

Structure and Superconductivity of High Pressure Synthesized Sr-Ca-Cu-O System ^{*1}

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A new superconducting cuprate $(\text{Sr}_{0.7}\text{Ca}_{0.3})_3\text{Cu}_2\text{O}_{5+\delta}$ has been synthesized under high pressure. CaO_2 has been used to make a homogeneous oxidizing atmosphere. X-ray diffraction measurements on the bulk sample revealed that $(\text{Sr}_{0.7}\text{Ca}_{0.3})_3\text{Cu}_2\text{O}_5$ (325-type) phase was found in the top surface of the columnar sample, $(\text{Sr}_{0.7}\text{Ca}_{0.3})_4\text{Cu}_3\text{O}_7$ (437-type) phase in the bottom surface and 325-type + 437-type mixed phase in a cross section parallel to the column axis. Segregations of 325-phase and 437-phase were supposed to take place in the upper and lower parts of the sample, respectively. Nearly single phase samples of 325-type and 437-type crystal were gained by grinding from the upper part and the lower part of the sample, respectively, using abrasive papers. Magnetic susceptibility measured by SQUID and electrical resistivity measurements showed that superconductive transition temperatures are 106 K in the 325-phase and 110 K in the 437-phase.

(Received April 25, 2001; Accepted July 19, 2001)

Keywords: superconducting cuprate, high pressure synthesis, segregation, X-ray diffraction pattern, magnetic susceptibility, electrical resistivity

1. Introduction

The superconducting transition temperature, T_c , of the layered cuprate has a relationship to the number of adjacent CuO_2 layers. As the number of layers in the superconducting cuprates is increased, T_c reaches a maximum at 3 or 4 layers.¹⁾ When the number of layers is further increased, T_c monotonically decreases. In this case, the structure converges towards the infinite layered (IL) structure, *i.e.*, the nonapical oxygen structure. It is interesting to find out whether the IL structure can be responsible for superconductivity or not. Using high-pressure synthesis, samples of $(\text{Sr}_{0.7}\text{Ca}_{0.3})_{0.9}\text{CuO}_2$ with the IL structure have been obtained as one of the series of $\text{Sr}_{1-x}\text{M}_x\text{CuO}_2$ for divalent $\text{M}=\text{Ba}$, Ca and small fractions of superconductivity are observed.²⁻⁵⁾

The powder sample of $\text{Sr}_{0.14}\text{Ca}_{0.86}\text{CuO}_2$ ⁶⁾ prepared in ambient pressure and a single crystal of $\text{Sr}_{0.74}\text{Ca}_{0.26}\text{CuO}_2$ ⁷⁾ have the IL structure, but could not be made superconducting.

H. Shaked *et al.* indicated that the superconductivity in high-pressure synthesized samples of the Sr-Ca-Cu-O system can be attributed to the phases $\text{Sr}_3\text{Cu}_2\text{O}_{5+\delta}$, $\text{Sr}_4\text{Cu}_3\text{O}_{7+\delta}$, and $\text{Sr}_5\text{Cu}_4\text{O}_{9+\delta}$ and not the IL structure.⁸⁾ Single-phase samples of $\text{Sr}_3\text{Cu}_2\text{O}_{5+\delta}$, $\text{Sr}_4\text{Cu}_3\text{O}_{7+\delta}$, and $\text{Sr}_5\text{Cu}_4\text{O}_{9+\delta}$ have never been prepared.

There are problems in the preparation of superconducting cuprate samples by the high-pressure synthesis. These problems are inhomogeneous distribution of oxygen in the samples, inhomogeneous distribution of temperature (/involving temperature gradient), and chemical reaction between the sample and the Pt capsule. The first problem appears when starting materials were sandwiched between two pellets of KClO_4 which acts as a source of oxygen. The inhomogeneous distribution of oxygen in the sample $(\text{Sr}_{0.7}\text{Ca}_{0.3})_{0.9}\text{CuO}_2$ make $(\text{Sr}_{0.7}\text{Ca}_{0.3})_3\text{Cu}_2\text{O}_5$ (325-type) phase or $(\text{Sr}_{0.7}\text{Ca}_{0.3})_4\text{Cu}_3\text{O}_7$ (437-type) phase at the position

close to the oxygen source and the IL structure at the position apart from it.⁸⁾

In the present paper, we report results obtained in our study of samples of $(\text{Sr}_{0.7}\text{Ca}_{0.3})_3\text{Cu}_2\text{O}_5$ by X-ray diffraction, magnetic susceptibility and electrical resistivity.

