JOURNAL OF SOLID STATE CHEMISTRY **131**, 177–180 (1997)
ARTICLE NO. SC977353

# BRIEF COMMUNICATION

# Synthesis and Characterization of a New Layered Cuprate $In_2Ba_2CuO_{6-\delta}$

T. Kijima, H. Sushida, T. Noguchi, M. Yada, and Masato Machida

*Department of Materials Science, Faculty of Engineering, Miyazaki University, Miyazaki 889-21, Japan*

Received April 26, 1996; in revised form November 18, 1996; accepted February 17, 1997

**A new cuprate with the composition $In_2Ba_2CuO_{6-\delta}$ ($\delta = 0.1$) has been synthesized in the temperature range 890–910°C in air. The cuprate crystallizes in an orthorhombic cell with the lattice parameters of $a = 5.545$, $b = 5.425$, and $c = 24.46$ Å. The resistivity of the cuprate at room temperature is as high as 8.1 MΩ cm. Chemical analysis and XPS data show that the indium-based cuprate contains 1.5 mol% of oxygen vacancies, probably located in the $CuO_2$ planes, which would lead to the high resistivity.** © 1997 Academic Press

## INTRODUCTION

The family of high-$T_c$ superconductors is based on a structure comprising $CuO_2$ planes interleaved with a variety of metal or metal/oxygen layers as separators and/or carrier reservoirs (1). The III group elements as carrier reservoirs characteristically form several homologous series of layered cuprate superconductors. The cuprates of this family were first found in 1988 in the Tl–Ba–Ca–Cu–O system in which $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$ and $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+3}$ were observed to be superconducting at temperatures up to 103–125 K (2–4). Recently, Takayama-Muromachi and his co-workers have used a high-pressure technique to synthesize new cuprate phases and have found some additional homologous series of superconducting cuprates with $T_c$ near or above 100 K: $BSr_2Ca_{n-1}Cu_nO_{2n+3}$ (5, 6), $AlSr_2Ca_{n-1}Cu_nO_{2n+3}$ (7), and $GaSr_2Ca_{n-1}Cu_nO_{2n+3}$ (8). In addition, Kasper (9) originally prepared the homologous layered compounds $In_2O_3(ZnO)_m$ ($m = 2$–5, 7), which was extended by Kimizuka and his co-workers (10–13) to the synthesis of a broad range of indium/zinc-based compounds $InMO_3(ZnO)_m$ ($M =$ Fe, Ga or Al, $m = 1$–13). For the indium-based cuprate system, however, a few studies appeared on the formation of perovskite-like dielectric compounds with a tetragonal structure, $InBa_2CuO_{4.5}$, $InBa_4CuO_{6.5}$, and $In_4Ba_3Cu_3O_{12}$ (14, 15). In this paper, we report the synthesis of a new layered cuprate, $In_2Ba_2CuO_{6-\delta}$ ($\delta = 0.1$), and discuss its electrically conducting properties in terms of its electronic structure.

## EXPERIMENTAL

The sample was prepared by the solid-state reaction of $In_2O_3$, $BaCO_3$, and CuO (99.99% Rare Metallic). The mixed powder, with nominal composition $In_2Ba_2CuO_6$, was heated at various temperatures from 850 to 950°C for 6 h in air, cooled in a furnace to room temperature, and then reground. The same procedure was repeated two times and then the calcined sample was pressed into a plate of $10 \times 5 \times 1\,mm^3$, followed by sintering at 800°C for 6 h. The oxidation state of copper and the oxygen content were determined by a combined use of total copper analysis by atomic absorption and iodometric titration of $Cu^{2+}$ and $Cu^+$ ions using the cuprate dissolved in hydrochloric acid solution. Powder X-ray diffraction measurements were made on a XD-3A Shimazu diffractometer using Cu$K\alpha$ radiation and silicon was used an external standard. Electron diffraction patterns were taken by a Hitachi transmission electron microscope operated at a voltage of 200 kV. Chemical composition analysis was conducted by energy-dispersive X-ray spectroscopy (EDX) under a Hitachi analytical scanning electron microscope. Resistivity measurement was conducted by the standard four- or two-probe DC method at room temperature. XPS spectra were measured at room temperature using a Shimazu ESCA-3300 spectrometer with Al$K\alpha$ X-rays as the exciting radiation.

## RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction pattern of the resulting solid with the nominal composition $In_2Ba_2CuO_6$ (**1**). Except for some peaks, all the observed diffraction peaks in the $2\theta$ range of 10–60° could be indexed by the least-squares

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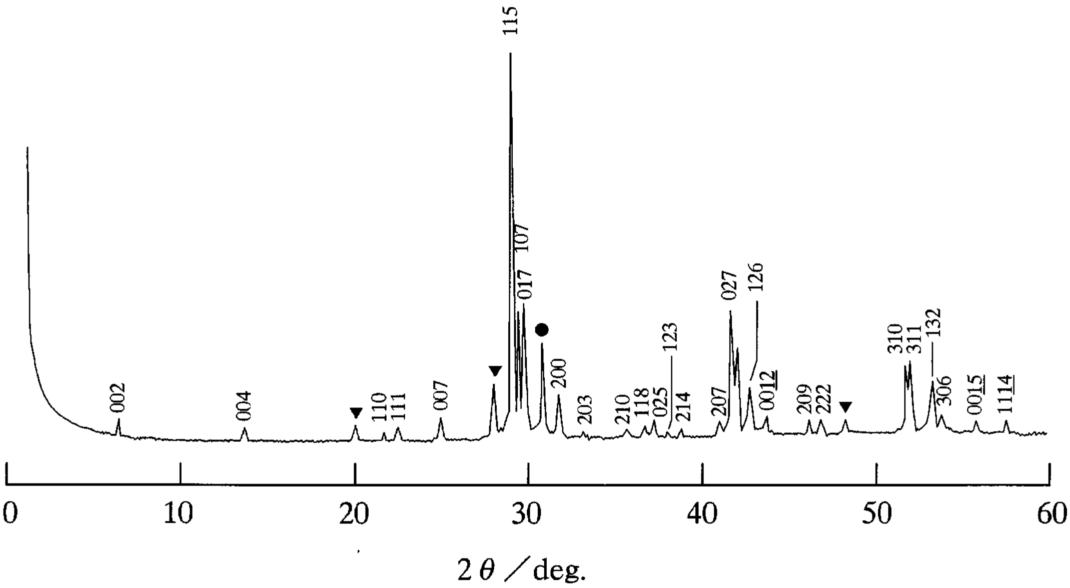

**FIG. 1.** X-ray diffraction pattern of **1** (Cu$K\alpha$). Indexes are given based on an orthorhombic cell with $a = 5.455$, $b = 5.525$, and $c = 24.46$ Å. Unindexed diffraction peaks are due to $In_2BaO_4$ (●) or unknown minor phase (▼).

fitting method on the basis of an orthorhombic unit cell with the lattice parameters $a = 5.455$, $b = 5.525$, and $c = 24.46$ Å (Table 1). These values are in good agreement with $a = 5.450$, $b = 5.503$, and $c = 24.49$ Å, determined from the electron diffraction patterns taken from the major solid in the same sample (Fig. 2). The major solid was observed to be lamellar in shape. The extra XRD peak at $d = 2.848$ Å, as well as that at $d = 2.929$ Å overlapped on the 017 reflection of the major phase, is attributable to $In_2BaO_4$. EDX analysis coupled with SEM observation showed that the resulting sample consists of one lamellar-shaped major phase with In, Ba, and Cu content of $37.4 \pm 1.9$, $42.4 \pm 5.8$ and $18.0 \pm 2.2$ mol% as well as some minor phases including one with the content of $37.1 \pm 0.8$, $51.4 \pm 1.8$ and $11.5 \pm 1.1$ mol% and one with the contents of $40.1 \pm 1.0$, $31.6 \pm 1.0$ and $28.4 \pm 2.0$ mol%. Taking into consideration the experimental error of the analytical data as well as the morphological observations, it would be reasonable to conclude that the major phase detected by XRD and ED analyses is a layered cuprate with the chemical composition $In_2Ba_2$

