Electron Diffraction and Microscopy of the Structures of La–Ba(Sr)–Cu–O and Ba–Y–Cu–O at Room and Liquid Helium Temperatures

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Electron Diffraction and Microscopy of the Structures of La-Ba(Sr)-Cu-O and Ba-Y-Cu-O at Room and Liquid Helium Temperatures

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Structural study of the superconducting oxides in the La-Ba(Sr)-Cu-O and Ba-Y-Cu-O systems has been made at room and liquid helium temperatures by electron diffraction and high resolution electron microscopy. $La_{1.9}Ba_{0.1}CuO_4$, which is not superconductive down to 4.2 K, is orthorhombic and belongs to the space group Pccm. $La_{1.8}Ba_{0.2}CuO_4$ with T_c=28 K and $La_{1.8}Sr_{0.2}CuO_4$ with T_c=36 K are tetragonal and belong to the space group I4/mmm. At liquid helium temperature, these oxides did not show any structural change. Oxides in the Ba-Y-Cu-O system with T_c=68 and 85 K are orthorhombic and belong to the space group Pmmm. (110) twins are formed in the structure. High resolution electron microscopy revealed the metal atom arrangement in these superconductive oxides.

1. INTRODUCTION

Recently, it has been shown that oxides in the La-Ba-Cu-O, La-Sr-Cu-O, and Ba-Y-Cu-O systems become superconductive at temperatures much higher than the transition temperatures of metallic materials. These oxides have crystal structures closely related with the perovskite structure. Many structural studies have been made mainly by X-ray powder diffraction of sintered polycrystalline specimens. Since X-ray diffraction is dificult to provide detailed information on the structure, the present authors have applied electron diffraction and electron microscopy for getting useful information about the crystal structure and structural defects. The results are described in this paper.

2. EXPERIMENTAL

Polycrystalline specimens of $La_{1-x}A_xCuO_4$ (A=Ba, x=0.1 and 0.2; A=Sr, x=0.2) were produced by sintering. X-ray diffraction showed that $La_{1.9}Ba_{0.1}CuO_4$ takes the La_2CuO_4 type of structure [1]. This oxide did not become superconductive down to 4.2 K. On the other hand, $La_{1.8}Ba_{0.2}CuO_4$ and $La_{1.8}Sr_{0.2}CuO_4$ became superconductive at 28 K for the former and at 36 K for the latter. Their structure was $LaSrVO_4$ (K_2NiF_4) type [1].

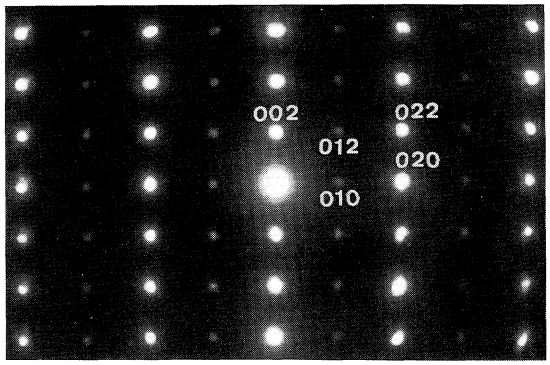
As the oxide with higher T_c, $YBa_2Cu_3O_{\sim 7}$ was prepared. Dependent upon the heat treatment, the specimen showed different T_c. Investigations were made for the specimens with T_c=68 and 85 K. X-ray diffraction showed that the structure is orthorhombic with a slight difference between the axial length a and b.

The produced specimens were crushed into fine powder, and fine flakes were mounted on carbon-coated microgrids for electron microscopic observations. Electron microscopes used are a JEM-200 CX operating at 200 kV and a high resolution 1 MV electron microscope operating at 1 MV. A superconductive cryo electron microscope (JEM-2000SCM) operating at 160 kV was used to investigate the structure at 4.2 K.

