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Crystal Structure and Superconductivity in the La-Ba-Ca-Cu-O System

(high-T_c superconductor／$La_2CaCu_2O_y$／$CaBaLaCu_3O_{7-\delta}$)

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Resistivity and X-ray measurements have been done on ceramic samples which have nominal compositions of $La_{2-x}A_xCaCu_2O_y$ or $La_{2-x}A_xSrCu_2O_y$ (A=Ba and Ca). The samples with nominal compositions of $La_{2-x}Ca_{1+x}Cu_2O_y$ (x=0.4) and $La_{2-x}Ba_xCaCu_2O_y$ (x=0.2 and 0.4) are metallic but not superconducting down to 22 K. They are found to have the same crystal structure as that for $La_2CaCu_2O_6$. However, when the amount of Ba doping is further increased, superconductivity appears near 80 K in samples with nominal compositions of $La_{2-x}Ba_xCaCu_2O_y$ (x=1.0, 1.2 and 1.4). The X-ray results show that the superconductivity is not caused by the Ba doping but by a structural change to $CaBaLaCu_3O_{7-\delta}$ which is tetragonal at all temperatures.

1. Introduction

Since the discovery of high-T_c superconductivity above 30 K in the La-Ba-Cu-O system [1] and above 90 K in the Y-Ba-Cu-O system [2], various types of superconducting oxides have been synthesized. They include $La_{2-x}A_xCuO_4$ (A=Ca, Sr, Ba) [1], $RBa_2Cu_3O_7$(R=Y or rare-earth metal) [2,3] and the Bi-Sr-(Ca)-Cu-O [4,5], Tl-Ba-(Ca)-Cu-O [6,7] and Nd-Ce-Sr-Cu-O [8] systems. The crystal structures of these oxides are composed of two-dimensional sheets of Cu-O pyramids or octahedra. A superconducting transition was found in another type of compounds, $Ln_{2-x}Ce_xCuO_{4-y}$ (Ln=Pr, Nd or Sm) [9], which have the sheets of Cu-O squares with no apical oxygen.

The compounds $La_2CaCu_2O_6$ [10] and $La_2SrCu_2O_6$ [10] also contain the sheets of Cu-O pyramids. In the structure of the compounds, each copper is coordinated by a pyramid of five oxygens. These pyramids share corner oxygens to form two-dimensional sheets that are stacked in pairs. An additional sheet of oxygen vacancies lies between the two sheets of pyramids and about 20% of the vacancies are filled with oxygen in the compound annealed in O_2. Considerable effort was done to make $La_2CaCu_2O_6$ or $La_2SrCu_2O_6$ superconducting by chemical doping. However, $La_2CaCu_2O_6$ and $La_{2-x}Sr_xCaCu_2O_6$ were made superconducting only by annealing them at high oxygen pressures.[11] Superconductivity was searched in another system $La_{2-x}Ba_xCaCu_2O_6$ but was not observed in the investigated range of $x \leq 0.3$.[12]

In this paper, the effect of Ba substitution for La is studied in $La_2CaCu_2O_6$ and $La_2SrCu_2O_6$ with a wider range of Ba／(La+Ba) .

2. Experimental

The samples were synthesized by solid-state reaction. The mixtures of appropriate amounts of powders La_2O_3, $BaCO_3$, $CaCO_3$, $SrCO_3$, and CuO were ground and heated in air at 930 ℃ for 10 h. The powders were finely ground and pressed into pellets. The pellets were sintered in air or flowing O_2. They were held at 1000 ℃ for 6 h, at 900 ℃ for 12 h, and then slowly cooled in the furnace at a rate of 1 ℃／min.

Phase identification of the samples was carried out by X-ray powder diffraction with Cu-Kα or Co-Kα radiation. The lattice constants were determined using Co-Kα radiation.

Electrical resistivity measurements were performed at temperatures between 22 and 300 K on bar samples which were cut from the pellets. A

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dc four-probe technique was employed using silver paint contacts. The temperature of the samples was measured by use of a (Au+0.07%Fe)-Chromel thermocouple.