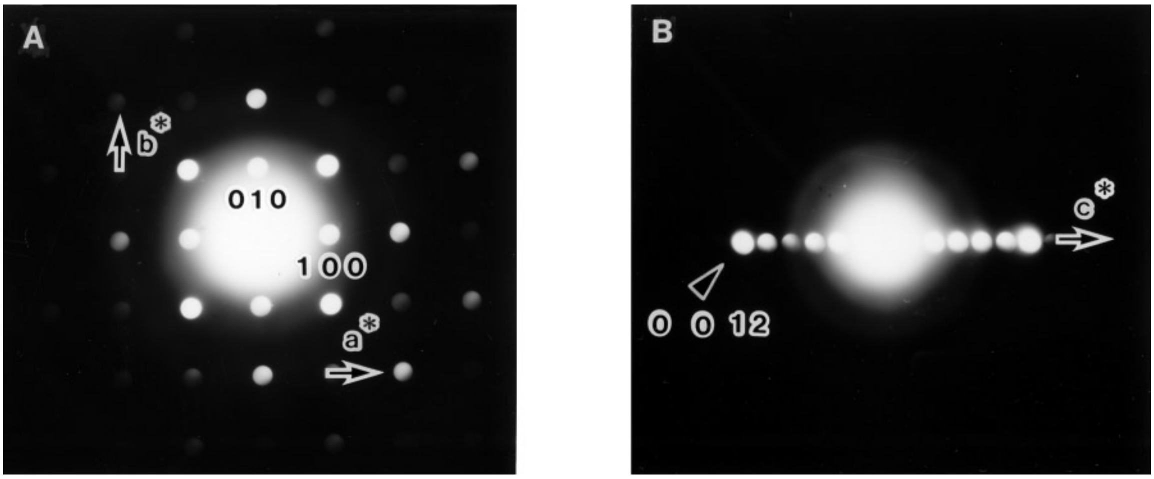

**FIG. 2.** The (a) $hk0$ and (b) 001 electron diffraction patterns of **1**.

**TABLE 1**
**Calculated and Observed X-Ray Diffraction Patterns of 1 (Indexed with the Lattice Parameters $a = 5.545$ Å, $b = 5.425$ Å, $c = 24.46$ Å)**

| Index ($h\,k\,l$) | $d_{cal}$/Å | $d_{obs}$/Å | $I/I_{max}$ |
|---|---|---|---|
| 002 | 12.23 | 12.29 | 4.3 |
| 004 | 6.115 | 6.163 | 3.1 |
| 104[a] | 4.108 | 4.272 | 2.9 |
| 110 | 3.878 | 3.883 | 3.2 |
| 111 | 3.830 | 3.830 | 5.6 |
| 112 | 3.697 | 3.709 | 5.5 |
| 007 | 3.494 | 3.485 | 5.8 |
| 008[a] | 3.057 | 3.128 | 15.8 |
| 115 | 3.039 | 3.024 | 100 |
| 107 | 2.956 | 2.960 | 32.9 |
| 017[a] | 2.938 | 2.929 | 35.0 |
| 116[a] | 2.810 | 2.848 | 25.4 |
| 200 | 2.773 | 2.780 | 11.5 |
| 203 | 2.625 | 2.619 | 2.8 |
| 210 | 2.469 | 2.470 | 3.2 |
| 118 | 2.401 | 2.400 | 4.8 |
| 025 | 2.372 | 2.374 | 5.1 |
| 123 | 2.335 | 2.331 | 1.7 |
| 214 | 2.289 | 2.288 | 2.8 |
| 207 | 2.172 | 2.171 | 4.3 |
| 027 | 2.143 | 2.143 | 31.8 |
| 126 | 2.092 | 2.093 | 18.4 |
| $00\underline{12}$ | 2.038 | 2.043 | 6.4 |
| 209 | 1.941 | 1.941 | 6.1 |
| 222 | 1.915 | 1.916 | 3.9 |
| $00\underline{13}$[a] | 1.881 | 1.869 | 3.6 |
| 310 | 1.750 | 1.748 | 19.7 |
| 311 | 1.745 | 1.743 | 22.0 |
| 132 | 1.703 | 1.703 | 18.4 |
| 306 | 1.683 | 1.687 | 9.5 |
| $00\underline{15}$ | 1.631 | 1.631 | 3.4 |
| $1\,1\underline{14}$ | 1.593 | 1.590 | 5.3 |

[a] Unindexible peaks.

