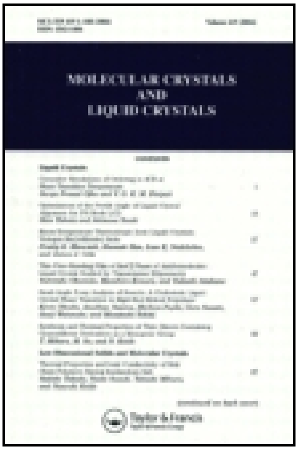

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Synthesis and Characterization of MI_2-Intercalated Bi-2212 Cuprates (M=Mn, Fe, Co, Cu, Zn)

Tsuyoshi Kijima [a], Hiroyuki Sushida [a], Yuhsuke Hara [a], Ryuhsuke Shiraishi [a], Mitsunori Yada [a] & Masato Machida [a]

[a] Miyazaki University, Dept of Materials Science, Miyazaki, 889-2192, JAPAN

Version of record first published: 27 Oct 2006

To cite this article: Tsuyoshi Kijima, Hiroyuki Sushida, Yuhsuke Hara, Ryuhsuke Shiraishi, Mitsunori Yada & Masato Machida (2000): Synthesis and Characterization of MI_2-Intercalated Bi-2212 Cuprates (M=Mn, Fe, Co, Cu, Zn), Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 341:2, 193-198

To link to this article: http://dx.doi.org/10.1080/10587250008026139

Mol. Cryst. and Liq. Cryst., 2000, Vol. 341, pp. 193-198
Reprints available directly from the publisher
Photocopying permitted by license only

Synthesis and Characterization of MI_2-Intercalated Bi-2212 Cuprates (M= Mn, Fe, Co, Cu, Zn)

TSUYOSHI KIJIMA, HIROYUKI SUSHIDA, YUHSUKE HARA,
RYUHSUKE SHIRAISHI, MITSUNORI YADA and
MASATO MACHIDA

Miyazaki University, Dept of Materials Science, Miyazaki, 889–2192 JAPAN

(In final form June 24, 1999)

A series of new layered cuprates with the composition $MI_{2+x}Bi_2Sr_2CaCu_2O_{8+y}$ (x=0.6–0.9; M=Mn, Fe, Co, Cu, Zn) have been synthesized by the reaction of $Bi_2Sr_2CaCu_2O_8$ with each transition metal under an atmosphere of iodine at 400°C. The new cuprates, lamellar in shape, are crystallized in a tetragonal unit cell with the lattice parameters of a = 5.393–5.402 Å and c = 43.32–43.96 Å. A structure model for these cuprates are proposed in which the monoiodide anions are intercalated in the Bi_2O_2 layer to form a bilayer accompanying $3d$ metal cations. All of the intercalated cuprates are non-superconducting to be as high as 0.74 – 2.52 MΩ · cm in resistivity at room temperature.

Keywords: layered bismuth cuprates; intercalation; transition metal iodides

INTRODUCTION

The high-Tc bismuth-based cuprate superconductors serve as the host materials to intercalate iodine and some other guest species. The first example was demonstrated by the intercalation of iodine into $Bi_2Sr_2CaCu_2O_8$ (Bi-2212) to form a modified superconductor $IBi_2Sr_2CaCu_2O_8$ (I-Bi2212) with iodine located between the Bi_2O_2 layers [1-3]. This approach was applied to the synthesis of silver-iodine and mercury-iodine intercalated Bi-2212 superconductors [4-7]. More recently, a similar reaction using lithium iodide and iodine resulted in the formation of a semiconducting layered cuprate $LiI_3Bi_2Sr_2CaCu_2O_8$ in which the iodine species are intercalated as I_3^- ions between the Bi_2O_2 layers [8]. In this paper, we report the synthesis of a series of new intercalation compounds, $MI_{2+x}Bi_2Sr_2CaCu_2O_{8+y}$ (x=0.6-0.9 ;

M=Mn, Fe, Co, Cu, Zn), propose their structure model, and discuss their electric properties in terms of their electronic structures.

