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Synthesis and Characterization of a New Layered Cuprate $LiI_3Bi_2Sr_2CaCu_2O_8$

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A new layered cuprate with the composition $LiI_3Bi_2Sr_2CaCu_2O_8$ has been synthesized by the reaction of $Bi_2Sr_2CaCu_2O_8$ with lithium iodide under an atmosphere of iodine at 300°C. The new cuprate is pale green and lamellar and crystallized in a tetragonal cell with the lattice parameters $a = 5.4038$ and $c = 44.179$ Å. A structural model for the cuprate is proposed in which the triiodide anions are stably intercalated in the Bi_2O_2 layer to form a tilted monolayer accompanying lithium cations. XPS data show that the electronic state of the intercalated triiodide anions is significantly perturbed through the interaction with the surrounding atomic species and that the lithium–iodine intercalation results in a significant narrowing of the valence band, leading to a resistivity of the cuprate as high as 0.777 kΩ cm at 30°C. Identification of the iodine species in $IBi_2Sr_2CaCu_2O_8$ is also discussed. © 1998 Academic Press

INTRODUCTION

The family of high-T_c cuprate superconductors consist of CuO_2 planes interleaved with a variety of metal or metal–oxygen layers as separators and/or carrier reservoirs (1). Among this family, the bismuth-based cuprates uniquely act as host materials to intercalate halogen and organic species in their weakly bound Bi_2O_2 double layers (2–5). The iodine-intercalated superconductor $IBi_2Sr_2CaCu_2O_8$ (I-Bi2212) was first synthesized by Xiang *et al.* by the reaction of $Bi_2Sr_2CaCu_2O_8$ (Bi-2212) with iodine (2). Subsequently, it was demonstrated that Bi-2212 takes up silver (or mercury) iodides or bromides to form a superconducting intercalate (6–9). Such intercalation of atomic or molecular guest species in metal oxides would provide a useful approach not only for understanding the mechanism of superconductivity but also for controlling the physical properties of metal oxides through the electronic host–guest interaction. In this paper, we report the synthesis of a new intercalation compound, $LiI_3Bi_2Sr_2CaCu_2O_8$, propose its structure model, and discuss its electrically conducting properties in terms of its electronic structure.

EXPERIMENTAL

The Bi-2212 material (**1**) was prepared by the solid-state reaction of a stoichiometric mixture of Bi_2O_3, $SrCO_3$, $CaCO_3$, and CuO (99.99%, Rare Metallic) with twice-repeated grinding and firing at 850°C for 12 h in air, followed by cooling to room temperature in a furnace. The formation of the single-phase Bi-2212 cuprate with the lattice parameters $a = 5.412$ and $c = 30.6$ Å was confirmed by X-ray diffraction (Fig. 1). The reaction of the Bi-2212 sample with lithium iodide under an atmosphere of iodine was carried out as follows. To a 1:1 mixed solid of Bi-2212 and LiI loaded in a Pyrex tube, iodine was added to keep the $Bi:LiI:I_2$ ratio constant at 2:2:1. After sealing in air, the mixture was heated at 170°C for 3 h and then maintained for 10 h at 200, 250, 300, or 350°C. The $Bi:LiI:I_2$ ratio of 2:1:1 was selected based on preliminary experiments with varying ratios as $x = 0.25$, 0.5, 0.75, and 1.0 and $y = 0.75$ and 1.0 in $Bi:LiI:I_2 = 2:x:y$. To prepare the I-Bi2212 sample (**2**) for reference, a 1:1 mixture of Bi-2212 and iodine (I_2) was sealed *in vacuo* and then heated stepwise at 170°C for 3 h and 190°C for 3 h. Samples for resistivity and/or XPS measurements were pressed into a plate of $10 \times 5 \times 1$ mm^3. Powder X-ray diffraction measurement was made at room temperature on a Shimadzu XD-3A diffractometer with Cu$K\alpha$ radiation. Thermogravimetric (TG) analysis was carried out on a Seiko TG/DTA320U with a heating rate 10°C min^{-1} in air. Scanning electron microscopy (SEM) as well as energy-dispersive X-ray spectroscopic measurement (EDX) was performed with a Hitachi H-4100 equipped with a Horiba EMAX-5770. Atomic absorption analysis was made on a Hitachi Z-8000 spectrophotometer. Resistivity measurement was conducted by the standard two-probe dc method. The plate samples mounted on double-sided carbon tape were utilized for XPS measurement at room temperature using a Shimadzu ESCA-3300 spectrometer with monochromated Al$K\alpha_{1,2}$ X-rays as the exciting radiation.

