis lengths became larger; the c-axis length of $InBa_2CuO_y$ was drastically increased from 8.09 Å to 8.36 Å with an increase in the oxygen content from 4.44 to 4.54. Based on the results of XRD pattern and oxygen content of the $InBa_2CuO_{4.54}$, we refined its crystal structure by using the Rietveld refinement software RIETAN-2000.

As shown in Fig.8, the observed XRD pattern coincided well with the one calculated by Rietveld analysis. The refined crystallographic data of the $InBa_2CuO_{4.54}$ are listed in Table 1(b) together with those of the $InBa_2CuO_{4.44}$ Table 1(a). The reliability factor of the $InBa_2CuO_{4.54}$ was R_{wp}=9.11%, R_p=7.00%, R_e=9.12%, R_I=5.21%, and R_F=4.00%, respectively. The S factor estimated by R_{wp} / R_e is about 1.0, showing that the crystallographic data refined by the Rietveld analysis is an appropriate one. In Fig.9, crystal structures of $InBa_2CuO_{4.44}$ and $InBa_2CuO_{4.54}$ are shown. Comparing the structure of the $InBa_2CuO_{4.54}$ with the $InBa_2CuO_{4.44}$, two clear differences were found; one is the increase in the occupancy of the O(4) and O(5) from 0.265 to 0.27, although the increase in the occupancy is rather small, indicating that the increased oxygen is doped to the oxygen sites in the CuO_2 plane. Another is the substitution of In and Cu each other. As shown in Table 1(b), about one third of the In(1) and Cu(2) sites are occupied by Cu and In, respectively. Since 8.3636 Å of the c-axis length of the $InBa_2CuO_{4.54}$ is close to 4.3780 Å, the double of its a-axis length, the inter-substitution will increase the symmetry of the crystal.

The inter-substitution also reveals that the CuO_2 plane is unstable when the a-axis length is as long as 4.18 Å. Since all the cuprate superconductors have CuO_2 planes, it will be difficult to make the $InBa_2CuO_{4.54}$ having incomplete CuO_2 planes superconducting.

In Fig.10, Resistivity as a function of temperature of the $InBa_2CuO_y$ (y=4.49 and 4.54) is shown, indicating that as the oxygen content becomes larger, the resistivity decreases. Although the $InBa_2CuO_{4.54}$ was not superconducting, the resistivity at room temperature of the $InBa_2CuO_{4.54}$ was 90.3 Ωcm, which corresponded to 1/400000 of that of the $InBa_2CuO_{4.44}$.

Conclusion

By annealing the InBa2CuOy under a pressure of 60MPa oxygen at 500℃ for 10 hours, its oxygen content increased from 4.44 to 4.54, together with a drastic increase in a c-axis length from 8.09 to 8.36 Å. About one third of In and Cu sites were substituted each other by annealing at a pressure of 60MPa oxygen. The resistivity of InBa2CuOy was drastically decreased from 28.8M Ωcm to 90.3K Ωcm at room temperature, indicating that a conducting a new phase of the InBa2CuOy was prepared.

Acknowledgments

A part of this work was supported by a grant from Yamagata Prefecture, Japan.

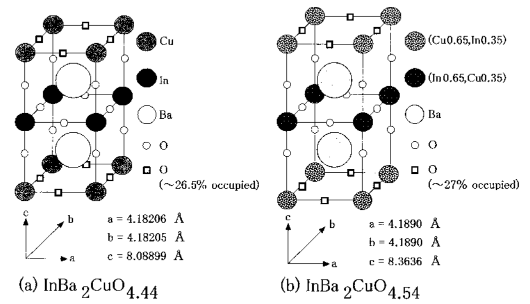

Fig.9 Structures refined by powder X-ray Rietveld analysis method. It was found by the Rietveld analysis that about one third of In and Cu sites were substituted each other by annealing under 60 MPa oxygen. Length of c-axis was increased from 8.0889 to 8.3636 Å, and oxygen contents were increased from 4.44 to 4.54.

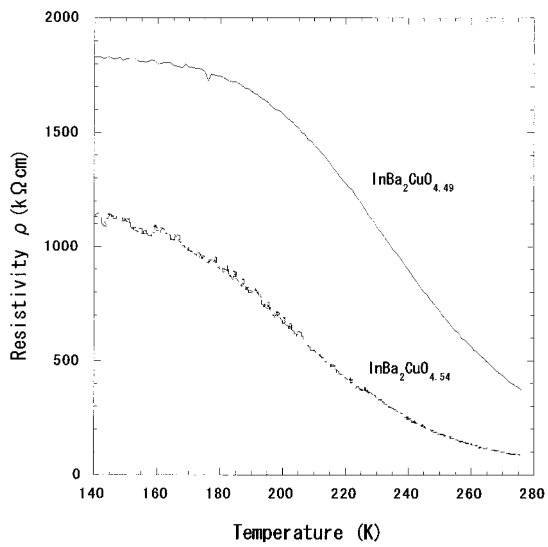

Fig.10 Results of resistivity vs. temperature measurement y=4.49 (50 MPa) and y=4.54 (60 MPa). Resistivity of $InBa_2CuO_{4.49}$ was 374 KΩcm at room temperature, and that of $InBa_2CuO_{4.54}$ was 90.3 KΩcm at room temperature, indicating that $InBa_2CuO_y$ becomes con ducting.

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(a) $InBa_2CuO_{4.44}$ (0MPa)

Atom	site	x	y	z	B(Å)	Occupancy
Ba	2t	0.5	0.5	0.24083	1.15242	1.0
In(1)	1a	0.0	0.0	0.0	0.17814	0.9809
In(2)	1c	0.0	0.0	0.5	3.83277	0.07
Cu	1c	0.0	0.0	0.5	1.1911	0.8073
O(1)	1b	0.5	0.0	0.0	0.5	1.0
O(2)	1e	0.0	0.5	0.0	0.5	1.0
O(3)	2q	0.0	0.0	0.30261	0.5	1.0
O(4)	1d	0.5	0.0	0.5	0.5	0.265
O(5)	1g	0.0	0.5	0.5	0.5	0.265

S/G:Pmmm(No.47)
a=4.182 b=4.182 c=8.089

Reliability factor
R_{wp}=10.31 R_p=7.97 R_e=8.51 R_I=2.75 R_F=2.29

(b) $InBa_2CuO_{4.54}$ (60MPa)

Atom	site	x	y	z	B(Å)	Occupancy
Ba	2t	0.5	0.5	0.24083	0.8254	1.0
In(1)	1a	0.0	0.0	0.0	0.5609	0.62483
Cu(1)	1a	0.0	0.0	0.5	0.5609	0.36456
In(2)	1c	0.0	0.0	0.5	7.0124	0.31058
Cu(2)	1c	0.0	0.0	0.5	7.0124	0.62001
O(1)	1b	0.5	0.0	0.0	0.5	1.0
O(2)	1e	0.0	0.5	0.0	0.5	1.0
O(3)	2q	0.0	0.0	0.30261	0.5	1.0
O(4)	1d	0.5	0.0	0.5	0.5	0.270
O(5)	1g	0.0	0.5	0.5	0.5	0.270

S/G:Pmmm(No.47)
a=4.190 b=4.190 c=8.363

Reliability factor
R_{wp}=9.11 R_p=7.00 R_e=9.12 R_I=5.21 R_F=4.00

Table 1 The refined crystallographic data of the $InBa_2CuO_{4.54}$ are listed in Table1 (b) together with those of the $InBa_2CuO_{4.44}$ Table 1 (a).