Superconductivity and crystal structure in the La-Ba-Cu-O system

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A series of samples with nominal compositions $La_{1-x}Ba_xCu_1O_{3-y}$ was prepared by solid-state reaction. The subsolidus phase relation in the CuO-rich region of the La-Ba-Cu-O system has been determined by an x-ray diffraction method. Two ternary compounds were confirmed to exist in the system. The tetragonal or pseudotetragonal phase $(Ba_{2-z}La_z)La_1Cu_3O_{7+\delta}$ has a wide homogeneous phase range from $z = 0.095$ to $z = 0.578$, and a crystal structure closely related to the structure of $Ba_2YCu_3O_{7-\delta}$. Superconductivity of compounds in this system was studied by resistivity and ac susceptibility measurements. The relation between crystal structure and the superconductivity is discussed.

I. INTRODUCTION

Extensive efforts have been made to study the copper-containing oxides with perovskite-related structures since high-T_c superconductivity in the La-Ba-Cu-O system was initially discovered by Bednorz and Müller.[1] Superconductivity with T_c at about 90 K was soon realized in the Y-Ba-Cu-O system and related systems.[2,3] In order to identify the reasons for superconductivity and explore new high-T_c superconducting materials, it is crucial to determine the phase relation and crystal structures of the superconducting compounds. The compounds with T_c about 40 K in the Ba(Sr)-La-Cu-O system have been revealed to have the K_2NiF_4-type structure, and the 90 K superconducting phase in the Y-Ba-Cu-O system was identified as the orthorhombic distorted perovskite $YBa_2Cu_3O_{7-\delta}$. An indication of higher T_c at about 70 K superconductivity in the La-Ba-Cu-O system was noticed in a previous study.[4] From the point of view of both theory and application, it is of great significance to study the crystal structure and the superconductivity of the La-Ba-Cu-O system.

Soon after superconductivity in the Y-Ba-Cu-O system was reported, we synthesized two samples with the nominal compositions $Y_2Ba_3Cu_5O_{15-y}$ and $La_2Ba_3Cu_5O_{15-y}$, respectively. While the Y-containing sample showed superconductivity with zero resistance and a substantial diamagnetic effect at 89 K, the La-containing sample had a resistivity-versus-temperature curve like that of a semiconductor and no superconducting transition was observed above 4.2 K. X-ray diffraction analysis revealed that the Y-containing sample had three phases, $Ba_2YCu_3O_{7-\delta}$, Y_2BaCuO_5, and CuO. The La-containing sample had a single phase, and its diffraction pattern could be indexed with a tetragonal cell ($a = 0.3922$ nm, $c = 3a$).

From the above experimental results, we inferred that $LaBa_2Cu_3O_{7+\delta}$ might be a high-T_c superconductor and that this compound could exist in a wide composition range due to the similar ionic radii of La and Ba. A possible explanation of the poor reproducibility of the high-T_c (70–90 K) La-Ba-Cu-O compound is the existence of a wide solid solution range and the strong composition dependence of the superconductivity of the compound. The present study is aimed at the confirmation of the above conjectures.

II. EXPERIMENT

High-purity La_2O_3 (99.95%), $BaCO_3$ (analytical reagent), and CuO (analytical reagent) were used as starting materials. Appropriate quantities of the starting materials were mixed, ground, and sintered in air at 960 °C in alumina crucibles for 12 h, reground, pressed into 10-mm-diam pellets and sintered a second time under similar conditions, then slowly furnace cooled to room temperature in about 10 h. Twenty samples were prepared with the compositions $La_{1-x}Ba_xCuO_{3-y}$ ($0 \leq x \leq 1$). $BaCuO_2$ was synthesized at a lower temperature (830 °C).

Powder x-ray diffraction patterns were obtained using a quadruple monochromatic Guinier–de Wolff camera. Cu $K\alpha$ radiation was used. Pure Si was added to the samples as interior standard for the measurements of the lattice constants. Intensity data were collected using a STADI-2-type diffractometer.

The resistivity and the ac susceptibility measurements were performed as described previously elsewhere.[2]

III. RESULTS AND DISCUSSIONS

A. The subsolidus phase relation of La-Ba-Cu-O system

The results of the x-ray diffraction phase analysis of $La_{1-x}Ba_xCuO_{3-y}$ are shown in Table I. In Table I and following discussions, 1:4:5 represents the compound with

TABLE I. Phase analysis results of the $La_{1-x}Ba_xCuO_{3-y}$.