2. Experiment

Samples with the nominal composition of $(\text{Sr}_{0.7}\text{Ca}_{0.3})_3\text{Cu}_2\text{O}_{5.9}$ were prepared and synthesized at a pressure of 5.4 GPa and a temperature of 1050°C. Starting materials Sr_2CuO_3 , Ca_2CuO_3 , CuO , and CaO_2 were mixed and pressed into a pellet ($\phi 6.0 \text{ mm} \times 4.6 \text{ mm}$). The pellet was loaded into a Pt capsule, which was surrounded by a BN separator, moreover, put into a cylinder form carbon heater, and then set into a pyrophyllite cell for pressure transmitting. This cell was compressed up to 5.4 GPa using a cubic-anvil-type apparatus. During compression, the pellet was heated to about 1050°C for 30 min by the carbon heater. Temperature was measured with an alumel-chromel thermocouple (Fig. 1). The sizes of the synthesized samples were about $\phi 5.6 \text{ mm} \times 4.2 \text{ mm}$.

To avoid the problem of inhomogeneous oxygen distribution, CaO_2 was utilized as one of the starting materials. Homogeneously oxidized samples were expected to be obtained. The nominal oxygen composition was adjusted by changing the ratio of $\text{CaO}_2/\text{Ca}_2\text{CuO}_3$. The real oxygen composition (5.3) was estimated from iodometry and compared with the

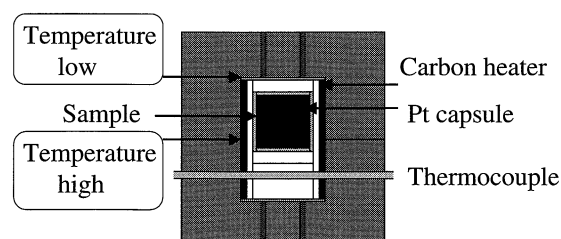


Fig. 1 Cross section of high pressure cell.

^{*1}This Paper was Presented at the Spring Meeting of the Japan Institute of Metals, held in Narashino, on March 29, 2001.

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nominal one (5.9). The value of 5.3 was obtained by subtracting the contribution of oxygen in the minor phase, CuO, from the measured one.

The surface layer of the samples was removed by abrasive papers because of the reaction of the surface with the Pt capsule. X-ray diffraction patterns from three surfaces, that is, the top and bottom surfaces after polishing and a cross section after cutting along the column axis, were measured. These X-ray patterns were identified with the intensity calculated using the structure models proposed by H. Shaked *et al.*⁽⁸⁾ and S. Adachi *et al.*⁽⁹⁾ and the data of the high pressure synthesized $\text{Sr}_2\text{CuO}_{3+\delta}$ refined from neutron powder diffraction.⁽¹⁰⁾

3. Results

The X-ray diffraction pattern from the cross section showed the existence of two-phases, 325-type + 437-type (Fig. 2), the pattern from the top surface showed 325-type structure (Figs. 3(a), 4), that from the bottom surface showed 437-type structure (Figs. 3, 4). Results of EPMA showed the value of

$(\text{Sr, Ca})/\text{Cu} = 1.5\text{--}1.33$ which meant the mixed phase was a 325-type and 437-type.

The inhomogeneous temperature distribution or the temperature gradient between the upper part and the lower part of the sample were supposed to make segregations of the two phases. In order to investigate the segregated phase, the same sample was synthesized with the same condition again. The upper part and the lower part were separated. X-ray diffraction patterns of the position of ③, ④ in the upper part of the sample (Fig. 2) showed 325-phase + 437-phase, those of ⑤, ⑥ in the lower part showed peaks of 437-phase + $(\text{Sr, Ca})_4\text{Cu}_6\text{O}_{10}$ (4610-phase). The 325-phase sample was gained by grinding the upper part of the sample with the abrasive paper from the bottom. This grinding was continued until the X-ray pattern of the bottom agreed with that of the top surface. The X-ray