EXPERIMENTAL

The Bi-2212 material (**1**) was prepared by the conventional solid state reaction of Bi_2O_3, $SrCO_3$, $CaCO_3$, and CuO (99.99% Rare Metallic). To a 1:1 mixed solid of Bi-2212 (0.35g) and powdered metal Mn, Fe, Co, Cu or Zn (0.76-0.90 g) loaded in a Pyrex tube, iodine (0.15g) was added at the Bi:M:I ratio of 2: 1 : 3. After being sealed in air, the mixture was heated at 170℃ for 3h prior to heating at 200, 250, 300, 350 or 400℃ for 10h. The solids were cooled to room temperature with a rate of about 5 ℃/min. The samples used for resistivity and/or XPS measurements were pressed into a plate of 10×5×1 mm^3.

Samples were characterized by powder X-ray diffraction (XRD) with CuK_α radiation, thermogravimetry (TG) with a heating rate 10℃ min^{-1} in air, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), atomic absorption analysis, XPS spectroscopy and resistivity measurement based on the standard two-probe dc method. The instruments used for these measurements were described in a previous report [8]. Ac susceptibility measurement was also conducted by the self inductance method in the temperature range of 12-293K.

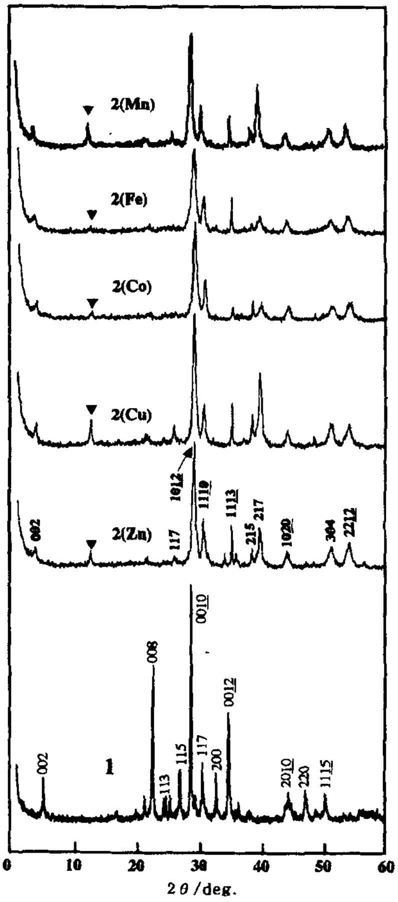

FIGURE 1 XRD patterns for **1** and **2**(M) along with indexes based on a tetragonal cell with the lattice parameters listed in TABLE I. Unindexed diffraction peaks are due to an unknown phase (▼).

RESULTS AND DISCUSSION

The reaction of Bi-2212 with iodine and the guest metals at temperatures below 200℃ for M=Mn, Fe, Cu and Zn and 250℃ for M=Co yielded the iodine-intercalated cuprate I-Bi2212 as a single or major phase. The reaction at higher temperatures led to one or more unidentified phases with or without CuI until at 400℃ the host phase in every system was totally converted into a well crystalline solid, **2(M)**, characterized by a relatively simple XRD pattern (Fig. 1). Almost all of the observed X-ray diffraction peaks in the 2θ range of 3-60° for **2(M)** could be indexed by the least square fitting of 2θ values on the basis of a tetragonal unit cell with the lattice parameters *a* and *c* summarized in TABLE I. Though the parameter *a* for all **2(M)** remained little changed in comparison with 5.40 Å for the host phase, the parameter *c* for the formers increased by 12.7 Å for M=Mn and 13.3 Å for the others, relative to 30.6 Å for the host phase, indicating the formation of a metal-iodine intercalated phase as a major phase in all of the systems.