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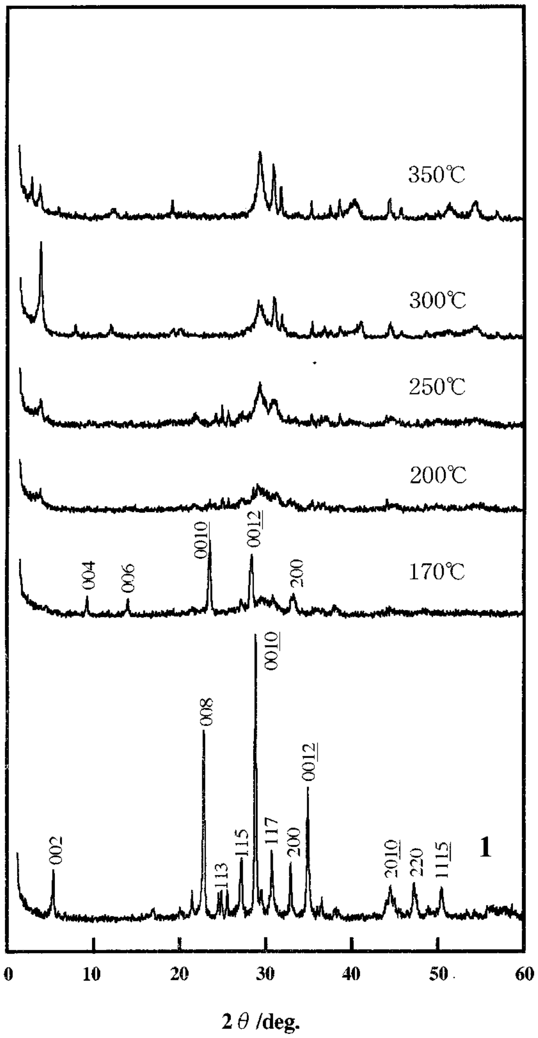

FIG. 1. X-ray diffraction patterns of **1** and its reaction products with a 1:1 mixture of LiI and I_2 obtained at various temperatures for 10 h (Cu*K*α). Indexes are given for both **1** (Bi-2212) and the major phase (I-Bi2212) in the 170°C product.

The spectra were calibrated using pump oil hydrocarbon on the sample surface (C 1*s* = 284.3 eV).

RESULTS AND DISCUSSION

Figure 1 summarizes the X-ray diffraction patterns of the resulting samples obtained by heating at 170°C or above. At 170°C, the Bi-2212 phase (**1**) reacted substantially with iodine alone to form I-Bi2212 as the major product. At 200°C, on the other hand, the host phase was totally converted into a poorly crystalline phase characterized by a weak diffraction peak at $2\theta = 3.95°$ and a broad band near $2\theta = 30°$. With further increase of reaction temperature, the solid increased in crystallinity until at 300°C it developed into a well crystalline phase (**3**) characterized by a sharp diffraction peak of $d = 22.3$ Å. The X-ray diffraction profile for the solid obtained at 350°C gave one more new diffraction peak at $2\theta = 3.02°$ along with higher order ones, indicating that the solid is a mixture of the major phase **3** and an extra phase with a long period of 29.3 Å.

