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117 K superconductivity in the Ba–Ca–Cu–O system

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Abstract

Superconductivity was observed at 117 K in the Ba–Ca–Cu–O samples synthesized at 950°C under 5.0 GPa for 1 h. The samples were multiphase. Electrical resistivity and DC magnetic susceptibility measurements revealed bulk superconductivity at $T_{conset}=117$ K, $T_{czero}=107.6$ K and $T_{cmag}=116.0$ K. Crystals having primitive tetragonal unit cells with the lattice parameters of $a=3.88$ Å, and $c=15.0$ Å, 18.3 Å and 21.6 Å were found by electron diffraction. The dominant peaks of the X-ray powder diffraction pattern were tentatively assigned to the hypothetical Cu-1234 ($a=3.85$ Å and $c=18.30$ Å) and Cu-1223 ($a=3.88$ Å and $c=14.94$ Å) structures. It is likely that these are new high-T_c superconducting phases.

1. Introduction

Intensive efforts have been made in the search for high-T_c superconductors among the A–Cu–O (A=Ca, Sr and/or Ba) compounds [1–5]. Previously, superconductivity at $T_{conset}=60$–90 K was reported in the Ba–Sr–Cu–O system [1]. Then, $(Sr_{0.7}Ca_{0.3})_{0.9}CuO_2$ samples of an "infinite layer" structure were reported to exhibit superconductivity at $T_{conset}=110$ K [2]. Adachi et al. [3,4] were successful in synthesizing superconducting Sr–Ca–Cu–O samples with T_c's in the range of 70 to 105 K. The Sr–Ca–Cu–O superconductors were found to have crystal structures other than the "infinite layer". It was found that they contained phases which were members of a new homologous series, "$02(n-1)n$", consisting of alternate stacking of rock-salt and "infinite layer" blocks. In the Sr–Ca–Cu–O samples, members with $n=2$, 3 and 4 were observed. Later, Hiroi et al. [5] and Laffez et al. [6] independently found an $n=1$ member of this homologous series in the Sr–Cu–O system having $T_{conset}=70\sim80$ K. It should be noted that all the superconducting A–Cu–O samples were synthesized at high temperatures under high pressures.

Here, we report superconductivity observed in samples of the Ba–Ca–Cu–O system which were prepared under conditions of a high temperature and a high pressure. The samples were multiphase, but strong diamagnetic signals which indicated superconductivity at $T_c=117$ K were observed. This value of T_c is the highest ever reported for A–Cu–O superconductors.

2. Experimental

The starting materials, i.e. BaO_2, CaO and CuO powders, were completely dehydrated. These powders were mixed to the nominal composition of Ba:Ca:Cu=2:3:4 and subsequently calcined at 920°C in flowing oxygen gas for a total heart-treatment time of 50 h. During calcination, intermediate

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grindings were carried out several times, and the sintered materials were slowly cooled to room temperature over a period of 6 h. The fresh calcined powder was pressed into a pellet of 2.7 mm diameter and 3 mm thickness, and then immediately put into a gold container. A graphite sleeve was placed outside of the container as a heater, and a pyrophyllite as the pressure-transmitting medium. High pressure was applied to the sample using a 700-ton cubic anvil press. The pressure scale was calibrated employing the phase transition points at room temperature of Bi(II–III) at 2.7 GPa and Tl(II–III) at 3.7 GPa. Temperature was controlled by changing the electrical power exerted on the graphite sleeve, and its value was read from a calibration curve on electrical power versus temperature which had been previously measured using a Pt–Pt13%Rh thermocouple. First, pressure was gradually increased to 5.0 GPa over a time span of 2 h, and then temperature was raised to 950°C. This condition was maintained for 1 h and the sample was cooled by reducing the electrical power to zero in 10 min, and finally pressure was released in 2 h. The structure of the samples was characterized by X-ray powder diffraction and electron diffraction. DC electrical resistivity was measured using a conventional four-probe method with a current of 1 mA. The DC magnetic susceptibility was determined using a SQUID magnetometer in an applied field of 10 Oe.