3. Results and discussion

Figure 1 shows the temperature dependence of the electrical resistivity for Ca-substituted samples with nominal composition of $La_{2-x}Ca_xCaCu_2O_y$ ($x=0.4$). The samples were prepared by sintering in air or in oxygen. For both samples, with decreasing temperature, the resistivity varies like a metal above $T\sim100$ K but increases at low temperatures.

Figure 2 represents the temperature dependence of the resistivity for samples which had nominal compositions of $La_{2-x}Ba_xSrCu_2O_y$ ($x=0.2$ and 1.0) and were sintered in O_2. As the temperature is lowered, the resistivities of both samples increase monotonically.

The resistivity versus temperature curves are plotted in Fig.3 for samples, sintered in flowing O_2, with nominal compositions of $La_{2-x}Ba_xCaCu_2O_y$ ($x=0.2$, 0.4, 1.0, 1.2 and 1.4). For $x=0.2$ and 0.4, with decreasing temperature, the resistivity decreases like a metal in the high-temperature region but slightly increases at low temperatures. A small change is seen in the resistivity around 30 K. X-ray diffraction showed that these resistivity changes are related with small traces of supercon-

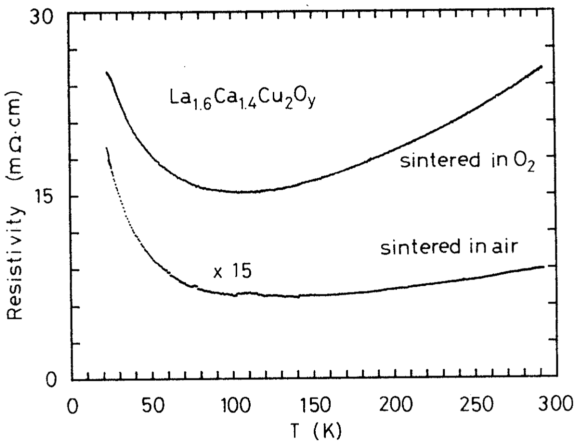

Fig.1. Temperature dependence of the electrical resistivity for Ca-doped $La_2CaCu_2O_y$ samples having nominal composition of $La_{2-x}Ca_xCaCu_2O_y$ ($x=0.4$).

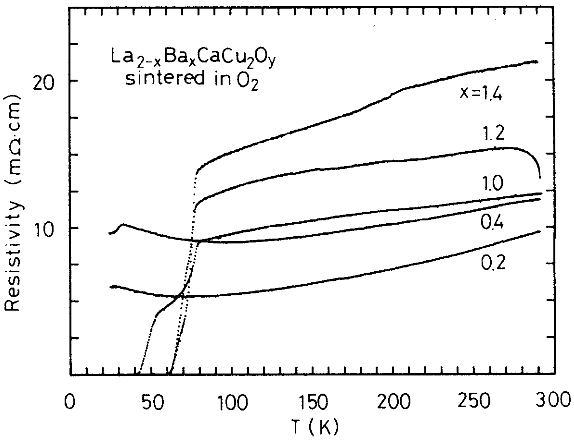

Fig.3. Temperature dependence of the electrical resistivity for Ba-doped $La_2CaCu_2O_y$ samples with nominal compositions of $La_{2-x}Ba_xCaCu_2O_y$ ($x=0.2$, 0.4, 1.0, 1.2 and 1.4). All the samples were sintered in O_2.

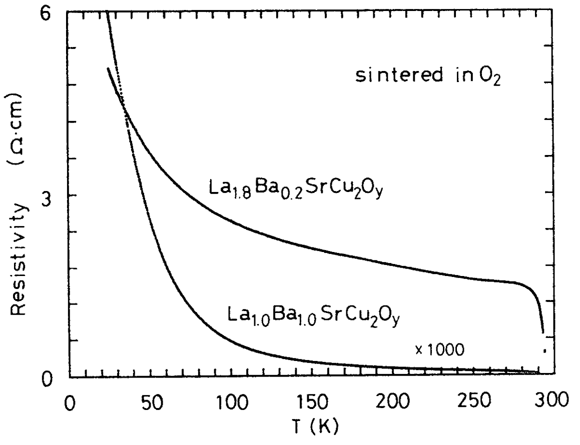

Fig.2. Temperature dependence of the electrical resistivity for Ba-doped $La_2SrCu_2O_y$ samples with nominal compositions of $La_{2-x}Ba_xSrCu_2O_y$ ($x=0.2$ and 1.0). The samples were sintered in O_2.

