Synthesis and Structural Study of $Sr_2CuO_{3+\delta}$ Superconductor under High Pressure *

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A single-phase $Sr_2CuO_{3+\delta}$ superconductor is synthesized under high temperature and high pressure, in which oxygen atoms only partially occupy the apical sites next to the CuO_2 planes and act as hole-dopants. The superconducting transition temperature with $T_c^{\max} = 75\,K$ is achieved in the material. Structure analysis from x-ray powder diffraction data show that this material crystallizes into a K_2NiF_4 structure with tetragonal unit cell of $a = 3.795(3)$ Å and $c = 12.507(1)$ Å. Energy-dispersive synchrotron x-ray-diffraction studies at ambient are performed on powder samples of $Sr_2CuO_{3+\delta}$ in a diamond-anvil cell at pressure up to 35 GPa. Anisotropic compressibility is found. Pressure-induced isostructural phase transition might exist as revealed by the discontinuous change of crystal cell volume V with pressure.

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Pressure tuning is a very powerful tool to search for novel HTS materials or to improve their physical properties.[1−11] It is well known that the superconducting transition temperature T_c of layered cooper oxides can be tuned by the application of high pressure. For example, T_c of Hg1223 increases from 134 K at ambient pressure to 164 K at above 30 GPa.[5] Sr-Cu-O system superconductors have been raising intensive interests since it contains only Sr and Cu cations and displays high T_c superconductivity. At ambient pressure, the stoichiometric Sr_2CuO_3 forms an orthorhombic structure with Cu-O chains along the a-axis.[12] Introducing extra O by applying high pressures leads to the formation of a K_2NiF_4-type tetragonal structure containing a CuO_2 plane as shown in Fig. 1. The $Sr_2CuO_{3+\delta}$ superconductor synthesized under high pressure is quite a unique cuprate which crystallizes into an oxygen-deficient La_2CuO_4 (i.e. K_2NiF_4) structure with partially occupied apical sites (Fig. 1), and the apical oxygen acts as hole dopant.[8−12] Using SrO_2 as an oxidizer, we have succeeded in fabricating the tetragonal single-phase $Sr_2CuO_{3+\delta}$ showing superconductivity at $T_c = 75$ K and T_c was enhanced about 95 K by post annealing.[13] The effect of the heat treatment at different temperatures on the structure and superconducting properties has been systematically studied. It is found that a remarkable enhancement of T_c in this superconductor is associated with the ordering of the apical oxygen atoms, not with a change of doped hole density as reported in Ref. [11]. It is worthwhile to study in detail the structure change under pressure in the $Sr_2CuO_{3+\delta}$ superconductor. This will deliver additional information about the axis and volume compressibility. Furthermore, the investigation of pressure induced structural change may give an insight into the effect of applied pressure on the magnetic and electronic properties of this material.

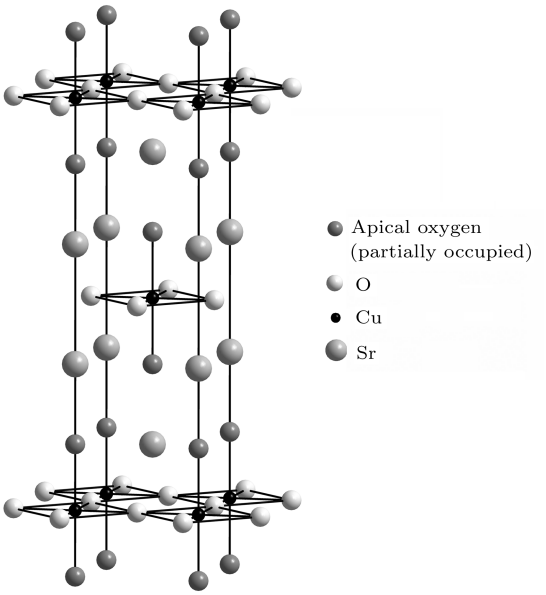

Fig. 1. Schematic view of the crystal structure of Sr_2CuO_{3+}. with K_2NiF_4-type tetragonal structure containing the CuO_2 plane, but the apical oxygen are partially occupied.