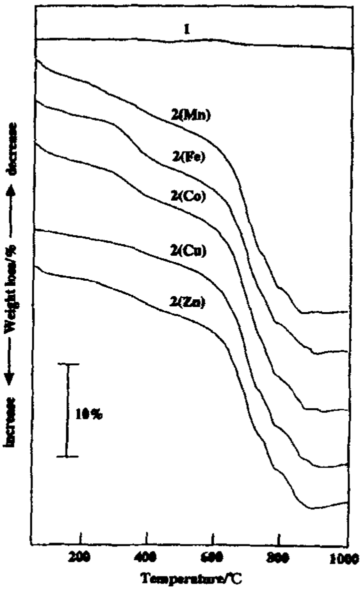

FIGURE 2 TG curves for 1 and 2(M).

The TG curves for **2(M)** showed three poorly resolved weight losses of 25.0-28.8% over a wide temperature range of 50-900 ℃ (Fig. 2 and TABLE I). The XRD patterns for **2(M)** were also observed to be little affected by heating the solids at any temperatures below 400℃. These facts indicate that the first weight loss at temperatures below 200℃ and the second one at

TABLE I Structural, compositional, thermogravimetric and physical properties of 2(M)

M	Lattice constant / Å		Composition / mole ratio[#]						Total wt loss /%		Resistivity / MΩ · cm
	a	c	Bi	Sr	Ca	Cu	M	I	Obs.	Calc[##]	
Mn	5.396(2)	43.32(2)	2.25	1.98	1.00	1.90	1.14	2.65	26.9	23.8	2.52
Fe	5.401(2)	43.94(3)	1.92	1.95	1.00	2.09	0.99	2.86	27.0	26.9	2.02
Co	5.393(3)	43.96(3)	1.97	1.97	1.00	2.01	1.16	2.84	28.8	26.2	1.52
Cu	5.402(2)	43.86(2)	2.15	2.18	1.00	2.13	1.07	2.62	25.0	25.7	0.74
Zn	5.390(3)	43.95(4)	2.20	2.17	1.00	2.00	1.17	2.91	25.3	25.1	0.87

[#] Determined by a combined use of EDX and atomic absorption analyses. [##] See text.

200-400 ℃ are due to desorption of two types of surface adsorbed iodine species with different thermal stabilities. The thermally more stable surface iodine species would be attributable to ones adsorbed directly on the surface of cuprate crystal, while the less stable ones may be additional iodine weakly held on the primary iodine layer at the surface. The succeeding large weight loss observed at higher temperatures for all of the samples would be assign-able to desorption of iodine species strongly held as an intercalant between the Bi_2O_2 layers.

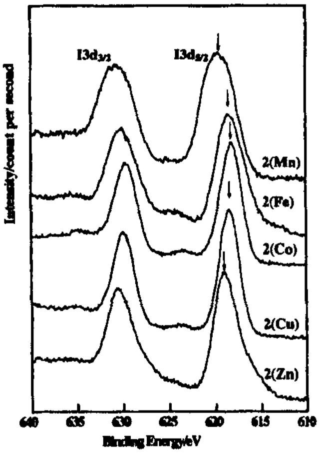

FIGURE 3 Iodine $3d_{3/2}$ and $3d_{5/2}$ XPS spectra for **1** and/or **2(M)** at room temperature.

The $I3d_{5/2}$ core level XPS spectra for **2(M)** with M=Mn, Fe, Co, Cu, and Zn showed a band centered at 619.5, 618.4, 618.1, 618.4 and 618.9 eV, respec-tively, as illustrated in Fig. 3. These binding energies are in close agreement with 618.6 eV for I^- in KI [8], indicating that the iodine species in these solids are intercalated essentially as the monoiodide ion I^-, but with a little perturbed electronic states.