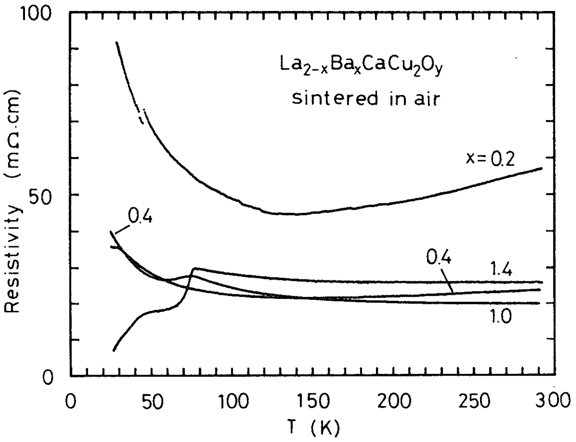

Fig.4. Temperature dependence of the electrical resistivity for Ba-doped $La_2CaCu_2O_y$ samples with nominal compositions of $La_{2-x}Ba_xCaCu_2O_y$ ($x=0.2$, 0.4, 1.0 and 1.4). The samples were sintered in air.

ducting phase, $La_{2-x}Ba_xCuO_y$, [1] included in the samples (see Fig.5). A sudden drop is observed in the resistivity for the samples with nominal compositions of $La_{2-x}Ba_xCaCu_2O_y$ (x=1.0, 1.2 and 1.4), indicating the occurrence of superconductivity at the onset temperatures of about 79, 78 and 78 K, respectively. There exist two transitions in the sample with nominal composition of $La_{1.0}Ba_{1.0}CaCu_2O_y$. The super-conducting transition is observed also in ceramic samples sintered in air, as shown in Fig.4. The temperature where the resistivity starts to drop is about 75.4 K for $La_{1.0}Ba_{1.0}CaCu_2O_y$ and 76 K for $La_{0.6}Ba_{1.4}CaCu_3O_y$

Figure 5 shows the X-ray (Cu-Kα) diffraction pattern for the sample with nominal composition of $La_{1.8}Ba_{0.2}CaCu_2O_y$. As indicated in the figure, strong peaks are well indexed on the basis of the structure of $La_2CaCu_2O_y$ or $La_2SrCu_2O_y$ [10]. Unlabeled peaks at 2θ =23°, 31° and 40.4° are identified as diffraction lines from $La_{2-x}Ba_xCu_2O_y$. [1] A very small peak around 2θ =51° cannot be explained and implies the formation of an unknown impurity phase. The X-ray pattern for the $La_{1.6}Ba_{0.4}CaCu_2O_y$ sample was similar to that for the $La_{1.8}Ba_{0.2}CaCu_2O_y$ sample although the peaks are relatively broadened.

Figure 6(a) displays the X-ray diffraction pattern for the sample with nominal composition of $La_{1.0}Ba_{1.0}CaCu_2O_y$. It is to be noted that the pattern is changed by increasing the amount of Ba. The observed peak positions for the $La_{1.0}Ba_{1.0}CaCu_2O_y$ sample approximately agree with those for $CaBaLaCu_3O_{7-\delta}$.[15,16] The compound $CaBaLaCu_3O_{7-\delta}$ is a synthesized superconductor with T_c of about 80 K, and its structure is isomorphic with $YBa_2Cu_3O_y$ and tetragonal at all temperatures [14,15]. In Fig.6(a), an extra peak is seen around 2θ =31.9°, indicating an inclusion of a small amount of additional phase expressed by La_2CuO_4 and/or $La_{2-x}Ca_xCu_2O_4$. Figure 6(b) shows the X-ray pattern for the sample with nominal composition of $La_{0.8}Ba_{1.2}CaCu_2O_y$. The pattern is similar to that for $La_{1.0}Ba_{1.0}CaCu_2O_y$ without the extra peak at 2θ =31.9°. A small peak, which is identified as the strongest diffraction line from CaO, is located around 2θ =37.3° for both samples having nominal compositions, $La_{1.0}Ba_{1.0}CaCu_2O_y$ and $La_{0.8}Ba_{1.2}CaCu_2O_y$.