3. Results and discussion

Fig. 1 shows the temperature dependence of electrical resistivity. A superconducting transition was clearly observed at $T_{\text{conset}}=117$ K and $T_{\text{czero}}=107.6$ K. The normal-state resistivity of the sample was metallic, being of the order of several mΩ cm, as reported for typical p-type high-T_c cuprate superconductors. Bulk superconductivity was confirmed from the DC magnetic susceptibility measurements as shown in Fig. 2. The susceptibility measurements were carried out in both modes of zero-field cooling (ZFC: shielding signal) and field cooling (FC: Meissner signal). The shielding signals became much stronger at lower temperatures. Assuming an average density of 6 g/cm^3 for the sample, and taking into account the demagnetizing field, the ZFC susceptibility was close to the value of full magnetic screening, i.e. $1/4\pi$, below 20 K. Also, the FC data revealed a large Meissner fraction. We prepared several samples and confirmed reproducibility of these results. Therefore, the existence of superconducting phases is solid. Moreover, the ZFC data shows two steps: one at 116 K corresponds to the superconducting transition determined from resistivity measurements as shown in Fig. 1 and the other takes place around 83 K. The temperature dependence of susceptibility changed drastically near 83 K, suggesting the possibility that at least two superconducting phases coexisted in the sample.

The X-ray powder diffraction pattern (Fig. 3) shows that the sample was multiphase. It is natural to expect that the superconductivity was due to the phases containing $Cu–O_2$ sheets in their crystal structures. Therefore the peak observed at $2\theta=47.14°$ ($d=1.926$ Å) could correspond to half of the Cu–Cu distance in the $Cu–O_2$ sheets. The indices are tentatively given for the Cu-1234 and Cu-1223 structures based on the discussion given in the following. Fig. 4(a) shows the electron diffraction pattern taken along the [001] direction for a certain grain in the sample. This pattern indicates that the observed crystal had a tetragonal symmetry with $a=3.88$ Å, being nearly equal to (1.926×2) Å. Fig. 4(b) is the diffraction pattern taken along the [110] direction, showing a period of 18.3 Å. From other diffraction patterns, we also observed the periodic structures of 15.0 and 21.6 Å. When the crystal was tilted around the c-axis, the 210 spot clearly appeared in the pattern taken along the [120] direction. Accordingly, a primitive lattice may be chosen for the structure of the analyzed crystal grain. Several tens of crystal grains in the sample were examined by electron diffraction. All the diffraction patterns taken along the [001] direction were similar to that shown in Fig. 4(a). No crystal grains containing body-centered lattices were observed. The observed crystal structures remind us the case of Hg(or Tl)-12$(n-1)n$ phases ($n=3$, 4 and 5) [7,8] whose c-axis parameters are approximately given by the formula: $c=9.5+3.2(n-1)$ Å. Using an analogy to these homologous series, the c-axis stacking periodicities for the present observation may be written as $c=8.4+3.3(n-1)$ Å with $n=3$, 4 and 5. Presently, we have no solid evidence that the analyzed crystal grains were all superconducting. However, we be-