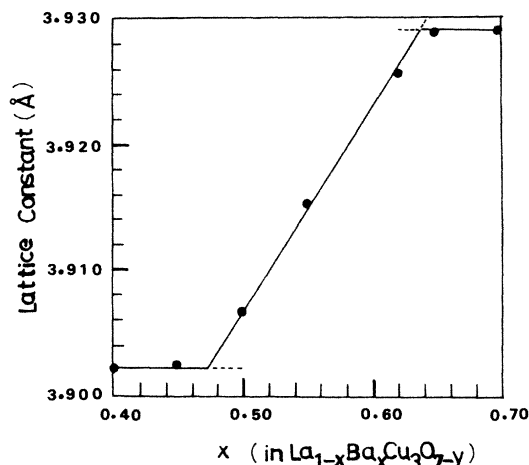| x range	Existing phase
$x = 0$	La_2CuO_4, CuO
$0 \leq x < 0.20$	La_2CuO_4, CuO, 1:4:5
$x = 0.20$	1:4:5
$0.20 < x < 0.474$	1:4:5, 2:1:3
$0.474 \leq x \leq 0.635$	2:1:3
$0.635 < x < 1$	2:1:3 + $BaCuO_2$
$x = 1$	$BaCuO_2$

FIG. 1. Lattice constant a vs x for $La_{1-x}Ba_xCuO_{3-y}$ (lattice constant $b=a,c=3a$).

a Ba:La:Cu ratio of 1:4:5 and 2:1:3 represents the solid solution which has an ideal composition with the Ba:La:Cu ratio 2:1:3.

The 2:1:3 phase has a tetragonal or pseudo-tetragonal symmetry with lattice constants given approximately by $a=b=c/3$. The solid solubility range of the 2:1:3 phase is determined by the lattice constant method to range from $x=0.474$ to $x=0.635$ (Fig. 1). The previously reported compound $La_3Ba_3Cu_6O_{14+\delta}$ is considered to be the solid solution of the 2:1:3 phase near the La-rich limit. No appreciable solid solution range of the 1:4:5 phase was detected by the x-ray diffraction method. As there is no other ternary compound existing in the CuO-rich region, the subsolidus phase relation can be determined as shown in Fig. 2.
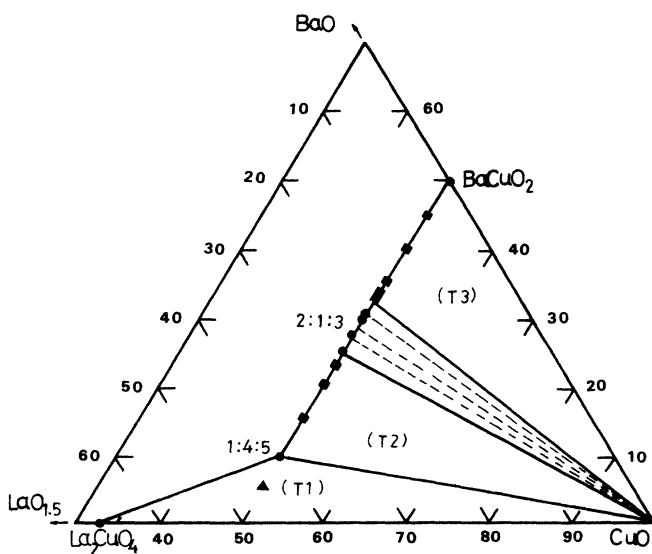

FIG. 2. The subsolidus phase relation in the CuO-rich region of the La-Ba-Cu-O system. $T1$: La_2CuO_4, 1:4:5, and CuO coexist. $T2$: 2:1:3, 1:4:5, and CuO coexist. $T3$: $BaCuO_2$, 2:1:3, and CuO coexist.

$T1$, $T2$, and $T3$ in Fig. 2 represent the three phase regions. In the $T1$ region, there are CuO, La_2CuO_4, and the 1:4:5 phase; the 2:1:3 and 1:4:5 phases and CuO coexit in the $T2$ region; and $BaCuO_2$, the 2:1:3 phase and CuO coexist in the $T3$ region.

