

**TEM STUDY OF THE IODINE INTERCALATED $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+x}$** **N.D. Drago¹, M. Déchamps^{2*}, L. Mazerolles³, P. Berthet² and A. Revcolevschi²**¹University of Bucharest, Faculty of Chemistry, Department of Physical Chemistry,
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(Refereed)

(Received July 25, 1996; Accepted August 8, 1996)

ABSTRACT

The partial substitution of Pb for Bi made it possible to prepare single phase 2223 and iodide intercalated I-2223 BiSrCaCuO compounds. Both compounds were studied by TEM, HRTEM, X-ray diffraction, and electrical resistivity. A change in symmetry occurs upon intercalation, likely a Bbmb to Pbm2 transition, and the change in the stacking sequence of the perovskite blocks was directly observed by HRTEM. Low temperature electrical resistivity measurements showed a metallic type conduction with critical temperatures of 105 K and 83 K, respectively. The resistivity at room temperature was $1.6 \times 10^{-3} \Omega\text{cm}$ for 2223 and $0.14 \Omega\text{cm}$ for I-2223.

KEYWORDS: A. layered compounds, A. superconductors, B. intercalation reactions, C. electron microscopy, D. crystal structure

INTRODUCTION

The high temperature superconductors of the $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_x$ type ($n = 1,2,3$) present strong anisotropic physical properties. In particular, electrical conductivity is metal-like in the (a,b) plane, whereas semi-conductivity is observed along the c axis. Their properties can be adjusted within some limits by modifying the crystallographic structure by intercalating

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various molecules. The purpose of this paper is to present a microstructure study of a $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+x}$ (2223) iodine intercalated compound.

These compounds have a layered structure formed by perovskite type blocks separated by Bi–O planes about 0.35 nm apart (1). There is no strong interaction between them, which explains the anisotropy of the physical properties. In this family three superconductor compounds are known, with critical temperatures (T_c) depending on the number of Cu–O planes in the perovskite block (e.g., for $n = 3$, $T_c = 110$ K). The exact nature of the interaction between the perovskite blocks is not well understood, but it is known that the properties of these compounds can be tuned by intercalating various molecules between the Bi–O planes (2). This intercalation increases the distance between the Bi–O planes up to 0.7 nm, which, as a result of a charge transfer process, leads to changes in the electrical properties and in anisotropy. The intercalation of iodine, bromine, benzene, IBr, AgI, HgI₂, Hg₂Cl₂, or even organo-metallic molecules has been already reported (3–11). Nevertheless, only the intercalation of iodine has been extensively studied.

RESULTS AND DISCUSSION

The Pb doped 2223 compound used in our measurements was synthesized according to a procedure described in the literature (12). Nominal cation stoichiometry was $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+x}$, the addition of Pb was used in order to stabilize the 2223 single phase structure. The stage-1 iodine-intercalated compound (I-2223) was prepared by sealing samples with iodine in evacuated Pyrex ampoules and annealing at 200°C for one day, according to the method of Xiang *et al.* (13). A stage- n compound includes one layer of intercalated molecules for each set of n pristine layers. The absence of any second phase in the 2223 and in the I-2223 materials was checked by X-ray diffraction.

Both the 2223 and I-2223 compounds are superconductors. Low temperature electrical resistivity measurements, carried out by a four point method, show a metallic-type conduction with critical temperatures of 105 K and 83 K, respectively. The resistivity at room temperature is $1.6 \times 10^{-3} \Omega\text{cm}$ for 2223 and 0.14 Ωcm for I-2223.

The unit cell parameters (determined by X-ray diffraction and electron diffraction) for pristine and I-2223 are $a = 0.543$, $b = 0.546$, $c = 3.691$ nm and $a = 0.54$, $b = 0.54$, $c = 2.207$ nm, respectively. The precision on a and b is lower for the I-2223 because of the specific broadening of the $hk\ell$ (h and $k \neq 0$) peaks. These values correspond to an expansion of the unit cell along the c axis of about 0.7 nm, in agreement with a stage-1 structure. Moreover, X-ray diffraction patterns of the two compounds present a systematic preponderance of the 00ℓ peaks, and the $hk\ell$ peaks (with h and/or $k \neq 0$) of the intercalated material are broader than those of the pristine material. The first observation results clearly from the two-dimensional character of their microstructure; the second can result either from an increased disorder in the (a,b) planes of I-2223 in relation to the well ordered 2223 (a,b) planes, or from an unusual Debye-Waller coefficient of the iodine in these planes. Low temperature X-ray diffraction experiments show that the broadening of the peaks does not depend upon temperature down to 140 K, and TEM observations, as shown hereafter, confirm that disorder and the small size of the crystallites are responsible for the peak broadening in the intercalated material.

Electron microscopy examination was carried out on crushed powders. TEM images clearly show the two-dimensional platelet-like microstructure of the 2223 (Fig. 1.a). They confirm that the platelets are parallel to the (a,b) plane, and consequently to the BiO planes.

