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LETTER TO THE EDITOR

High-Temperature X-Ray Diffraction Study on Stability of the Infinite-Layer $SrCuO_2$

Xingjiang Zhou, Cheng Dong, Fei Wu, Hong Chen, Guangcan Che, Yushu Yao, and Zhongxian Zhao

National Laboratory for Superconductivity, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China

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The stability of the infinite-layer $SrCuO_2$ upon heating in air has been investigated by high-temperature X-ray diffraction. Above 300°C the infinite-layer $SrCuO_2$ reacted gradually with CO_2 in air to form $SrCO_3$; at a temperature over 400°C, the infinite-layer $SrCuO_2$ transformed into orthorhombic $SrCuO_2$, with an abrupt decrease of the amount of the infinite-layer phase in the sample. The lattice parameters *a* and *c* of the infinite-layer $SrCuO_2$ showed different thermal expansion coefficients, i.e., $da/dT = 3.329 \times 10^{-5}$ and $dc/dT = 5.801 \times 10^{-5}$ Å/°C. © 1994 Academic Press, Inc.

INTRODUCTION

At ambient pressure, $SrCuO_2$ crystallizes into an orthorhombic structure consisting of double edge-sharing Cu–O chains (1). This orthorhombic $SrCuO_2$ transforms at high pressure into the tetragonal infinite-layer phase, which consists of infinite stacking of CuO_2 layers separated only by the alkaline earth ions (Sr^{2+}) (2). Starting from the parent infinite-layer compound $SrCuO_2$, superconductivity has been realized under high pressure by partially replacing Sr^{2+} with trivalent ions (3–5) or by introducing vacancies into the Sr site (6–8). The investigation of the infinite-layer superconductors has aroused much interest due to their unique properties and possessing the simplest structures of all the high-temperature cuprate superconductors.

The infinite-layer $SrCuO_2$ is high-pressure phase metastable. At ambient pressure, one may expect the tetragonal infinite-layer $SrCuO_2$ phase to become unstable at high temperature. In the present paper, we report on the stability of the infinite-layer $SrCuO_2$ phase upon heating in air as determined by differential thermal analysis (DTA) and high-temperature X-ray diffraction.

EXPERIMENTAL

The samples were prepared from appropriate amounts of $SrCO_3$ and CuO mixed and calcined at 960°C for 48 hr with an intermediate grinding. X-ray diffraction analysis indicated that the calcined powder with the composition $SrCuO_2$ consisted of a single orthorhombic $SrCuO_2$ phase. The calcined powder was then pressed into pellets with a diameter of 8 mm and a thickness of 4 mm. The pellets wrapped with silver foil were finally treated under a pressure of 3.5 GPa at 800–1100°C for 30–45 min in a belt apparatus. A detailed description of the synthesis and superconductivity of the infinite-layer $Sr_{1-x}CuO_2$ is reported elsewhere (9).

Nearly single-phase samples of infinite-layer $SrCuO_2$ could be obtained at lower annealing temperatures under high pressure. These samples were ground into powders and used for differential thermal analysis and high-temperature X-ray diffraction. A DTA of both the infinite-layer and the orthorhombic $SrCuO_2$ samples was carried out in air at a heating rate of 10°C per minute with Al_2O_3 as the standard. For the high-temperature X-ray diffraction analysis, the fine powder was pressed into a pellet with a diameter of 14 mm and a thickness of 1 mm. Then the pellet was attached to a nickel support by a high-temperature cement and inserted into the sample chamber of the high-temperature attachment for the X-ray diffractometer (MXP18A-HF type). The heating rate of the sample was 5–10°C per minute between room temperature and 700°C, holding 5 min at a given temperature before the X-ray diffraction pattern of the sample was collected.

RESULTS AND DISCUSSION

Figure 1 shows the DTA curves of the infinite-layer $SrCuO_2$ and the orthorhombic $SrCuO_2$. The infinite-layer $SrCuO_2$ shows two extra peaks, one at 423°C and the other at 1034°C. The peak at 423°C is exothermic, while the peak at 1034°C is endothermic. At ambient pressure, transformation of the infinite-layer $SrCuO_2$ can be expected to give off heat, and the peak at 423°C may correspond to the destabilization of the infinite-layer $SrCuO_2$.

