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Polytypoid structure of Pb-modified Bi-Ca-Sr-Cu-O superconductor

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Pb addition has been found to improve the superconducting properties of a Bi-Ca-Sr-Cu-O superconductor. We report zero resistance at 104 K in a $Bi_{1.4}Pb_{0.6}Ca_2Sr_2Cu_3O_y$ alloy with no steps in the resistivity. Pb replaces Bi in the unit cell, as determined by x-ray microanalysis. The superconducting phase has the same structure as the alloy without lead, with the c parameter uniformly 38.2 Å. The Cu+Ca content of these regions has also been found to be higher than in the undoped sample, indicating that the periodicity is determined by the composition leading to polytypoids. Such polytypoid structures appear to correlate well with the critical temperatures.

INTRODUCTION

The discovery of a new family of superconducting oxides, Bi-Sr-Cu-O by Michel *et al.*[1] has further fueled the excitement in this area of research since the initial discovery of the Y-Ba-Cu-O compounds. Further improvements by Maeda, Tanaka, Fukutomi, and Asano[2] and Chu *et al.*[3] resulted in resistive and diamagnetic anomalies in the Bi-Ca-Sr-Cu-O system near 110 K, although zero resistance was obtained only around 75-80 K. Subsequently other groups have reported similar results, with zero resistance primarily occurring around 75-80 K.[4-8] Previously we reported transmission-electron-microscopy (TEM) results[9,10] suggesting that the steps in the susceptibility and resistivity may be due to the presence of a compound with $c = 38.2$ Å ($T_c \sim 110$ K) along with the $c = 30.5$ Å ($T_c \sim 80$ K) compound. High-resolution TEM showed that the regions with $c = 38.2$ Å exist as "slabs" inside the $c = 30.5$ Å regions. The $c = 38.2$ Å regions were richer in Cu+Ca than the $c = 30.5$ Å regions. Subsequently it has been found that the controlled addition of Pb to the alloy leads to the elimination of the resistive step, although the step in the diamagnetic susceptibility still remains.[11] In this Brief Report, we report preliminary results of TEM experiments on the lead-substituted samples.

Samples of nominal composition $Bi_2Sr_2Ca_2Cu_4O_y$ and $Bi_{1.4}Pb_{0.6}Sr_2Ca_2Cu_3O_y$ were prepared by solid-state reaction. Appropriate amounts of Bi_2O_3 (purity of 99.9%), PbO (99.999%), $CaCO_3$ (99.9%), $SrCO_3$ (99.999%), and CuO (99.9%) were well mixed and ground in an agate mortar. The powders were prefired in air at 800 °C for 16 h, reground, and pressed into pellets. The pellets were sintered at the temperatures and for the time period given in Fig. 1, followed by furnace cooling to 350 °C and subsequently removed to the laboratory bench. Bars approximately $2 \times 1 \times 10$ mm^3 were cut from the center of the pellets for the resistivity measurements. Stainless-steel springs, arranged in a four-point configuration, were glued with silver paint. A 0.5-1.0-mA rms current was supplied at 40 Hz and the sample's voltage drop was detected by a lock-in amplifier. The minimum detectable resistively was 0.5 $\mu\Omega$ cm. dc susceptibility measurements were performed using a SQUID magnetometer at a field of 20 Oe. Samples for TEM were prepared by the argon ion milling technique under conditions described earlier,[10] in order to obtain foils with the c axis in plane. High-resolution TEM (HRTEM) was carried out in a JEOL 200CX at 200 kV and analytical TEM (ATEM) was carried out in a Philips 400TEM at 100 kV.