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High-pressure synthesis of $Sr_2CuO_{3+\delta}$ superconducting samples was performed using a cubic-anvil-type apparatus. The details of the present route have been described elsewhere.[11] Sr_2CuO_3, SrO_2, and CuO were mixed in a balanced way according to the nominal composition $Sr_2CuO_{3+\delta}$ at various molar ratios in a dry glove box. The materials were then subjected to high-pressure synthesis under 6 GPa at 1100°C for 1 h. Crystal structure was analysed by means of XRD using Cu $K\alpha$ radiation. The dc magnetic susceptibility was measured with a SQUID magnetometer in an external magnetic field of 20 Oe. The in-site high pressure x-ray energy dispersive diffraction experiment on $Sr_2CuO_{3+\delta}$ sample was carried out at room temperature in a diamond anvil cell at Beijing Synchrotron Radiation Facility (BSRF). The culet of diamond is 500 μm in diameter and the hole in a T301 stainless steel gasket is 250 μm in diameter. The powder sample is loaded into the hole in the gasket and platinum powder is covered with the sample as an inner pressure standard.

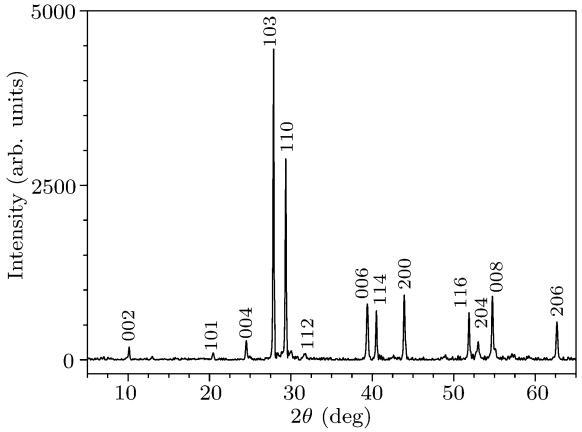

Fig. 2. X-ray powder diffraction pattern for the sample $Sr_2CuO_{3+\delta}$ with nominal $\delta = 0.4$.

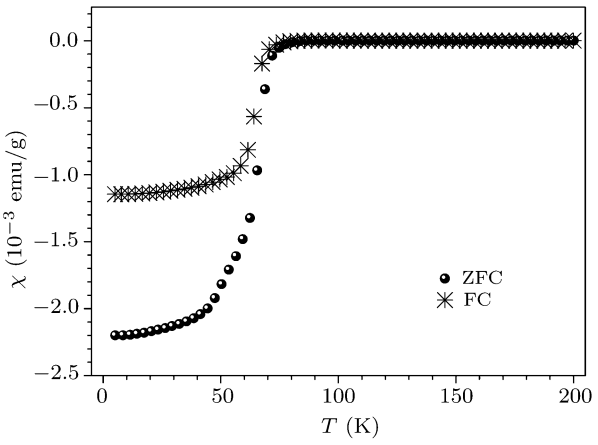

Fig. 3. Temperature dependence of the dc magnetic susceptibility in both the zero-field-cooling and field-cooling modes for as-prepared $Sr_2CuO_{3+\delta}$.

A series of $Sr_2CuO_{3+\delta}$ samples were prepared under high-pressures by changing the initial amount of SrO_2. The superconducting phase was found in the range $0.1 < \delta < 0.6$ and a maximum $T_c \approx 75$ K occurs at $\delta = 0.4$ as shown in Fig. 3. Figure 2 presents the x-ray diffraction pattern of $Sr_2CuO_{3+\delta}$ ($\delta = 0.4$) with tetragonal structure (space group $I4/mmm$), indicating an apparent single-phase pattern with lattice parameters $a = 3.795(3)$ Å, $c = 12.507(1)$ Å.

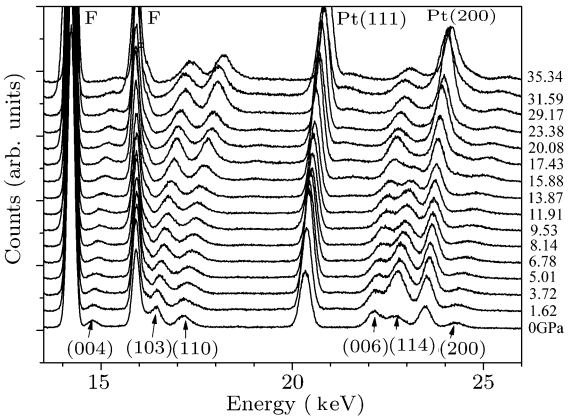

Fig. 4. Energy dispersive x-ray diffraction spectra for the $Sr_2CuO_{3+\delta}$ sample at room temperature.