EDX analysis, coupled with atomic absorption analysis for Ca, Mn, Fe, Co, Cu and Zn yielded the molar ratios of Bi, Sr, Ca, Cu, I, and M for **2(M)**, listed in TABLE I. If we represent the chemical composition of **2(M)** as $Bi_{2+a}Sr_{2+b}CaCu_{2+c}(MI_2)_d(I_2)_fO_{8+g}$ by assuming that the guest metal ions are incorporated as their divalent ion, the total weight loss could be calculated based on the following pyrolytic reaction:

$$Bi_{2+a}Sr_{2+b}CaCu_{2+c}(MI_2)_d(I_2)_fO_{8+g} + (d/2)O_2 \rightarrow Bi_{2+a}Sr_{2+b}CaCu_{2+c}M_dO_{8+g+d} + (d+f)I_2$$

The total weight losses thus calculated are in fairly good or essential agreement with their observed values (TABLE I). The chemical compositions of **2(M)** are thus given approximately by $MI_{2+x}Bi_2Sr_2CaCu_2O_{8+y}$ with x=0.6-0.9 corresponding to the amount of surface adsorbed iodine species.

SEM images showed that the major solid in **2(M)** is lamellar in shape as in the host cuprate. On the basis of the above X-ray, TG, XPS, SEM and chemical analysis data, a structure model could be proposed for the M-I intercalated phases, as illustrated in Fig. 4. The Bi^{3+} and O^{2-} ions in the Bi_2O_2 layer are located in a NaCl-like cell with the O-O distance of 5.4 Å along the -O-Bi-O- sequence and with the Bi-Bi distance of 3.8 Å along the

-Bi-Bi- sequence.The intercalated iodine species would be arranged as a bilayer of monoiodide anions in the Bi_2O_2 layer, along with the guest metal cations occupying half the four tetrahedral sites coordinated by every four mono-iodide ions in the upper and lower sheets. This model is consistent with the X-ray results that the observed increase of ca. 6.65 Å in $c/2$ value, relative to the host phase, for **2(M)** with M=Fe, Co, Cu and Zn is in good agreement with $(1+\sqrt{3}/2)$ times 3.6 Å for I-Bi2212 or 6.7 Å, obtained by assuming the closest packing of bilayered monoiodide anions. The smaller increase of 6.35 Å in $c/2$ value for **2(Mn)** might be attributed to a slight interlayer shrinkage due to a weak, covalent I-O interaction between any adjacent iodine and Bi-O layers, as suggested from the relatively higher binding energy of 619.5 eV observed for the $I3d_{5/2}$ band in the same sample.

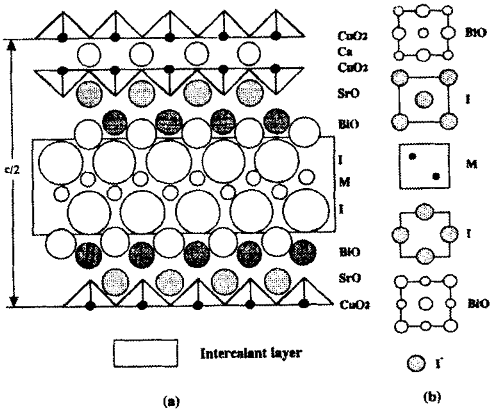

FIGURE 4 Schematic representation of the probable arrangement of 3d metal cations and iodide anions in the Bi_2O_2 double layer of Bi-2212 cuprate: (a) macro layer projected perpendicular to the c axis and (b) stacking sequence of atomic layers interleaved between the Bi_2O_2 double layer.