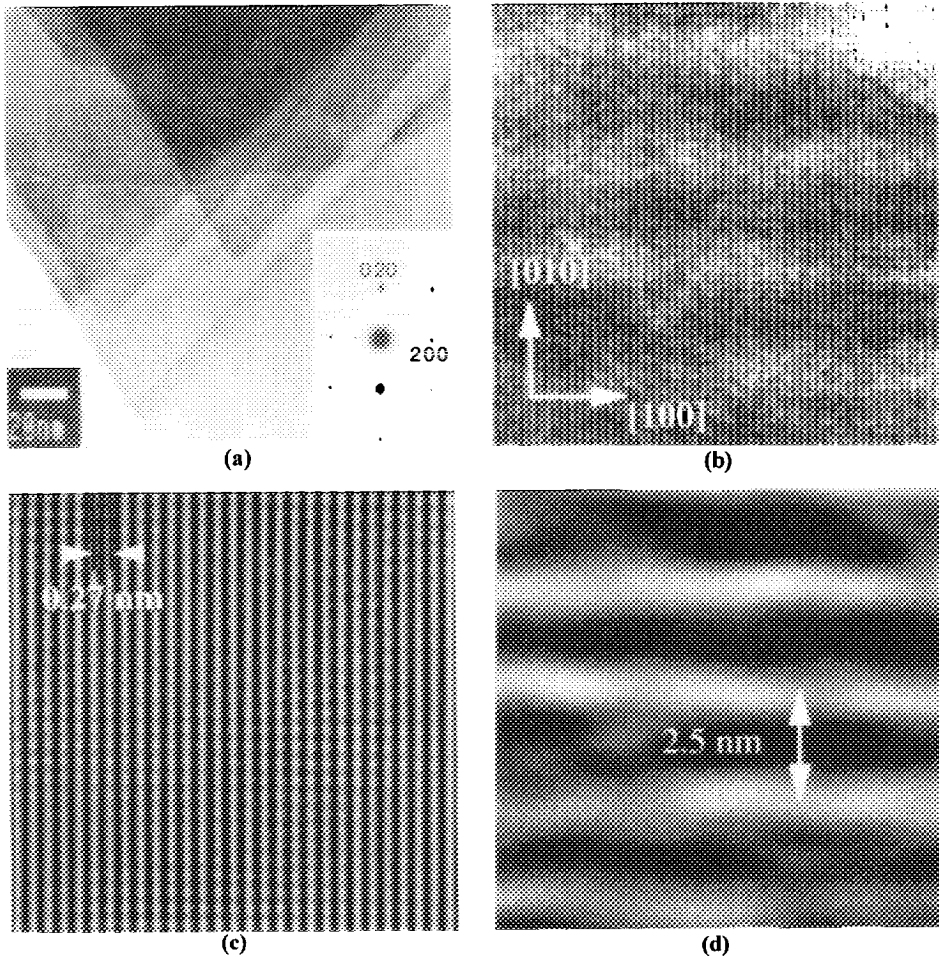


FIG. 1

(a) Bright field picture and electron diffraction pattern of the 2223 non intercalated compound. The platelet-like microstructure is evident as well as a periodic contrast. The platelets are parallel to the (a,b) plane and the modulation vector (period $\cong 3.5$ nm in this sample) is parallel to b (the satellite spots originated by the modulation are not perceptible in the inserted reproduction of the diffraction pattern). (b) HRTEM image taken along c. The main characteristics of the basic lattice and of the modulation are shown respectively in the reconstructed images of the lattice (c) and of the incommensurate structure (d).

A periodic contrast is observed perpendicular to the b direction. It is likely due to an incommensurate modulation along b (Fig. 1.d) which causes the satellites systematically observed around the $h00$, $0k0$ and $hk0$ ($h,k = 2n$) spots. Occasionally, other spots can be observed. The period of 0.27 nm ($\cong a/2 \cong b/2$) and the distribution of the contrast observed on the HRTEM pictures (edges of the square cell // $[100]$ and $[010]$, Fig. 1.b-c) are

consistent with a $1/2 a$ or $1/2 b$ translation of the perovskite blocks layers according to an A–B–A... stacking sequence along c .