B. The crystal structure and property of the 1:4:5 phase

The 1:4:5 phase is a mixed-valence copper oxide with a tetragonal distorted perovskite structure ($a=0.8644$ nm, $c=3.867$ nm, space group $P4/m$). Michel, Er-rakho, and Raveau[5] found that the oxygen content of the 1:4:5 phase is almost constant, and they formulated this compound as $La_4Ba_1Cu_5O_{13.4}$. The present study demonstrates that the Ba:La:Cu ratio is also constant, so the 1:4:5 compound is a compound with a definite composition. The 1:4:5 compound is a good metallic conductor, but no superconductivity transition was observed in the resistivity and ac susceptibility measurements. This fact supports the theoretical model which stresses the crucial importance of the layered structure or two-dimensional characteristics of the high-T_c materials, because the 1:4:5 compound has no superstructure along the c-axis direction or in other words, there is no oxygen-depleted lanthnide layer separating the Cu-O planes.

C. The crystal structure of the 2:1:3 phase

It should be mentioned here that the La-Ba-Cu-O system was investigated by Michel et al.[5] previously and two compounds with (La+Ba):Cu ratio 1:1 were formulated as $La_4Ba_1Cu_5O_{13.4}$ and $La_3Ba_3Cu_6O_{14+\delta}$, respectively.[5,6] The phase diagram of the La-Ba-Cu-O system has been studied by Che et al.[7] and the compound $LaBaCu_2O_{5-y}$ with the same La:Ba:Cu ratio as $La_3Ba_3Cu_6O_{14+\delta}$ was indexed with a tetragonal cell ($a=0.3917$ nm, $c=1.175$ nm) which is different from the cell given by Michel et al.[5] ($a=0.5525$ nm, $c=1.1721$ nm). A similar discrepancy also occurs in the current literature.[8,9] A series of x-ray diffraction experiments also enabled us to solve this problem. In the following discussion, we denote the smaller cell as 2:1:3 and the larger one as 3:3:6 for clarity.

The main difference between the 2:1:3 and the 3:3:6 phase is the oxygen-defect arrangements. The calculated diffraction patterns of the 2:1:3 and the 3:3:6 structure were almost the same except for some superstructure diffraction lines with relative intensities less than 1%. The diffraction line with lattice space $d=0.554$ nm may be considered as the (100) diffraction of the 3:3:6 phase, but it might come from the secondary harmonic (110) diffraction of the 2:1:3 phase. It is difficult to determine which model should be adopted from a single x-ray pattern from a Guinier-type camera. A series of x-ray diffraction experiments was made in order to solve this problem. The experimental conditions and results are listed in Table II. In Table II, the diffraction intensity of the (002) plane of the 2:1:3 phase with $d=0.588$ nm is also listed for comparison.

A tube voltage of 15 kV cannot give any secondary harmonic radiation from Cu $K\alpha$ ($\lambda=0.15418$ nm, $\lambda/2$

TABLE II. X-ray diffraction conditions and the results for the sample $La_{0.4}Ba_{0.6}CuO_{3-y}$.

| | X-ray diffraction condition | | | | Relative intensity | |
Radiation	Tube voltage (kV)	Tube current (mA)	Filter	Time (h)	$d=0.554$ nm	$d=0.588$ nm
Cu Kα	30	20	· · ·	8	Very weak	Very weak
Cu Kα	15	20	· · ·	24	Not observed	Very weak
Cu Kα	36	25	Fe	24	Middle	Not observed

$=0.07709$ nm), because the shortest x-ray wavelength is determined by the tube voltage, $\lambda = 1240/V$ (nm). The diffraction intensity with $d=0.554$ nm disappears when a 15-kV tube voltage is applied, while the superstructure line (002) of the 2:1:3 phase still appears. When the tube voltage is increased to 36 kV and an Fe filter is used to increase the relative intensity of the secondary harmonic radiations, the intensity of the diffraction at $d=0.554$ nm becomes stronger and the diffraction at $d=0.588$ nm disappears. These results clearly show that the diffraction at $d=0.554$ nm is the secondary harmonic diffraction of the (110) plane of the 2:1:3 structure ($d=0.277$ nm $=0.554$ nm/2), but not the (100) diffraction of the 3:3:6 model. So the 2:1:3 structure is correct, at least for the samples prepared with processes similar to that which we adopted, and the 3:3:6 model seems incorrect. Electron diffraction study of the samples $La_{1-x}Ba_xCuO_{3-y}$ ($x=0.6$, $x=0.65$) supports the x-ray diffraction result.[10]

As the tetragonal unit cell of the 2:1:3 phase is correctly determined, it can be inferred that its crystal structure is closely related to the structure of $Ba_2YCu_3O_{7-\delta}$. The Ba-Y-Ba order along the c-axis direction is simply replaced by Ba-La-Ba order in the La system, but some of the Ba atoms may be substituted by La due to the similar ionic radii of La and Ba. For the La-rich limit, each Ba site has about 0.28 La atom on the average. Considering the solubility range of the 2:1:3 phase, the formula of this phase can be written as $(Ba_{2-z}La_z)La_1Cu_3O_{7+\delta}$ with z range from 0.095 to 0.578.