Except for two extra peaks, all of the observed X-ray diffraction peaks for **3** in the 2θ range of 3–60° could be indexed by the least-squares fitting method on the basis of a tetragonal unit cell with the lattice parameters $a = 5.4038$ and $c = 44.179$ Å (Fig. 2 and Table 1). The SEM image of **3** demonstrated that the major solid consists of lamellar particles ~1 μm in size. EDX analysis, coupled with atomic absorption analysis for Li and Cu, showed that the molar ratio of Bi, Sr, Ca, Cu, I, and Li for the major phase is 2.16:2.03:1.00:1.99:3.06:1.07. This analytical result gives the empirical composition $Li_{1.07}I_{3.06}Bi_{2.16}Sr_{2.03}Ca_{1.00}Cu_{1.99}O_8$, which corresponds to the nominal composition $LiI_3Bi_2Sr_2CaCu_2O_8$ for the reaction mixture. It is therefore suggested that the new intercalate **3** is obtainable essentially as a stoichiometric single phase by heat treatment at 300°C and that the iodine species are intercalated as the I_3^- ion.

The thermogravimetric (TG) curve for **1** showed a slight weight loss of as little as 0.4% at temperatures above 600°C, as shown in Fig. 3. This is presumably due to release of excess oxygen incorporated in the Bi_2O_2 double layers. The TG curve for **2**, on the other hand, showed two weight losses due to desorption of iodine over the two temperature ranges 146–400 and 658–892°C. In the first stage, the solid **2** was partly deiodinated into a poorly crystalline layered cuprate but isostructural with the host phase. The partial deiodination was succeeded by the complete regeneration of the host phase in the second stage. The total weight loss of 12.6% (w/w) observed for **2** was in good agreement with 12.5% expected for $IBi_2Sr_2CaCu_2O_8$ (I-Bi2212). These facts indicate that the cuprate **2** contains two types of iodine species,

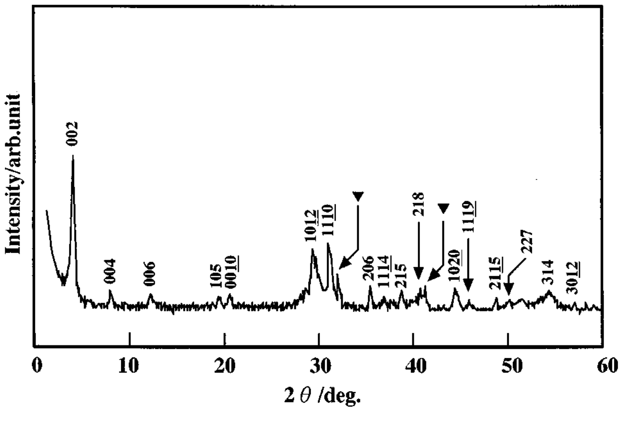

FIG. 2. Indexes of X-ray diffraction peaks for **3** based on tetragonal cell with $a = 5.4038$ and $c = 44.179$ Å. Unindexed diffraction peaks are due to an unknown phase (▼).

TABLE 1

Calculated and Observed X-Ray Diffraction Patterns of 3 (Indexed with the Lattice Parameters $a = b = 5.405$ Å and $c = 44.12$ Å)

Index (*hkl*)	d_{cal} (Å)	d_{obs} (Å)	I/I_{max}
002	22.06	22.36	100
004	11.03	11.06	11
006	7.354	7.357	15
105	4.609	4.579	15
$00\underline{10}$	4.412	4.389	16
$10\underline{12}$	3.040	3.045	53
$11\underline{10}$	2.889	2.886	71
1111[a]	2.767	2.807	35
206	2.536	2.532	28
$11\underline{14}$	2.431	2.436	18
215	2.331	2.330	21
218	2.214	2.220	18
$00\underline{20}$[a]	2.206	2.198	29
$10\underline{20}$	2.042	2.044	25
$11\underline{19}$	1.985	1.982	13
$21\underline{15}$	1.867	1.869	16
227	1.829	1.828	10
314	1.689	1.687	23
$30\underline{12}$	1.618	1.619	12

[a] Unindexable peaks.

one weakly and the other strongly held in the solid; the molar ratio of the former and latter species can be taken as 1.8 : 1 from the weight loss data. In contrast to the TG curve for **2**, the TG curve for **3** showed three poorly resolved weight losses over the wide temperature range 100–900°C. The slight weight loss at temperatures below 250°C indicates that almost all of the loaded iodine species are likely incorporated in the crystal lattice of the solid. This indication is also consistent with the fact that little iodine was observed to adhere to the inner wall of the glass tube during the reaction. X-ray diffraction and atomic absorption analyses revealed that on heating at 850°C the solid is pyrolyzed into the initial structure of Bi-2212 type but 8.5% of the intercalated Li moiety is left undesorbed. The total weight loss of 30.4% (w/w) observed for **3** was in good agreement with 30.9% (w/w), expected for the conversion of $Li_{1.07}I_{3.06}Bi_{2.16}Sr_{2.03}Ca_{1.00}Cu_{1.99}O_8$ into $Li_{0.091}Bi_{2.16}Sr_{2.03}Ca_{1.00}Cu_{1.99}O_8$.