Figure 1 shows the resistivity and susceptibility (shielding experiment) versus temperature plots for the two alloys. Note that the Pb-doped sample does not show a step in the resistivity while the undoped sample does. Both the samples are comprised of almost similar fractions of the 110- and 75-K polytypoids, as evidenced from the susceptibility plots. Figures 2(a) and 2(b) show HRTEM images of the superconducting phase in the undoped and doped samples, respectively, in the [310] zone axis. Since the sample tilt was limited to ± 10°, lower-index zone axes were not accessible in this microscope. In Fig. 2(a), the regions with $c = 38.2$ Å and $c = 30.5$ Å are indicated. In an earlier paper also it was shown that such regions of $c = 38.2$ Å exist over several tens of unit cells. Figure 2(b) shows a HRTEM image in the case of the Pb-doped sample, in the [310] zone axis. The c parameter was measured to be 38.2 Å. This periodicity is very uniform unlike that in the undoped sample which showed frequent variations in the c parameter inside each grain. Figure 3(a) shows a lattice fringe image close to a grain boundary of the undoped sample. It is seen that adjacent to the grain boundary the c parameter is lower than that inside the grains. In the case of the Pb-doped sample, the c parameter is uniformly 38.2 Å up to the grain boundary, as evidence from the lattice fringe in Fig. 3(b).

The existence of regions of different c parameter periodicities can also be derived by convergent-beam electron diffraction (CBED), as described previously.[9,10]

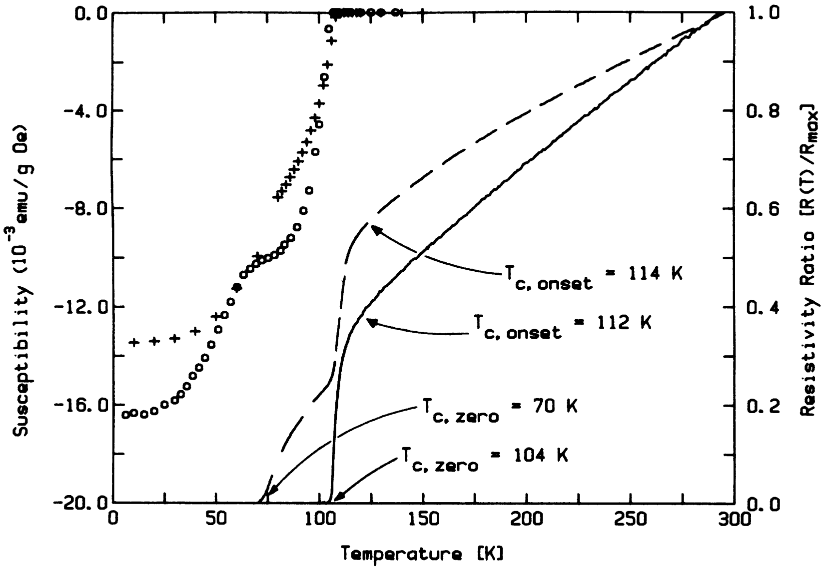

FIG. 1. A plot of resistivity and susceptibility vs temperature for the two sample used in this study. +, ——: $Bi_2Sr_2Ca_2Cu_4O_y$, 870–875 °C, 72 h; ○, ---: $Bi_{1.4}Pb_{0.6}Sr_2Ca_2Cu_3O_y$, 860–865 °C, 60 h.

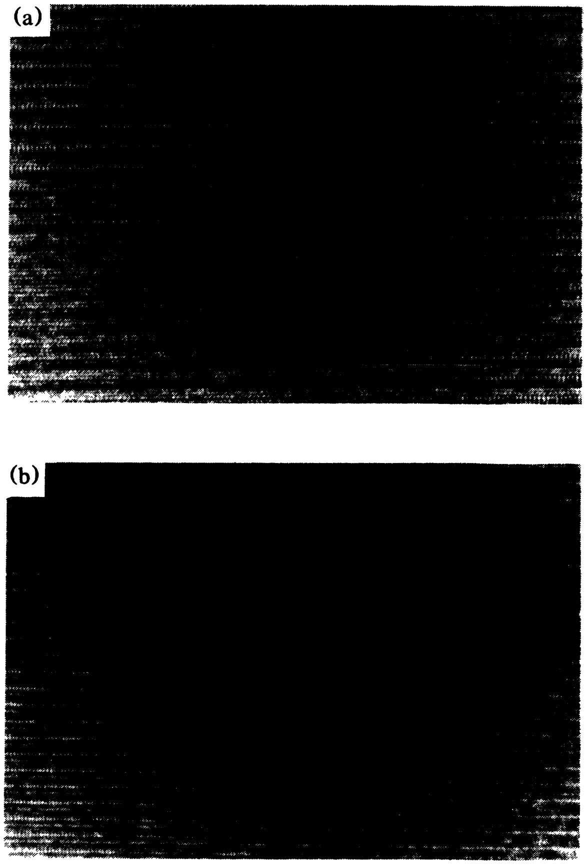

FIG. 2. (a) [310] zone axis high-resolution image of the undoped sample showing the presence of interpenetrating regions of $c = 30.5$ Å and $c = 38.2$ Å. (b) [310] zone axis high-resolution image of the Pb-doped sample showing a uniform c parameter of 38.2 Å.