CuO$_{6-\delta}$. This major phase might coexist with more than three extra phases including In$_4$Ba$_3$Cu$_3$O$_{12}$ and In$_6$Ba$_9$Cu$_2$O$_{20}$, although the latter two minor phases could not be detected by the XRD data. The resulting solid was gray and the major cuprate was stably formed in the narrow temperature range 890–910°C. The new orthorhombic phase is different from any of the tetragonal cuprates earlier reported, InBa$_2$CuO$_{4.5}$ ($a = 4.1778$, $c = 8.103$ Å), InBa$_4$CuO$_{6.5}$ ($a = 4.1585$, $c = 29.587$ Å), and In$_4$Ba$_3$Cu$_3$O$_{12}$ ($a = 12.1226$, $c = 8.5083$ Å) (13).

The physical properties of **1** were compared with those of InBa$_2$CuO$_{4.5}$ (**2**) and Bi$_2$Sr$_2$CuO$_6$ (**3**). The latter two cuprates were prepared by heating their nominal compositions at 920 and 830°C, respectively, for 6 h. In contrast to $5.9 \times 10^{-4}$ MΩ · cm for **3**, the resistivity of **1** at room temperature is as high as 8.1 MΩ · cm, but it is slightly lower than 25.5 MΩ · cm for **2**. Iodometric titration combined with atomic absorption analysis yielded a value of $+1.82$ for the overall oxidation number of copper in **1**. The XRD and EDX data suggest that the overall composition of extra phases is the same as that of the major phase and that their total amount may be as much as about 10%. This leads to the copper oxidation number of $+1.80$ for the major phase in **1** if we assume that the average oxidation number of copper for the extra phases is $+2.0$. The chemical composition of the major phase is thus reasonably given by In$_2$Ba$_2$CuO$_{6-\delta}$ ($\delta = 0.1$). The copper oxidation number of $+1.8$ for this phase is fairly close to $+1.78$ for **2**, but much less than $+1.99$ for **3**. The quantitative data on the copper oxidation state were consistent with Cu2p$_{3/2}$ XPS spectra of these three samples (Fig. 3a): the binding energy of 934.0 eV for **3** corresponds to the $+2$ state of copper, whereas the lower values of 933.0 for **1** and 932.6 eV for **2** are indicative of lower oxidation states of copper. This indication is also in harmony with the marked decrease in intensity of the shake-up band near 942 eV for both the indium-based cuprates. Additional XPS spectra showed that the valence bands of the indium-based cuprates are narrower in width and higher in threshold binding energy than that for the bismuth-based analogue, leading to an increase in the band gap (Fig. 3b). If we assume that the crystal structure of the present layered cuprate is similar to that of the bismuth-based 2201 cuprate, the lattice parameters of $a = 5.545$ and $b = 5.425$ Å for **1** can be related by $a' = 1/4\sqrt{a^2 + b^2}$ to $a' = 1.939$ Å roughly corresponding to the planar Cu–O bond length in the CuO$_2$ plane. This Cu–O bond length may be slightly expanded in comparison to those usually observed for the superconducting cuprates. The chemical composition data indicates that the new cuprate **1** contains 1.5 mol% of vacancies in oxygen sites. According to Khorlanov *et al.*, InBa$_2$CuO$_{4.5}$ is structurally similar to $\alpha$-ScBa$_2$CuO$_{4.5}$ whose structure contains a large number of oxygen vacancies to form $[\mathrm{CuO}_{1/2}\square_{3/2}]^+$ planes (14). This fact suggest that oxygen vacancies in **1** are likely located in the CuO$_2$ planes. Such an arrangement of oxygen vacancies, together with the slightly expanded intraplane Cu–O length would be responsible for the localization of valence electrons in the CuO$_2$ plane, resulting in the increase in band gap responsible for the high resistivity of the indium-based cuprates.