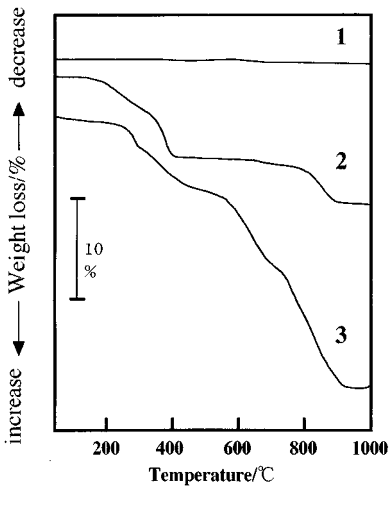

FIG. 3. TG curves for **1**, **2**, and **3**.

On the basis of the X-ray and SEM observations as well as the compositional data, it is most likely that monovalent triiodide anions are intercalated in the Bi_2O_2 double layer, with an accompanying equimolar amount of Li^+ cation. The ionic radii of Li^+, I^-, and O^{2-} ions are 0.74, 2.15, and 1.4 Å, respectively. Referring to the ionic and van der Waals radii of iodine as well as the crystallographic data for some triiodide salts such as CsI_3 (10), the triiodide molecular ion has a van der Waals diameter of 4.3 Å, a length of 10.2 Å, and a value of 5.9 Å for the terminal I–I distance. The Bi^{3+} and O^{2-} ions in the BiO layer are located in a NaCl-like cell with an O–O distance of 5.4 Å along the –O–Bi–O– sequence and with a Bi–Bi distance of 3.8 Å along the –Bi–Bi– sequence. If the triiodide molecular ions are arranged as a bilayer with their axes parallel to the BiO layer and oriented along the –Bi–Bi– sequence, the maximum value of the I/Bi ratio is $3 \times (3.82/10.2)$ or 1.1, being much less than the observed value of 1.5. The van der Waals thickness of the intercalated bilayer, given by $(2 + \sqrt{3}) \times 2.15$, or 8.0, is also much greater than half the difference between the c values of **3** and its host phase, given by $(44.18 - 30.6)/2$, or 6.8 Å. Thus, we propose a most probable structure model in which the triiodide ions are arranged along the –O–Bi–O– sequence to form a monolayer with their axes tilted by 63° relative to the BiO layer, with Li^+ ions located in a position surrounded by any four triiodide ions, as illustrated in Fig. 4. This atomic and molecular packing model reasonably explains the observed Bi : Li : I ratio of 2 : 1 : 3 and the increase of 6.8 Å in $c/2$ value relative to the Bi-2212 phase. There is a well-known tendency that a family of MI_3-type compounds are stably formed as a bulk crystal only for M^+ ions with a large ionic radius such as K^+ and Cs^+ ions (10). Within the Bi_2O_2 layer, however, the monolayered I_3^- assemblies accompanying relatively small Li^+ cations would be stably held due to the electrostatic interaction with the surrounding atomic species.