An apparent difference between the crystal structure of the 2:1:3 phase in La and Y systems is the different degree of the orthorhombic distortion. The former is tetragonal or pseudotetragonal with the lattice constant $a=b=c/3$ within the experimental resolution, but the latter is clearly orthorhombic with the lattice constants $a < b \doteq c/3$. The origin of the different degree of orthorhombic distortion is the oxygen atom arrangements. Several models of $Ba_2LaCu_3O_{7+\delta}$ have been tested by making comparisons between experimental intensities and calculated ones. A detailed crystal structure analysis with given atomic parameters will be described elsewhere. Figure 3 shows the suggested structure model for $(Ba_{2-z}La_z)La_1Cu_3O_{7+\delta}$. In this figure, we can clearly see that the symmetry of the 1:2:3 phase depends mainly on the ordering of the oxygen in the Cu(1) plane. If oxygen atoms in the Cu(1) plane occupy sites randomly, the symmetry of the structure is tetragonal; if oxygen ordering occurs, with oxygen preferably occupying the $(0, \frac{1}{2}, 0)$ position rather than the $(\frac{1}{2}, 0, 0)$ position, the symmetry of the structure becomes orthorhombic. It is difficult to determine the degree of the

oxygen ordering by x-ray diffraction, and a neutron-diffraction technique is required. Such a neutron-diffraction study of this compound recently was done by Segre et al.[11]

D. The superconductivity of the 2:1:3 phase

The 2:1:3 phase is a superconductor and the transition temperature depends on several factors, such as the La:Ba ratio, oxygen content, and oxygen ordering. The composition dependence of T_c is not simply linear in the homogeneous region, but the general trend is that T_c increases with the increase of the Ba content. The samples showing high T_c have a La:Ba ratio near 1:2. Figure 4 shows the resistance versus temperature curves for samples $La_{1-x}Ba_xCuO_{3-y}$ with five different x values from 0.5 to 0.7. According to the variation of T_c with the composition, we can see that the samples with compositions in the $T3$ region of Fig. 1 show remarkably higher T_c than in the $T2$ region. The superconductivity of the sample in the $T1$ region is resulting from the $La_{2-x}Ba_xCuO_4$ phase.

The sample with $x=0.70$ has the highest zero-resistance temperature in Fig. 4. This sample and the sample with $x=0.68$ have $BaCuO_2$ as a second phase. It is possible that a small amount of the second phase can accelerate the sintering process. Sample C, which has a composition close to the Ba-rich limit of the 1:2:3 phase, shows a nonlinear resistivity decrease around 100 K, though its zero-resistance temperature is lower than the
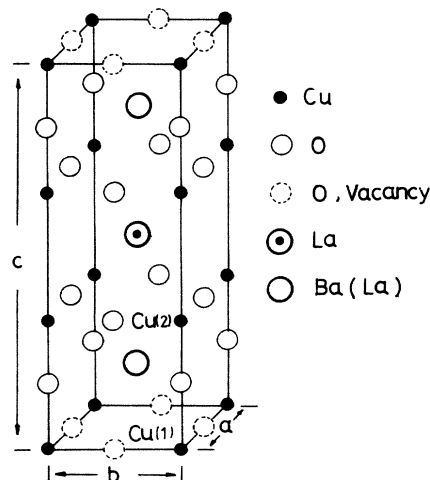

FIG. 3. Unit cell of the compound $(Ba_{2-z}La_z)La_1Cu_3O_{7+\delta}$ (pseudotetragonal with lattice constant $a=b=c/3$).
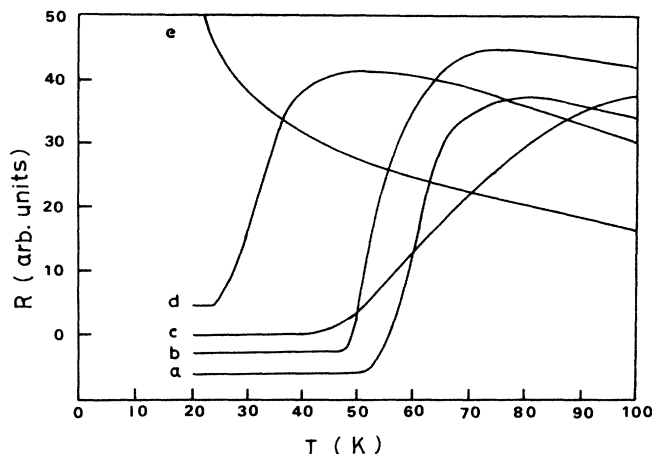
FIG. 4. Resistance vs temperature curves for $La_{1-x}Ba_x$-CuO_{3-y}, (a) $x = 0.70$, (b) $x = 0.68$, (c) $x = 0.65$, (d) $x = 0.60$, and (e) $x = 0.50$ (curves are zero offset along the resistance axis for clarity).