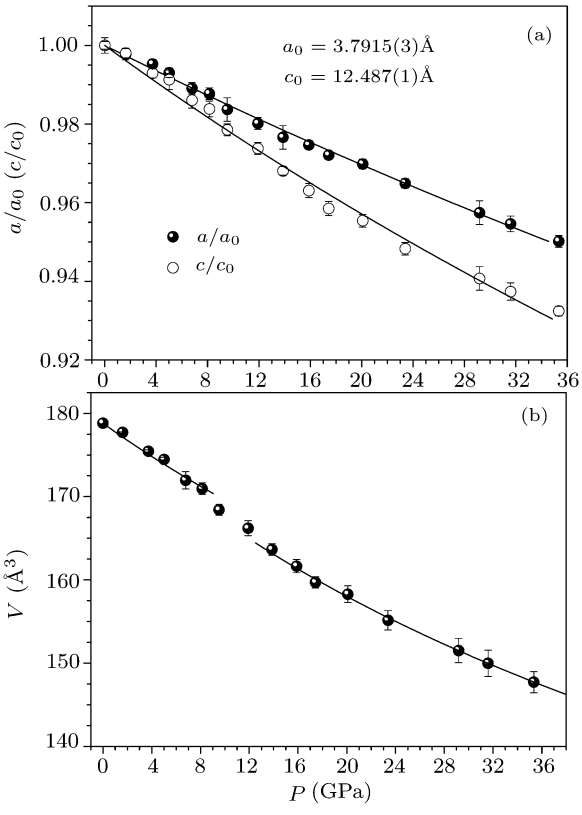

Fig. 5. Lattice parameters and volume versus pressure for the $Sr_2CuO_{3+\delta}$ sample.

The energy-dispersive x-ray diffraction patterns at fixed angle were collected at Beijing Synchrotron Radiation Facility (BSRF). Diffraction peaks agreed well with powder-diffraction patterns of the tetragonal unit cell as shown in Fig. 2. All diffraction peaks except fluorescence peaks shift to higher-energy with increasing pressure as shown in Fig. 4. When pressure returns to ambient pressure, the peaks almost recover their original sites. In addition, the intensity of some diffraction peaks such as (114) is strong with increasing pressure below 11 GPa, while vanishes with pressure above 15 GPa, showing novel change in crystal structure. The relationships of lattice parameters and volume versus pressure for the $Sr_2CuO_{3+\delta}$ sample are shown in Figs. 5(a) and 5(b). It can be clearly seen in Fig. 5(a) that the crystal lattice is anisotropically compressed. The crystal structure of $Sr_2CuO_{3+\delta}$ is significantly distorted from ideal geometry under high pressure due to partially occupied apical oxygen. The unusual change of some diffraction peaks such as (114) with pressure might originate from the lattice distortion caused by the anisotropic compression of the unit cell, and it is also resulted from the possible structural transition in $Sr_2CuO_{3+\delta}$ sample. From Fig. 5(b), it is found that the changes of volumes below 8 GPa and above 13 GPa are different, which is possibly due to the isostructural phase transition in the $Sr_2CuO_{3+\delta}$ sample. Fitting the data to the Birch–Murnaghan equation,

$$P(\mathrm{GPa}) = \frac{3}{2} \times B_0 \times \left[\left(\frac{V_0}{V}\right)^{\frac{7}{3}} - \left(\frac{V_0}{V}\right)^{\frac{5}{3}}\right] \times \left\{1 - \left(3 - \frac{3}{4} \times B_0'\right) \times \left[\left(\frac{V_0}{V}\right)^{2/3} - 1\right]\right\}.$$

Here the pressure derivative $B_0' = 4$, the bulk modulus $B_0 = 169$ GPa below 8 GPa, and $B_0 = 126$ GPa above 13 GPa are obtained. The structure type has no change in the whole pressure region, while the volume has a discontinuity with pressure, which indicates the gradual phase transition process resulting from the electronic structure phase transition. The changes of electronic structure could induce the changes of the crystal structure, which contributes to the isostructural phase transition. However, we could not obtain more information of the phase transition on $Sr_2CuO_{3+\delta}$ samples from our XRD patterns. The detailed structure study is needed based on more accurate high pressure angle resolved x-ray or neutron experiments.

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