The electronic structure of the LiI_3-incorporated cuprates obtained was examined by X-ray photospectroscopy, as shown in Fig. 5. It is known that the I_3^- ion is essentially a resonating system consisting of an I^- ion and an I_2 molecule and that the 3*d* core-level spectra for most triiodide salts show only a single, sharp line, as observed at 619.5 eV for CsI_3 or 619.0 eV for $[CoPc]I_3$ (11), or a narrow asymmetric band, as one composed of 2 : 1 double-component peaks at 619.65 and 618.45 eV for CsI_3 (12). In contrast,

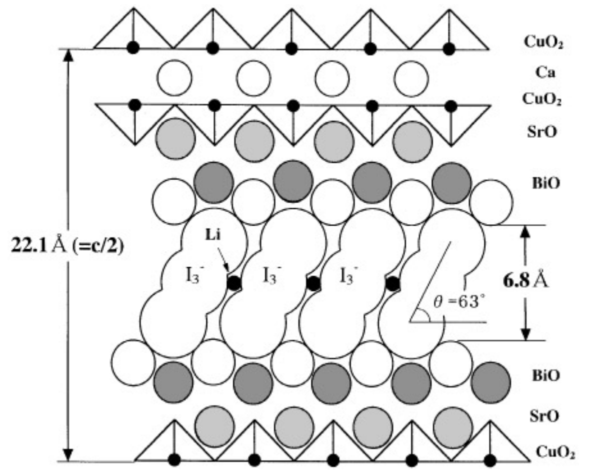

FIG. 4. Schematic representation of the probable arrangement of triiodide ions in the Bi_2O_2 double layer of Bi-2212 cuprate.

both the I $3d_{5/2}$ and $3d_{3/2}$ spectra for **3** show a wide, asymmetric band which can be deconvoluted into two peaks of intensity ratio ca. 3:2 with different binding energies (Fig. 5a). The binding energy of 620.2 eV for the higher energy component in the I $3d_{5/2}$ band is nearly equal to 619.9 eV for solid I_2 (12), and the value of 617.8 eV for the lower energy component is rather decreased relative to 618.6 eV for I^- in the standard sample of KI. The peak broadening and marked asymmetric tailing to lower binding energy suggest that the electronic state of the intercalated I_3^- ions is significantly perturbed through the interaction with the surrounding oxygen, bismuth, and/or lithium atoms in the crystal lattice, probably leading to partial transfer of electron from the triiodide species to oxygen atoms in the BiO layer. On the other hand, the I $3d$ core-level spectrum for **2** indicates two main peaks at about 617.8 and 629.3 eV corresponding to the $3d_{5/2}$ and $3d_{3/2}$ levels, respectively, both with an additional peak shifted by 4.9 or 5.7 eV to higher binding energy (Fig. 5a). The lower and higher binding energy components in each band are attributable to monoiodide ion I^- as in KI and iodine in a highly oxidized state as in KIO_4, respectively, according to Choy *et al.* (13). It should also be noted that the peak intensity ratio of about 2:1 for both components in each band coincides with the above-described molar ratio of two types of iodine species with different chemical stabilities in the bulk sample. In contrast to a previous explanation by Choy *et al.* (13), both types of iodine species spectroscopically detected should thus be taken to exist in the host lattice, in which the anionized species would be weakly held through ionic bonding and the oxidized species would be strongly held through covalent I–O bonding.

The solid **3** was pale green and its resistivity was as high as 7.7×10^2 Ω cm at 30°C. This is in striking contrast to the known metal iodide intercalates $AgIBi_2Sr_2CaCu_2O_8$ (6–8)