3. RESULTS AND DISCUSSIONS

3.1 Structure of La_{1-x}(Ba or Sr)$_x CuO_4$ at Room Temperature

In accordance with the previous study [1], electron diffraction investigations showed that $La_{1.8}$(Ba or Sr)$_{0.2}CuO_4$ is bct with a_t=3.779 (or 3.774) and c_t=13.171 (or 13.221) A, and belong to the space group I4/mmm. In contrast to this, $La_{1.9}Ba_{0.1}CuO_4$ is orthorhombic with a_o=5.354, b_o=5.408 and c_o=13.264 A. Thus, $a_o \sim b_o \sim \sqrt{2}a_t$. As shown in Fig. 1, diffraction patterns give weak reflection spots with indices h0l and 0kl (h, k= odd; l=even), which are forbidden for the La_2CuO_4 structure belonging to the space group Fmmm. Investigations lead to the conclusion that the appropriate space group is Pccm and that the weak reflections are due to the metal and some of the oxygen atoms displaced slightly in the c plane from the positions in the La_2CuO_4 structure. Figure 2 is a [1$\bar{1}$0] structure image of $La_{1.9}Ba_{0.1}CuO_4$, where the arrangement of metal atoms are clearly seen in accordance with the structure model. $La_{1.8}$(Ba or Sr)$_{0.2}CuO_4$ gave similar structure image under the beam incidence along [100].



Fig, 1. [100] diffraction pattern of $La_{1.9}Ba_{0.1}CuO_4$.

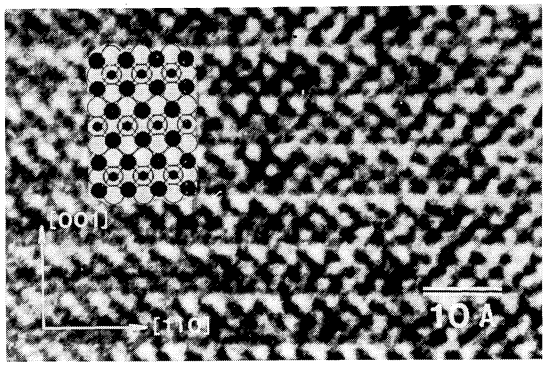


Fig. 2. [1$\bar{1}$0] structure image of $La_{1.9}Ba_{0.1}CuO_4$. In the inset, large solid circles are Ba or La atoms, small solid circles Cu atoms, and open circles O atoms.

3.2 Structure of La_{1-x}(Ba or Sr)$_x CuO_4$ at Liquid Helium Temperature

It is important to know the structure at the superconducting state. Therefore, the structure at liquid helium temperature was investigated. Many diffraction patterns and lattice images were taken under various incident beam directions. Any noticeable change could not be found. This shows that no structure transition takes place at the superconducting transition.

Lattice parameters at 4.2 K were measured by using gold as a reference material. The result for $La_{1.9}Ba_{0.1}CuO_4$ is a_o=5.336R(Au), b_o=5.409R(Au), and c_o=13.225R(Au) A, and the result for $La_{1.8}Sr_{0.2}CuO_4$ is a_t=3.807R(Au) and c_t=13.237R(Au) A. Here, R(Au) is the ratio of lattice parameter of gold at 4.2 K to that at room temperature, and is estimated at 1-0.0026 from the thermal contraction data. The thermal contraction is almost uniform in all the directions.

3.3 Structure of $YBa_2Cu_3O_{\sim 7}$ at Room Temperature

Two structure models have been presented for the structure of the superconductive phase $YBa_2Cu_3O_{\sim 7}$. One is orthorhombic with a=3.822, b=3.833, and c=11.690 A [2], and the other is orthorhombic with $a \sim b' \sim \sqrt{2}a \sim \sqrt{2}b$ [3]. Since the latter is a superstructure of the former, it should give superstructure spots. Careful investigations were made but any trace of the superstructure spots could not be found. Therefore, the former model can be said to be correct. The appropriate space group is Pmmm.

Since a and b are different slightly, the (110) type of twins is formed [4]. Figure 3 is a [001] diffraction pattern, where the reflection spots split in two. Figure 4 is a [001] lattice image, where the (100) and (010) lattice fringes kink at the (110) twin boundary.