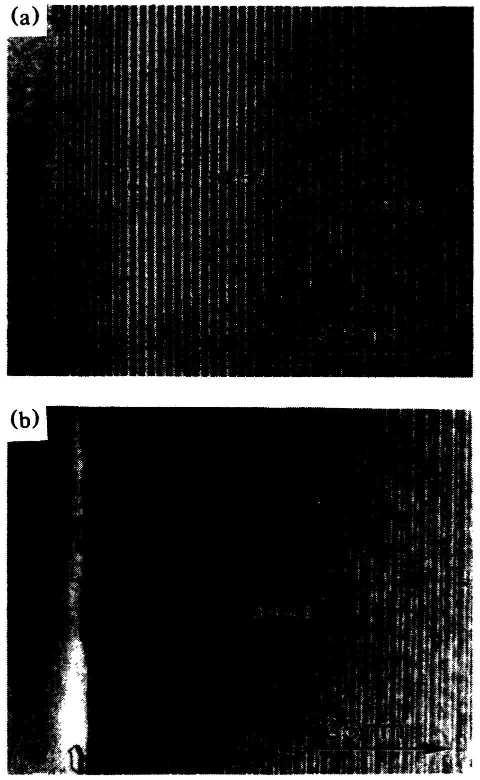

FIG. 3. (a) High-resolution lattice fringe image of the undoped sample showing the decrease in the c parameter close to the grain boundary; the 24-Å spacing corresponds to the polytypoid with no Ca while the 30.5 and 38.2 Å correspond to the cation sequences shown in Fig. 5. (b) High-resolution lattice fringe image of the Pb-doped sample showing the uniform c parameter up to the grain boundary.

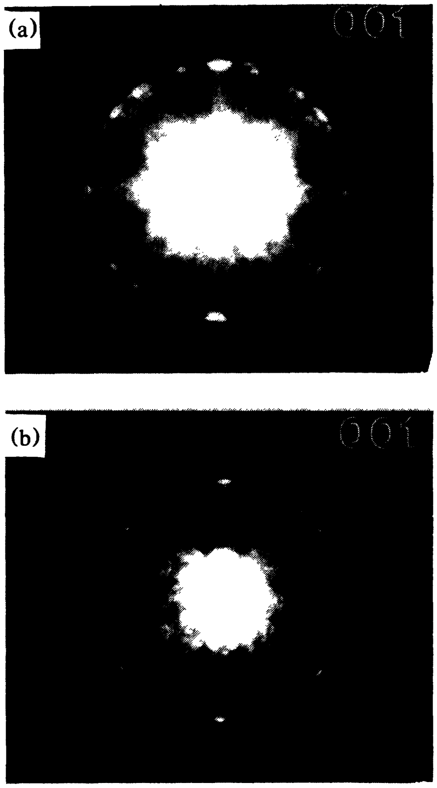

FIG. 4. (a) [001] zone axis convergent beam electron diffraction (CBED) pattern from the undoped sample showing the higher-order Laue zones (HOLZ) from the diameter of which the c parameter was calculated to be 30.5 Å; (b) [001] zone axis CBED pattern from the Pb-doped sample from which the c parameter was calculated to be 38.2 Å. Note the width in the diameter of the first order ring in (a) suggesting a range of c parameters selected by the probe of nominal size of 500 Å.