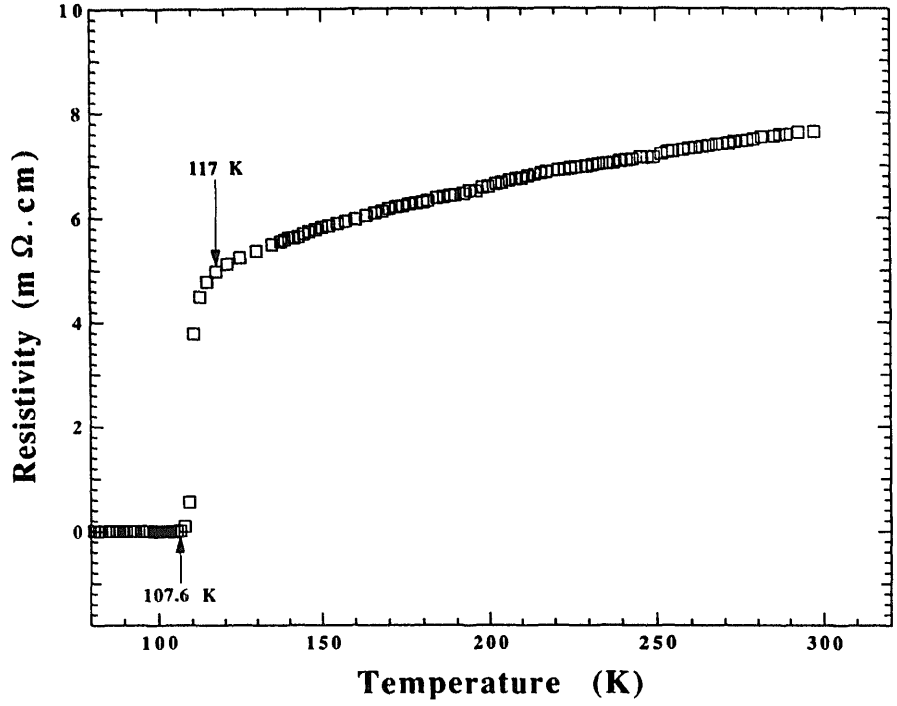

Fig. 1. Temperature dependence of electrical resistivity of the sample.

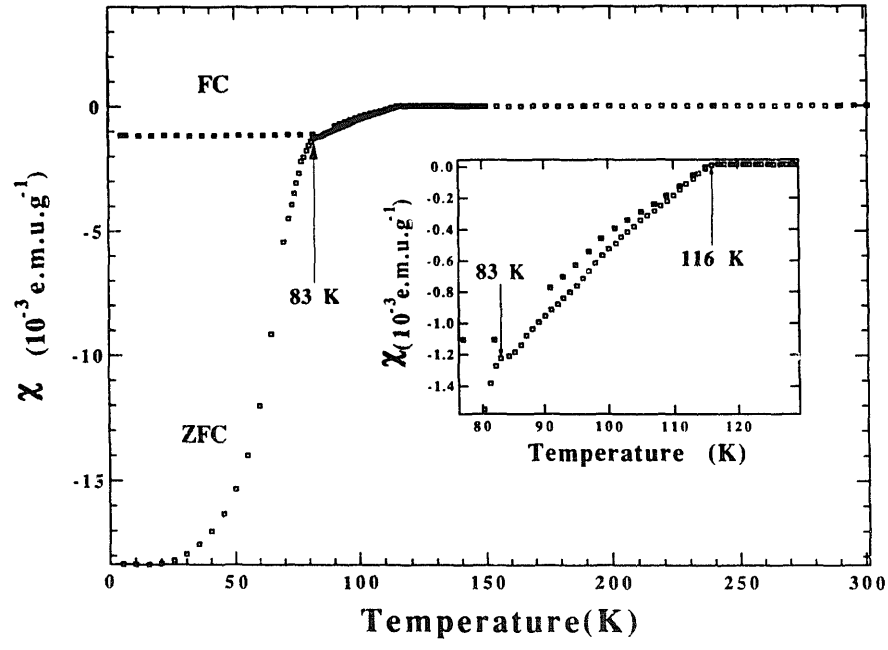

Fig. 2. Temperature dependence of the DC magnetic susceptibility of the sample in an external field of 10 Oe. The inset shows an enlarged portion in the temperature range of 75–130 K.

lieve that one of the phases which has a similar structure to the Hg(or Tl)-12($n-1$)n (n=3, 4 and 5) phases may be responsible for the observed 117 K superconductivity. Upon this analogy, indices for both the Cu-1234 structure with a=3.85 Å and c=18.30 Å, and the Cu-1223 structure with a=3.88 Å and