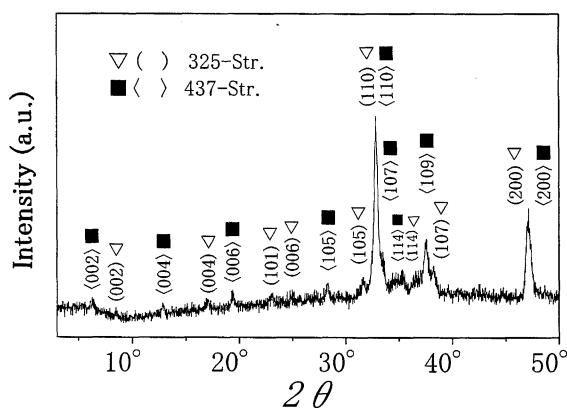


Fig. 2 X-ray diffraction pattern from the cross section of the $(\text{Sr}_{0.7}\text{Ca}_{0.3})_3\text{Cu}_2\text{O}_{5.3}$ sample. Two phases exist on this surface.

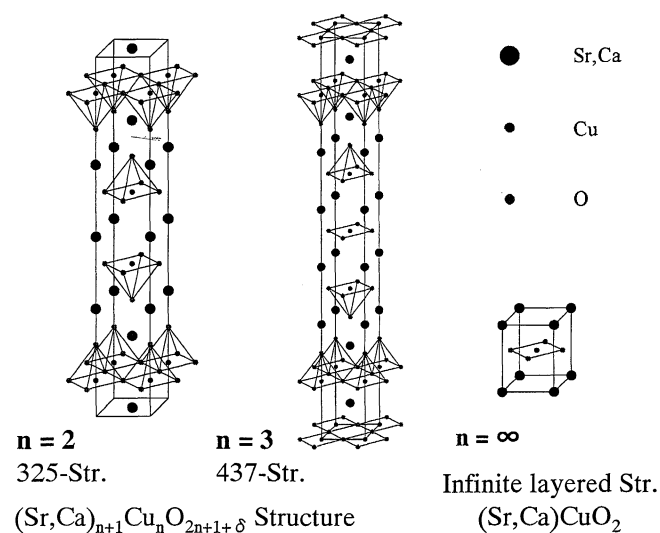


Fig. 4 Crystal structure of 327-type, 437-type and infinite layered structure.

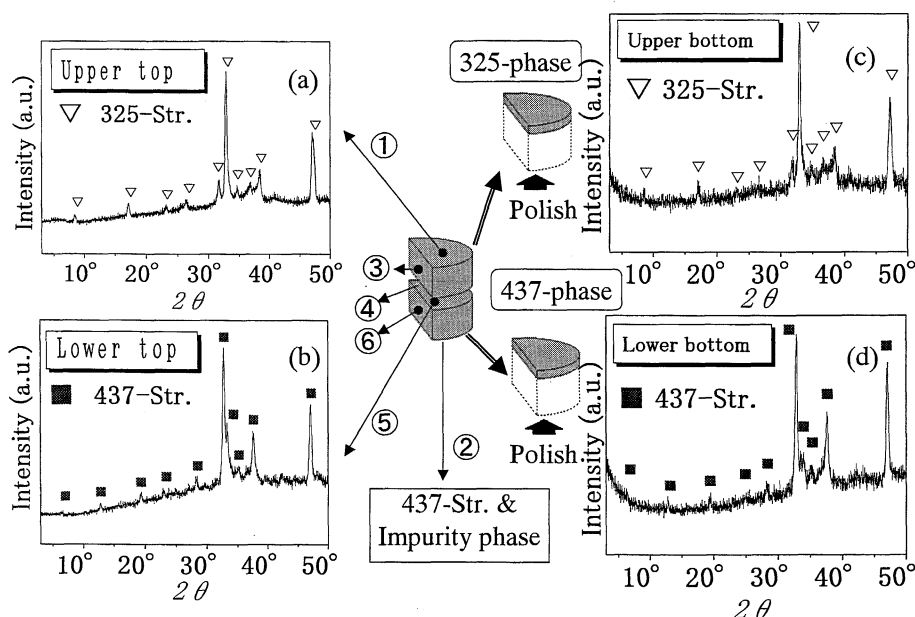


Fig. 3 X-ray diffraction patterns of the respective top and bottom surfaces of the upper and lower parts of the $(\text{Sr}_{0.7}\text{Ca}_{0.3})_3\text{Cu}_2\text{O}_{5.3}$ sample.