CBED patterns were acquired under the same lens setting from both doped and undoped samples. Figure 4(a) shows a [001] CBED pattern from the undoped sample while Fig. 4(b) is a [001] pattern from the Pb-doped sample. The c parameter determined from the higher-order Laue zone (HOLZ) rings was 30.5 Å for (a) and 38.2 Å for (b), thus corroborating the HRTEM results. Another interesting feature in the pattern in Fig. 4(a) is that the first-order ring is broadened, suggesting that there is a distribution of c parameters within the probe size of about 500 Å. However, in the case of the Pb-doped sample, this is not observed, consistent with the observation of constant 38.2 Å periodicity.

Energy dispersive x-ray (EDX) microanalysis of the two samples showed that the Cu+Ca content of the Pb-doped sample is higher in the $c = 38.2$ Å region than that of the $c = 30.5$ Å regions in the undoped sample. The quantitative data are given in Table I. The Cu+Ca content of this region agrees well with the composition reported for the 38.2 Å region in the earlier paper.[10] By comparing the composition of the $c = 38.2$ Å polytypoid in the unleaded and in the leaded samples (as determined by EDX microanalysis), it was found that Pb replaces Bi in the unit cell. In this case, the Cu, Ca, and Sr contents were the same, while the Pb content made up for the decrease in the Bi content.

TABLE I. Microanalysis data for the undoped and Pb-doped samples.

Element	Undoped sample	Pb-doped sample
Cu	35.66	40.55
Ca	15.36	18.16
Sr	22.32	22.09
Bi	26.65	15.58
Pb	· · ·	3.62

It may be pointed out that this phenomenon of adjustment of structural periodicity without change in crystal structure to accommodate compositional changes is not unusual in ceramic alloys and results in structures referred to as polytypoids.[12]

DISCUSSION

In this paper it has been shown that the steps in the susceptibility remain while the steps in the resistivity disappear when Pb is added to the alloy. Inside each grain the composition and hence the c parameter is uniform unlike the undoped sample, which shows frequent fluctuations in the Cu+Ca content and the c parameter.[10] In subsequent experiments, it has been found, by direct atomic imaging, that the increase in the c parameter from 30.5–38.2 Å is due to the insertion of two Cu-O and two Ca layers inside the intergrowth structure, as speculated earlier by us and by several others.[7,10,13-15] Figure 5 shows a model of the structure consistent with the observed data. The 30.5 Å and the 38.2 Å periodicities differ only in the number of intercalated Cu+Ca layers in the structure. This is also consistent with the x-ray microanalysis results in Table I. It is important to note that it is possible, by suitable modification of the alloy composition (and heat treatment), to obtain a superconducting compound with a uniform composition comprising three Cu-O units between the Bi bilayers. The observation of a step in the susceptibility plot can be rationalized in terms of the presence of the two polytypoids with $c = 30.5$ Å ($T_c \sim 65$–75 K) and $c = 38.2$ Å ($T_c \sim 110$ K), either inside the same grain or as discrete grains of uniform c parameters. The HRTEM re-

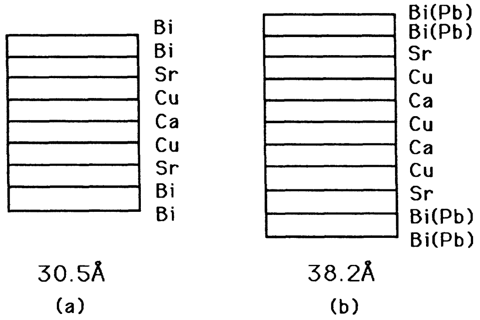

FIG. 5. Schematic model showing the [001] cation stacking sequence in the Bi(Pb)-Ca-Sr-Cu-O alloy for (a) $c = 30.5$ Å and (b) $c = 38.2$ Å.

sults suggest that the latter is more likely in the case of the Pb-doped sample while both occur in the undoped sample. The presence of the step in the resistivity plot in the case of the undoped sample suggests that the presence of regions of reduced c parameter near the grain boundaries [Fig. 3(a)] leads to a loss of connectivity. This is due to the change in T_c from 20 K ($c = 24.6$ Å) to 110 K ($c = 38.2$ Å) with distance from the boundary corresponding to each polytypoid. Due to the homogeneous composition (and hence c parameter) in the Pb-doped sample [Fig. 3(b)] connectivity between the grains is attained and the step in the resistivity plot vanishes.