As a result of the intercalation reaction, the color of **1** (Bi-2212) changed from black to dark brown (M=Mn, Co), dark red (M=Fe) or pale green (M=Cu, Zn). In contrast to the superconducting host phase with Tc=78K, the ac susceptibility of **2(M)** for M=Mn, Fe, Co, Cu and Zn showed no Meissner effect at tempera-tures of 12-293 K (Fig. 5). This is also consistent with their resistivities of as high as 0.56-2.52 MΩ · cm at room temperature (TABLE I). The superconductiviy of the host cuprate Bi-2212 is related essentially to the excess oxygen incorporated in the Bi_2O_2 layer to supply hole carriers in the CuO_2 layers. In the present M-I intercalated phases, on the other hand, the excess oxygen in the Bi_2O_2 layer is likely excluded upon intercalation of MI_2 and the intercalated M-I species greatly ionized into M^{2+} and I^- ions to allow no significant electron transfer from the CuO_2 layers. This would result in a considerable increase of the electron count on copper, or decrease of the carrier in the CuO_2 layer, leading to a high resistivity. XPS data actually showed that the binding energy for the $Cu2p_{3/2}$ band is decreased from 933.9 eV for the host cuprate to 932.0-933.3 eV for **2(M)**, indicative of a little reduced state of copper for the intercalated cuprates. An essentially the same electronic scheme as above would apply to the high resistivity of $LiI_3Bi_2Sr_2CaCu_2O_8$ with I_3^- ions intercalated as a tilted monolayer accompanying Li^+ ions [8]. In contrast, the maintenance of superconductivity upon intercalation of metal iodides in Bi-2212 was observed for $AgIBi_2Sr_2CaCu_2O_8$ [4-6] and $(HgI_2)_{0.5}Bi_2Sr_2CaCu_2O_8$ [7]. One dimensional Fourier analysis demonstrated that the guest species in these two modified cuprates are intercalated as AgI or HgI_2 molecules to form a double layer of iodine [5,7], although their definite structures have not been yet established. The covalent / ionic mixed character of the intercalated Ag-I and Hg-I species might be available for permitting the charge transfer between the guest and host block [9], leading to superconductivity.

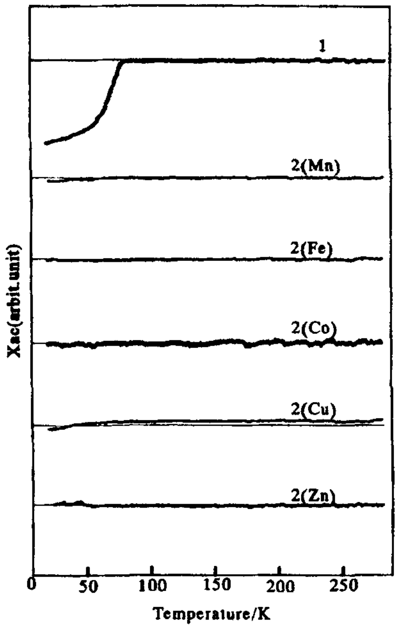

FIGURE 5 Ac susceptibility as a function of temperature for **1** and **2(M)**.

References

[1] X. D. Xiang, S. Mckernan, W. A. Vareka, A. Zettl, J. L Corkill, T. W. BarbeeIII, and M. L. Cohen, *Nature,* **348,** 145 (1990).

[2] X. D. Xiang, A. Zettl, W. A. Vareka, J. L Corkill, T. W. Barbee III, and M. L. Cohen, *Phys. Rev. B,* **43,** 1496 (1991).

[3] X. D. Xiang, W. A. Vareka, A. Zettl, J. L Corkill, and M. L. Cohen, *Phys. Rev. Lett.,* **68,** 530 (1992).

[4] H. Kumakura, J. Ye, J. Shimoyama, H. Kitaguchi, and K. Togano, *Jpn. J. Appl. Phys.,* **32,** L894 (1993).

[5] J. -H. Choy, N. Park, S.-J. Hwang, and Y.-L. Kim, *Synth. Metal.,* **71,** 1551 (1995).

[6] Y. Muraoka, M. Nagoshi, Y. Morioka, M. Kikuchi, K. Hiraga, N. Kobayashi, and Shono, *Physica C,* **263,** 193 (1996).

[7] J.-H. Choy, N.-G. Park, S.-J. Hwang, and D.-H. Kim, *J. Am. Chem. Soc.,* **116,** 11564 (1994).

[8] T. Kijima, H. Sushida, M. Yada, and M. Machida, *J. Solid State Chem.,* **141,** 452 (1998).

[9] J. -H. Choy, S.-J. Kwon, S.-J. Hwang, Y.-L. Kim, and W. Lee, *J. Mater. Chem.,* **9,** 129 (1999).