Figure 5 is a [100] structure image, where Ba, Y and Cu atoms are imaged, although O atoms are not. In accordance with the structure model, Y and Ba atom planes are stacked in the c direction in the order of -Y-Ba-Ba-Y-, and between every atom plane Cu atom planes exist.

Sometimes, (001) planar defects are observed as indicated by arrows in the figure. The defect is formed by the replacement of Cu atom plane by the Ba atom plane. This replacement is considered to be not so difficult, since if such a replacement takes place periodically the La_2CuO_4 type of structure is formed. Quenched specimens from 900°C contain many such defects, and their diffraction patterns show strong [001] streaks.

Acknowledgment

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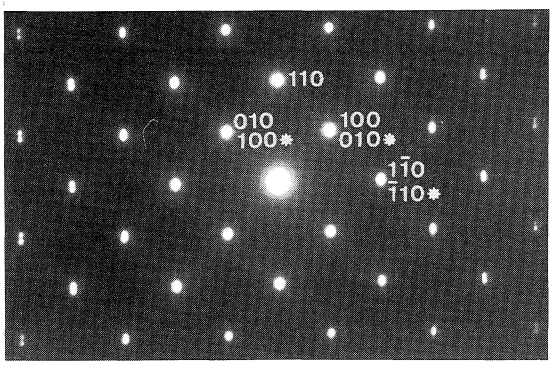

Fig. 3. [001] diffraction pattern of $YBa_2Cu_3O_{\sim 7}$ showing (110) twinning. Asterisk: twin.

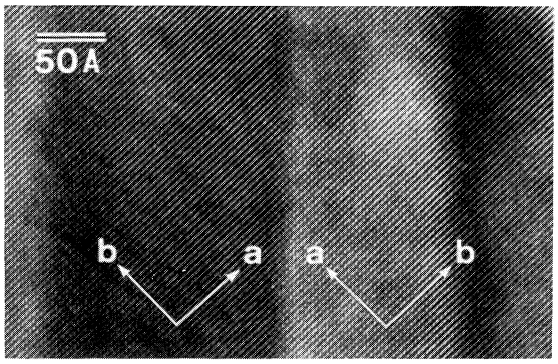

Fig. 4. [001] lattice image of $YBa_2Cu_3O_{\sim 7}$. (100) lattice fringes are kinked at the (110) twin boundary.

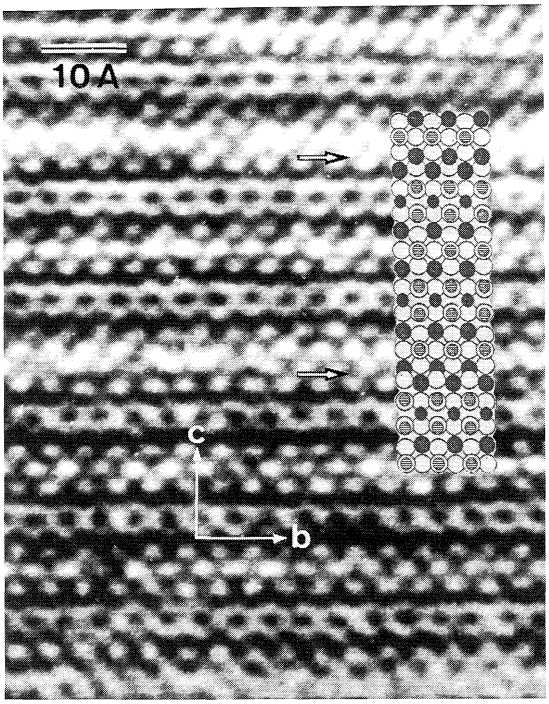

Fig. 5. [100] structure image of $YBa_2Cu_3O_{\sim 7}$. Structure model is inserted. Large solid circle: Ba, small solid circle: Y, hatched circle: Cu, open circle: O. Arrows indicate planar defects.