FIG. 5. Resistance vs temperature curve for $Ba_2LaCu_3O_{7+\delta}$. Sample A was prepared at 950°C in air and furnace cooled. Sample B was prepared at 950°C in air and annealed at 250°C for 16 h.

above-mentioned two samples. This is an indication of superconductivity with T_c about 100 K in the La-Ba-Cu-O system. Further study is needed to optimize the preparation methods and heat treatments to obtain the better superconductors in this system. The sample with $x = 0.6$ has a much lower T_c, and the sample with $x = 0.5$ is a semiconductor. Thus, we can control the La:Ba ratio to adjust the properties of the 2:1:3 phase in this system.

When the composition is fixed, the samples annealed at low temperature for a longer time than described above show higher T than others. Figure 5 shows the resistance versus temperature curve of the sample with a nominal composition $LaBa_2Cu_3O_{7+\delta}$. Sample A was prepared using the above-mentioned method. Sample B was prepared with a similar method but was annealed at 250°C for 16 h. While sample A is a semiconductor above 4.2 K, sample B is a superconductor with an onset temperature of 90 K and nearly zero resistance at 67.5 K. A possible explanation is that annealing at low temperature for a long time results in oxygen ordering in the Cu(1) plane and the crystal structure changes from tetragonal to orthorhombic.

Apparently oxygen ordering is crucial to the superconductivity in this system. From these experimental studies of the 1:4:5 and the 2:1:3 phases in the La system, we can find a clue to the origin of high-T_c superconductivity. The nonsuperconductivity of the 1:4:5 phase, which is a
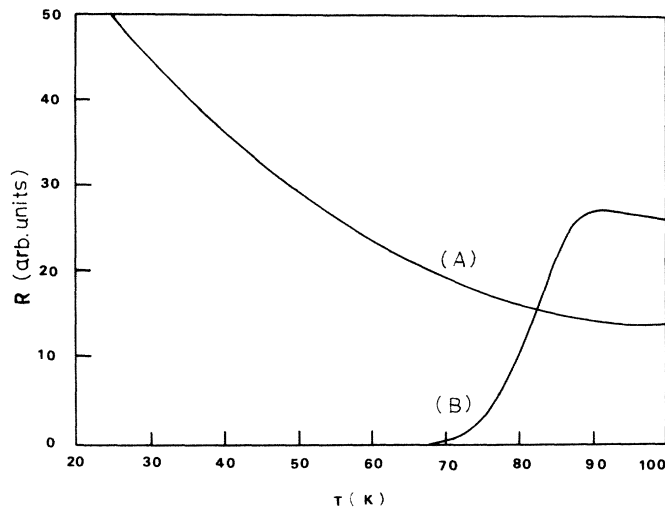
mixed-valence copper oxide, suggests the importance of the two-dimensional feature of the Cu-O planes separated by oxygen-depleted lanthanide layers, and the superconductivity of the annealed 2:1:3 phase and the nonsuperconductivity of the unannealed phase suggests the importance of the one-dimensional character of the "fence-like" CuO chain. Both the one-dimensional and two-dimensional character seems necessary to high-T_c superconductivity around 90 K.

IV. CONCLUSIONS

In the $La_{1-x}Ba_xCuO_{3-y}$ system, the 2:1:3 phase is a superconductor. This phase has a homogeneous range from $x = 0.474$ to $x = 0.635$. Its crystal structure is similar to that of $Ba_2YCu_3O_{7-\delta}$. The superconducting transition temperature of the 2:1:3 phase depends on composition, oxygen content, and oxygen ordering. Long-term annealing at low temperature is required for the preparation of high-T_c La-Ba-Cu-O materials. The authors believe that a superconductor with zero-resistance temperature above 77 K can be obtained after further research in the La-Ba-Cu-O system. In addition, the variation of the superconductivity of the 2:1:3 phase with composition and oxygen ordering in the La system is instructive to theoretical study of the mechanism of high-T superconductivity.

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