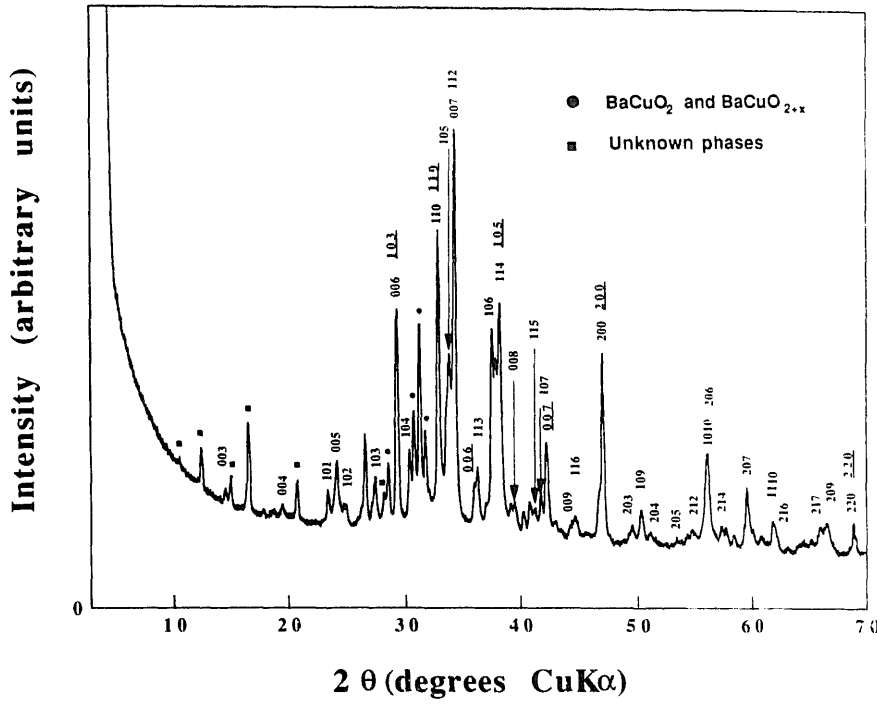

Fig. 3. X-ray powder diffraction pattern for the sample. The dominant peaks are tentatively indexed for the hypothetical Cu-1234 (a=3.85 Å and c=18.30 Å) and Cu-1223 (underlined) (a=3.88 Å and c=14.94 Å) structures. Solid circles are for $BaCuO_2$ and $BaCuO_{2+x}$. Solid squares indicate unknown phases.

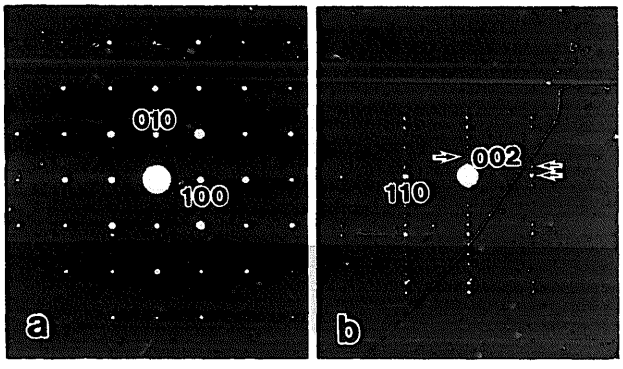

Fig. 4. Electron diffraction patterns for a certain grain in the sample: (a) taken along the [001] direction and (b) taken along the [110] direction. Double arrows indicate a distance of 18.3 Å in real space.

c=14.94 Å were tentatively ascribed to the dominant peaks in the X-ray diffraction pattern shown in Fig. 3. The peaks denoted by solid circles are from $BaCuO_2$ [9] and $BaCuO_{2+x}$ [10]. The remnants marked with solid squares were attributed to unknown phases. Of course, there still exist other possibilities: the nature of multiphase samples makes it difficult to identify the superconducting phase. Finally, it should be noted that Ihara et al. [#1] recently reported 117 K superconductivity for a sample with the nominal composition of $AgBa_2Ca_3Cu_4O_y$ which was synthesized at a high temperature and a high pressure. However, it is not known at this moment whether there are any common features between the present superconducting phase(s) and that in $AgBa_2Ca_3Cu_4O_y$. More efforts should be made for the identification of the superconducting phase(s).

4. Summary

By using a high-pressure technique, Ba–Ca–Cu–O polycrystalline samples were synthesized at 950°C under 5.0 GPa for 1 h. Superconductivity of T_{conset}=117 K and T_{czero}=107.6 K was observed by electrical resistivity measurements. The DC magnetic susceptibility data confirmed that the samples exhibited bulk superconductivity below T_{cmag}=116 K. An electron diffraction study showed that the ob-

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served crystals had primitive tetragonal unit cells with lattice parameters of $a=3.88$ Å and $c=8.4+3.3(n-1)$ Å with $n=3$, 4 and 5. The X-ray diffraction pattern was likely to contain peaks from the Cu-1234 structure with $a=3.85$ Å and $c=18.30$ Å, and also from the Cu-1223 structure with $a=3.88$ Å and $c=14.94$ Å. These are considered to be new superconducting phases.

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