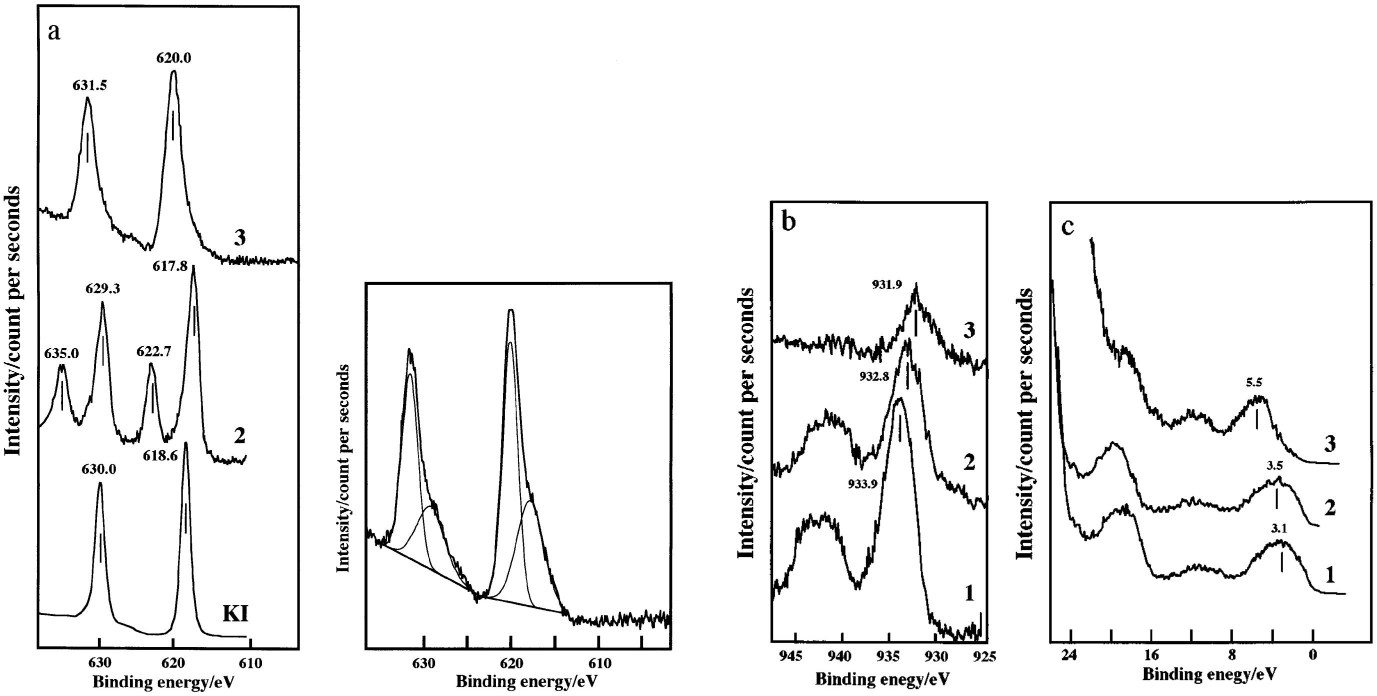

FIG. 5. X-ray photoelectron spectra of **1**, **2**, **3**, and/or KI at room temperature: (a) iodine $3d_{3/2}$ and $3d_{5/2}$ bands, (b) copper $2p_{3/2}$ bands with high-energy satellites, and (c) low-energy bands, including their valence bands.

and $(HgI_2)_{0.5}Bi_2Sr_2CaCu_2O_8$ (9), both of which are black and remain superconducting. The oxidation states of copper for **1**, **2**, and **3** were compared based on the Cu $2p_{3/2}$ XPS spectra of these samples (Fig. 5b). Referring to iodometric data for $In_2Ba_2CuO_{6-\delta}$ ($\delta = 0.1$), which give the Cu $2p_{3/2}$ band at 933.0 eV (14), the binding energy of 933.9 eV for **1** corresponds to the +2 state of copper, whereas the lower values of 932.8 and 931.9 eV for the latter two samples are indicative of a less oxidated state of copper. The superconducting nature of Bi-2212 is related to the excess oxygen incorporated in the Bi_2O_2 double layers to supply hole carriers for the CuO_2 layers. The replacement of the excess oxygen by the intercalation of LiI_3 in the Bi_2O_2 layer as well as the electron transfer from the intercalated triiodide to oxide would result in a considerable increase of the electron count on copper, or decrease of hole carrier, in the CuO_2 layer. The intercalation of LiI_3 also results in a significant narrowing of the valence band with an accompanying increase in threshold binding energy, in contrast to the intercalation of iodine alone, which has little influence on the band, as suggested from the low-energy region of the XPS spectra (Fig. 5c). Since the lattice parameter of $a = 5.404$ Å for the LiI_3-intercalated cuprate **3** is nearly equal to those for the other two analogues, the marked narrowing of the valence bandwidth for the former would arise from the expansion of the oxygen to copper distance along the c-axis in the CuO_2 layer to induce the localization of valence electrons. The band gap increased by such a valence-band narrowing, as well as the decrease in the carrier content in the CuO_2 layer, would be responsible for the high resistivity of the LiI_3-intercalated cuprate.

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