In an attempt to induce superconductivity in the In$_2$Ba$_2$CuO$_6$ system, mixed solids with the nominal composition of In$_2$Ba$_{2-x}M_x$CuO$_6$ ($M$ = K, La; $x$ = 0–1.0) were prepared in the same procedure as above. The X-ray diffraction patterns of the resulting solids gave the 002 reflection in a limited range of $x$, leading to the solid solution ranges of $0 \leq x \leq 0.4$ for $M = \mathrm{K}$ and $0 \leq x \leq 0.3$ for $M = \mathrm{La}$. In both systems, the resistivity of the resulting mixed solids showed a tendency to rather increase with an increase in $x$, probably due to an increase in width of the valence band induced by the partial atom replacement in the Ba sites.

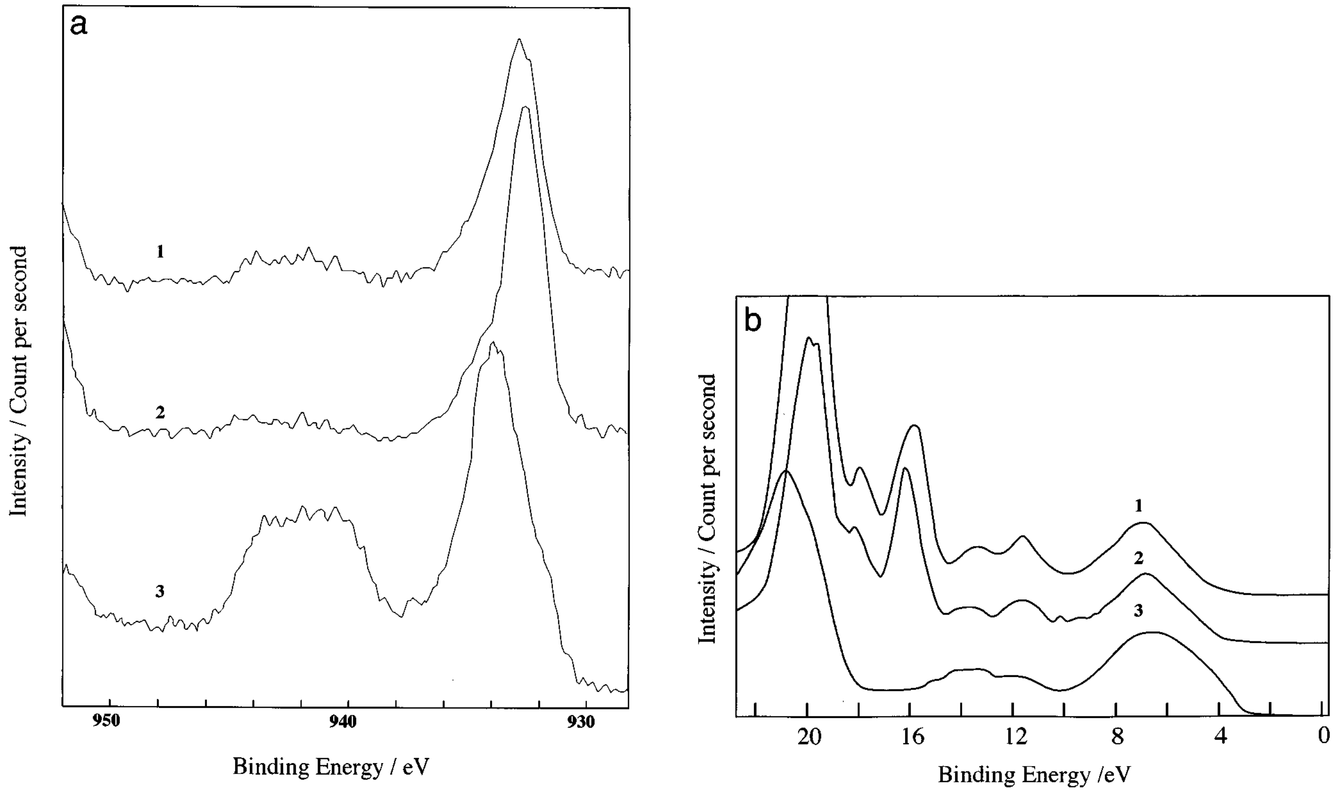

**FIG. 3.** X-ray photoelectron spectra of **1**, **2**, and **3** at room temperature: (a) copper $2p_{3/2}$ bands with high energy satellite lines and (b) low energy bands including their valence bands.

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