While in the 2223 compound a well-ordered crystalline structure is preserved over large domains (>300 nm), the large number of misoriented microdomains revealed by moiré patterns (Fig. 2.a) shows that the I-2223 structure is strongly affected by intercalation. Moreover, although the iodine intercalated compound is not very stable under the electron

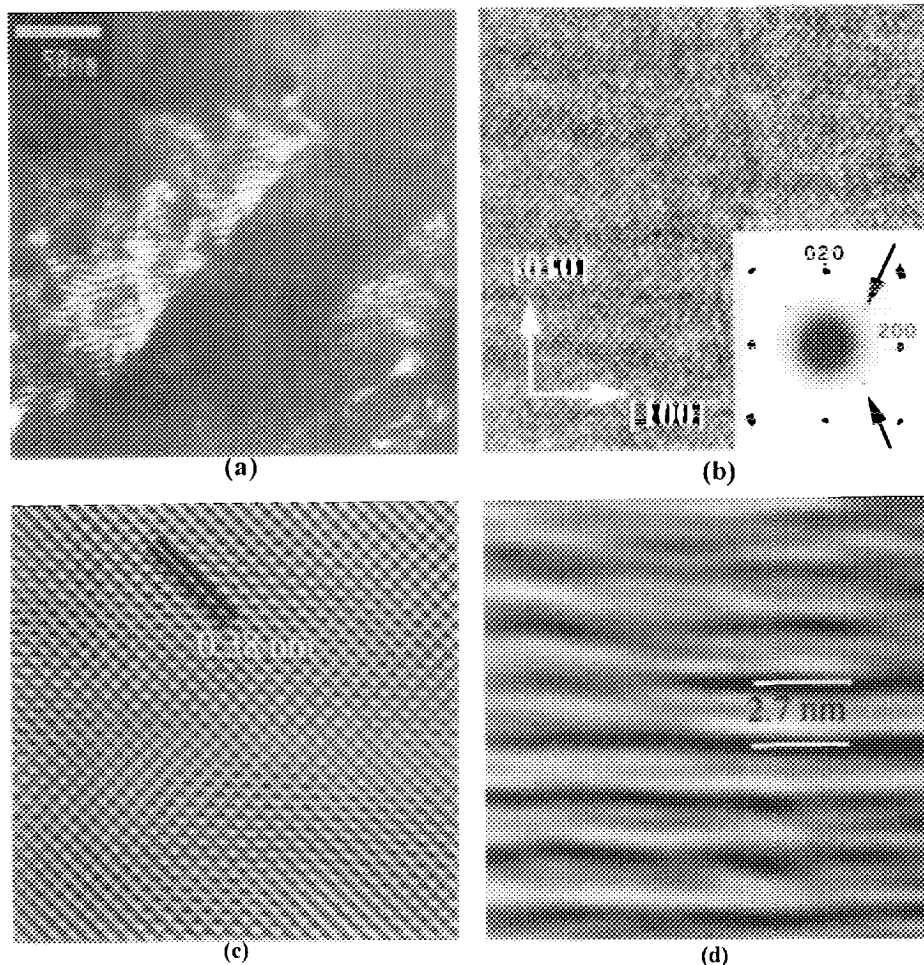


FIG. 2

(a) 020 dark field picture of the I-2223 intercalated compound. Rough periodic contrasts are moiré patterns. Their small extension and irregularity indicate that the platelets, and consequently the Bi–O planes, are not well ordered and are locally misoriented in relation to each other. (b) HRTEM picture and electron diffraction pattern. The 110 and $\bar{1}\bar{1}0$ diffraction spots (arrows), in particular, appear systematically, which is consistent with a change in symmetry in relation to the pristine material. The main characteristics of the basic lattice and of the modulation appear respectively in the reconstructed images of the lattice (c) and of the incommensurable structure (d).

beam, it was possible to obtain diffraction patterns which showed that a change in the space group occurs upon intercalation (Fig. 2.b). This change in symmetry is likely the same as that observed upon intercalation in the 2212 compound (14), i.e., a Bbmb to Pbm2 transition. Kijima et al. (14) have attributed the Pma2 space group to I-2212. This choice is the right one from a crystallographic point of view, but we have chosen the Pbm2 nonstandard setting in order to conserve the modulation direction parallel to the b axis cell in the two compounds. The period of 0.38 nm ($= a\sqrt{2}/2$) and the contrast distribution (edges of the square cell // $[110]$ and $[\bar{1}\bar{1}0]$, Fig. 2.c) are consistent with an alignment of the perovskite blocks along c according to an A-A-A... stacking in the intercalated compound. Satellite spots due to the modulation were also observed, but usually with a larger period than in the nonintercalated 2223 (Fig. 2.d). The change in magnitude of the modulation vector relative to the pristine could be provoked either by a reorganization of the B-O distances, or by a charge transfer in the Bi-O planes due to the intercalated iodine which might modify the oxidation state of Bi and, consequently, the Bi-O distances. Reports of modulation along the c axis as well as a model of the modulation vector amplitude and direction in superconductor oxides have been reported (15) but are not discussed here.

CONCLUSION

For such a complex system, important physical and structural changes occur upon intercalation: conductivity, crystallographic parameters, symmetry, stacking sequence of the perovskite blocks, inter and intra platelet (Bi-O planes) misorientation and, as the properties of the intercalated compound are affected by these defects, especially the usual and superconductive electrical properties, a correlation between the structure of the intercalation compounds and their properties must be regarded in connection with the whole set of structural changes and not just as a function of copper charge, as is often the case.

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