ACKNOWLEDGMENTS

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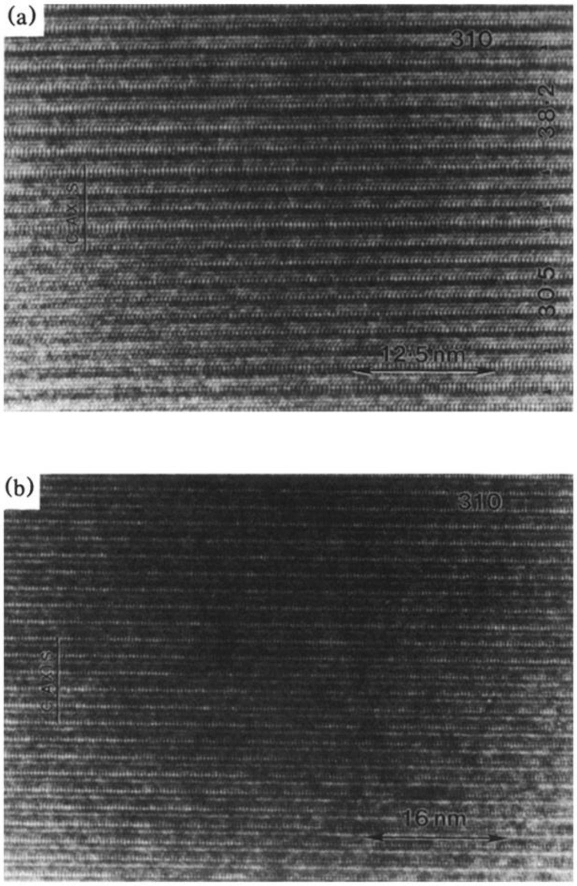

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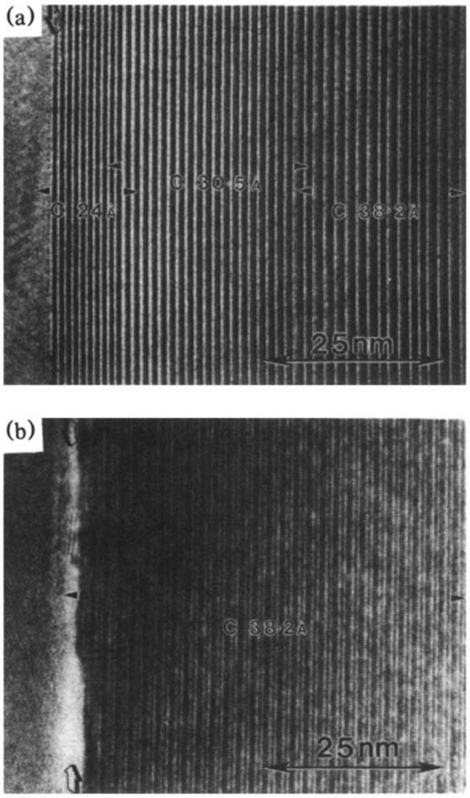

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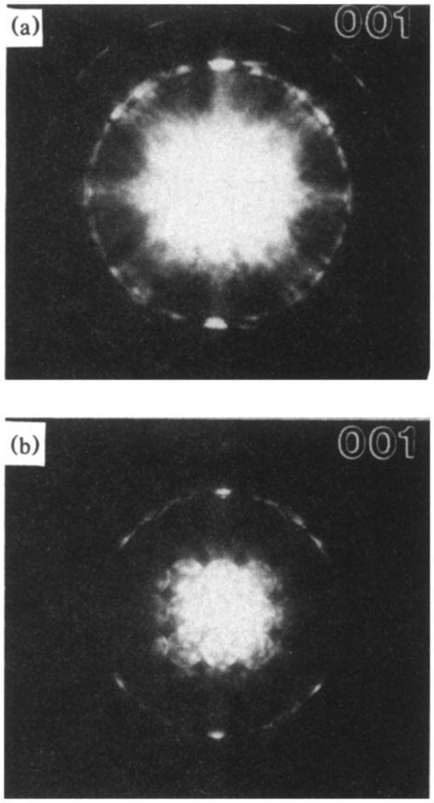

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