The lattice constants determined by X-ray diffraction for the single or major phase in the samples of nominal compositions $La_{2-x}Ba_xCaCu_2O_y$ are listed in Table I, together with the reported data on $La_{1.9}Ca_{1.1}Cu_2O_{5.95}$ and $CaBaLaCu_3O_{7-\delta}$. The lattice constants for $La_{1.8}Ba_{0.2}CaCu_2O_y$ and $La_{1.6}Ba_{0.4}CaCu_2O_y$ are close to those for $La_{1.9}Ca_{1.1}Cu_2O_{5.95}$. In contrast, the lattice constants for major phases in the samples of $La_{0.8}Ba_{1.2}CaCu_2O_y$ and $La_{1.0}Ba_{1.0}CaCu_2O_y$ coincide rather with those for $CaBaLaCu_3O_{7-\delta}$ [15,16]. The agreements of

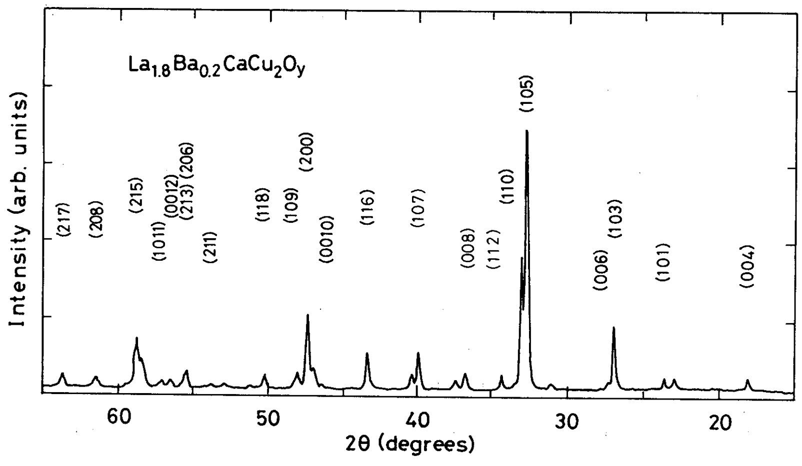

Fig.5. X-ray (Cu-Kα) powder diffraction pattern at room temperature for a sample of $La_{1.8}Ba_{0.2}CaCu_2O_y$ which was prepared by sintering in O_2.