pattern almost showed a single phase of 325-type structure, but (004) peak of 437-type structure remained in the bottom of the polished sample. EPMA results for several points of the sample showed the ratio $(\text{Sr, Ca})/\text{Cu} \sim 1.5$. In the same way as the upper part, the 437-phase sample was gained by grinding the lower part of the sample from the bottom. The grinding was continued until the X-ray pattern of the bottom agreed with that of the lower top surface. The X-ray spectrum almost showed a 437-phase, but involved a little peak of 4610-phase. EPMA results showed the ratio $(\text{Sr, Ca})/\text{Cu} = 0.66\text{--}1.33$. The DC magnetic susceptibility was measured for these samples on warming in an applied field of 10 Oe after zero field cooling (Fig. 4(a)), and the electrical resistivity was measured by the usual four-terminal method (Fig. 4(b)).

4. Discussion and Conclusion

The synthesized sample of $(\text{Sr}_{0.7}\text{Ca}_{0.3})_3\text{Cu}_2\text{O}_{5.3}$ had the segregations of the 325-type structure phase in the upper part and the 437-type structure in the lower part. These segregations resulted from the temperature distribution in the sample. For the thermocouple passing through the cell as shown in Fig. 1, the Pt capsule center in the cell was above (or did not coincide with) the center of the carbon heater where the temperature was estimated to be the highest. This configuration was considered to make the temperature of the lower part higher than that of the upper part. The segregations were separated by grinding, and then a 325-type single phase sample and a 437-type single phase sample were gained. For the case of 325-phase, the magnetic susceptibility data showed $T_c = 106\text{ K}$, volume fraction = 32.8%, and the electrical resistivity measurement showed the superconducting transition at 106 K (Figs. 5(a), (b)). For the case of 437-phase, the magnetic susceptibility data showed $T_c = 110\text{ K}$, volume fraction = 29.4%, and the electrical resistivity measurement showed the superconducting transition at 110 K (Figs. 5(a), (b)).

The 325-type structure and the 437-type structure contain pyramid type CuO_2 layers with apical oxygen. These structures are similar to that of the cuprate superconductor of the Bi-system and the Tl-system. The superconductivity of the sample with 325-type and 437-type structure was observed. The small fraction superconductivity of IL structure samples, which was previously reported,⁴⁾ might be attributed to small fractions of $(\text{Sr}_{0.7}\text{Ca}_{0.3})_3\text{Cu}_2\text{O}_5$ and $(\text{Sr}_{0.7}\text{Ca}_{0.3})_4\text{Cu}_3\text{O}_7$. We conclude that the materials with the structure containing many CuO_2 layers without apical oxygen like the IL structure (Fig. 4) do not develop superconductivity. This conclusion is consistent with that of H. Shaked *et al.*,⁸⁾ who did not recognize the superconductivity of the IL structure except electron doped superconductivity.

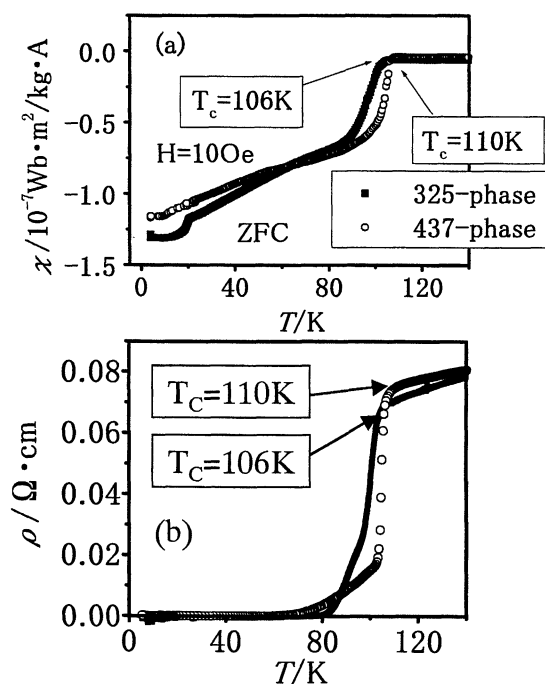


Fig. 5 Zero field cooled dc magnetic susceptibility and electrical resistivity as a function of temperature for the 325-phase and the 437-phase of the $(\text{Sr}_{0.7}\text{Ca}_{0.3})_3\text{Cu}_2\text{O}_{5.3}$ sample.

Acknowledgments

The authors would like to thank A. Matsumuro (of the University of Nagoya) for his helpful advice concerning high-pressure synthesis.

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