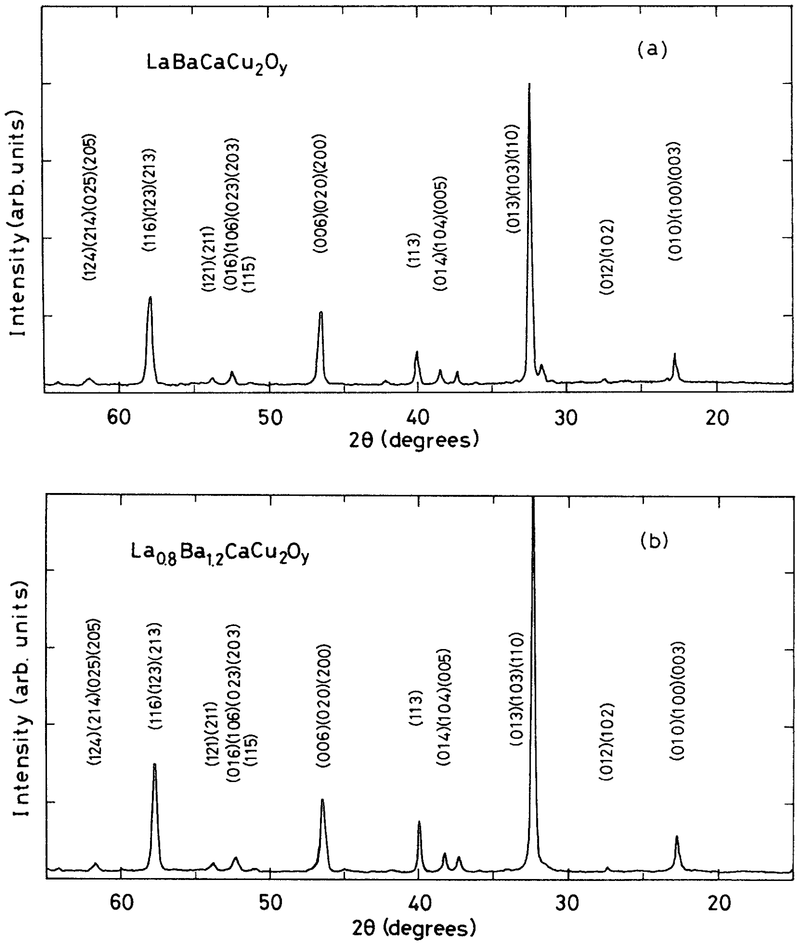

Fig.6. X-ray (Cu-Kα) powder diffraction patterns at room temperature for samples of nominal compositions: (a) $La_{1.0}Ba_{1.0}CaCu_2O_y$ and (b) $La_{0.8}Ba_{1.2}CaCu_2O_y$. The samples were sintered in O_2.

the X-ray pattern and lattice parameters between the superconducting phase and $CaBaLaCu_3O_{7-\delta}$ show that the superconducting phase in the samples with nominal compositions of $La_{1.0}Ba_{1.0}CaCu_2O_y$, $La_{0.8}Ba_{1.2}CaCu_2O_y$ and $La_{0.6}Ba_{1.4}CaCu_2O_y$ is $CaBaLaCu_3O_{7-\delta}$.

Table I shows that the unit cell volume V increases with the increase of the Ba doping concentration as expected from simple ionic radius consideration. This means that the solubility limit of Ba in $La_2CaCu_2O_y$ extends to x=0.4. However, when the amount of Ba is further increased, i.e. for $x \geq 1.0$ in $La_{2-x}Ba_xCaCu_2O_y$, the sample cannot retain the original crystal structure. This leads to the change in the crystal structure which causes the superconductivity around 80 K.

Table I. Lattice parameters for samples with nominal compositions of $La_{2-x}Ba_xCaCu_2O_y$ (x =0.2, 0.4, 1.0 and 1.2) and for compounds, $La_{1.9}Ca_{1.1}Cu_2O_{5.95}$ and $CaBaLaCu_3O_{7-\delta}$. V is the unit cell volume.

sample	a (Å)	c (Å)	V (Å^3)
$La_{1.8}Ba_{0.2}CaCu_2O_y$	3.82_9	19.52_9	$286._3$
$La_{1.6}Ba_{0.4}CaCu_2O_y$	3.83_5	19.63_9	$288._8$
$La_{1.9}Ca_{0.1}CaCu_2O_{5.95}$[10]	3.82_5	19.40_4	$283._9$
$La_{1.0}Ba_{1.0}CaCu_2O_y$	3.88_9	11.66_7	$176._5$
$La_{0.8}Ba_{1.2}CaCu_2O_y$	3.90_1	11.70_2	$178._1$
$CaBaLaCu_3O_{7-\delta}$[15]	3.8655	11.6354	173.9

4. Conclusion

The effect of Ba doping for La in $La_2CaCu_2O_6$ was studied by preparing ceramic samples. For the samples of $La_{2-x}Ba_xCaCu_2O_y$ (x=0.2 and 0.4), the crystal structure was the same as that for the original compound $La_2CaCu_2O_6$. The Ba doping induced an expansion of the unit cell volume, but did not bring about superconductivity. The samples with nominal compositions of x=1.0, 1.2 and 1.4 were metallic and exhibited superconductivity near 80 K. The X-ray diffraction patterns for the superconducting samples were not of the $La_2CaCu_2O_y$ type and included peaks resulted from a tetragonal superconductor $CaBaLaCu_3O_{7-\delta}$. In addition, from the agreement of the lattice parameters with those for $CaBaLaCu_3O_{7-\delta}$, it was concluded that the appearance of superconductivity was due to the structural change.

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