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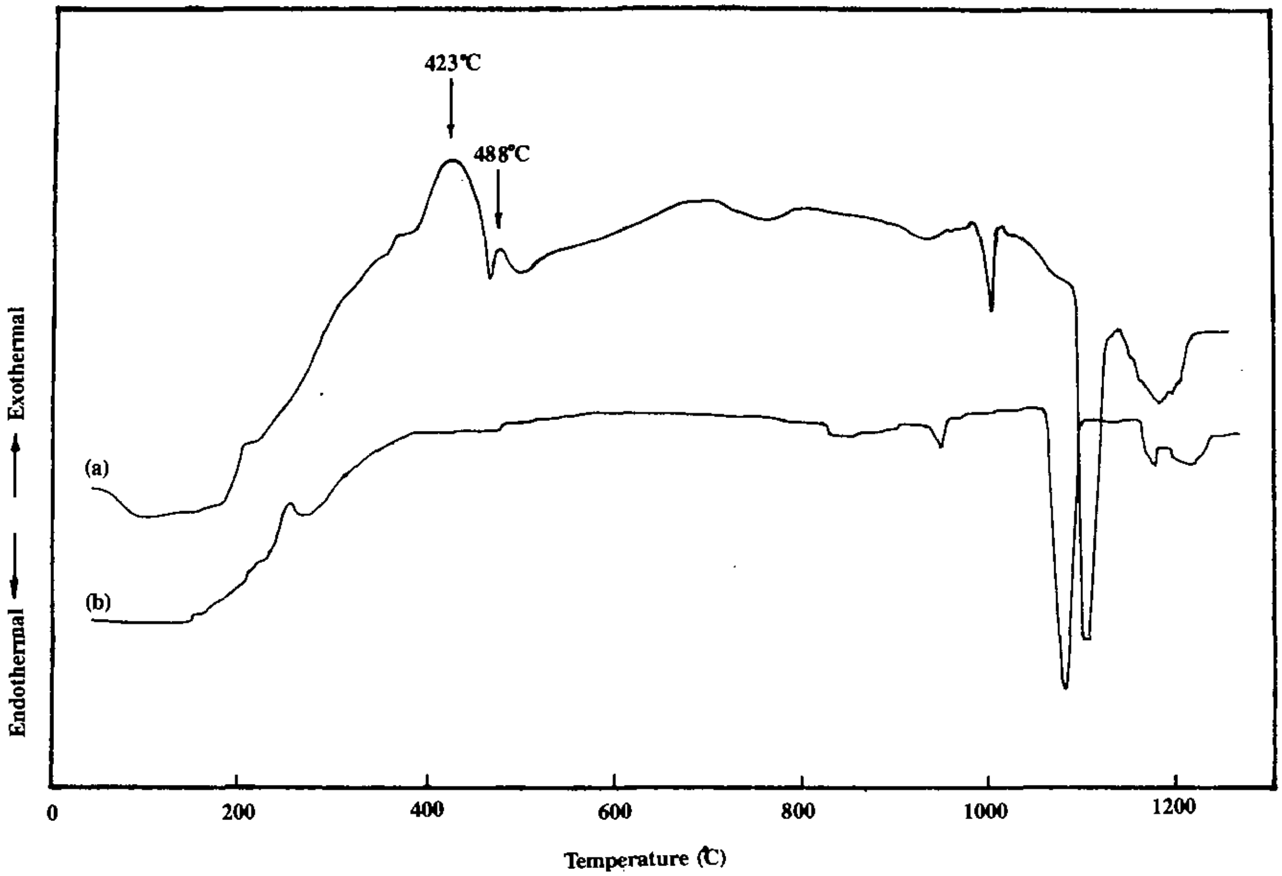

FIG. 1. DTA curves for (a) the infinite-layer $SrCuO_2$ and (b) orthorhombic $SrCuO_2$.

Figure 2a shows the X-ray diffraction profiles of the infinite-layer $SrCuO_2$ taken at various temperatures between room temperature and 700°C in air. It is clear that the as-prepared sample consists of a nearly single infinite-layer $SrCuO_2$ phase with its corresponding peaks indexed in the figure. The expanded view of the (002) peak of the infinite-layer $SrCuO_2$ at different temperatures is also included in Fig. 2b, which clearly shows the peak position shift and the amount change of the infinite-layer phase with temperature. The diffraction profiles of the sample showed no obvious change between room temperature and 300°C. At 300°C, new peaks appeared in the diffraction pattern, and above 400°C these peaks became remarkable. These new peaks can be attributed to the formation of $SrCO_3$. As the temperature was increased further to 500°C, a new phase other than $SrCO_3$ appeared, which was indexed to the orthorhombic $SrCuO_2$ phase. The amount of the infinite-layer phase in the sample decreased abruptly with increasing temperature above 400°C, and at 600°C the infinite-layer phase in the sample had almost disappeared completely.

Figure 3 shows the variation of the lattice parameter and unit-cell volume of the infinite-layer $SrCuO_2$ between room temperature and 600°C. It is clear that between

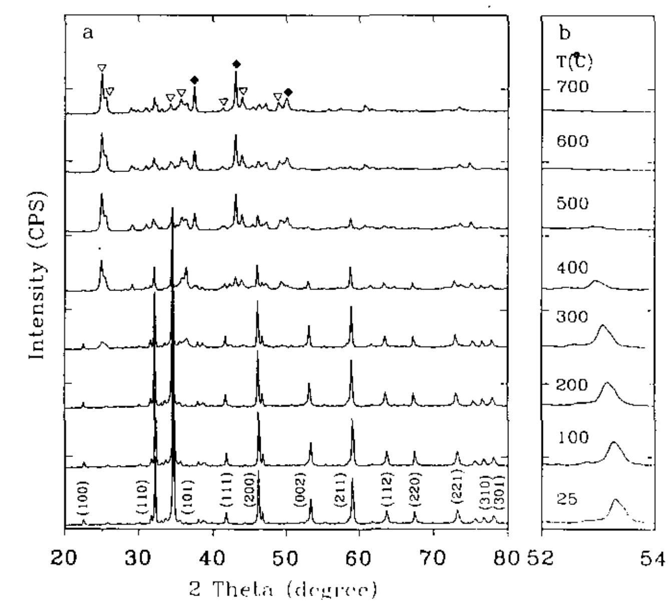

FIG. 2. (a) X-ray diffraction patterns of the infinite-layer $SrCuO_2$ sample taken at different temperatures. The infinite-layer phase has been indexed. (∇) represents $SrCO_3$ and (♦) orthorhombic $SrCuO_2$. (b) Expanded view of the (002) peak of the infinite-layer $SrCuO_2$ at different temperatures.

room temperature and 400°C the lattice parameters a and c and the corresponding cell volume all increase linearly with temperature. The least-squares fit of the lattice parameters a and c with temperature leads to $a = 3.392 \times 10^{-5} T + 3.926$ and $c = 5.801 \times 10^{-5} T + 3.3430$, in which the units of the lattice parameters and temperature are Å and °C, respectively; the expansion coefficient of c is larger than that of a. Above 400°C, the variation with temperature of the lattice parameters a and c of the infinite-layer phase deviates obviously from linear.

From Fig. 2, it has been shown that the infinite-layer $SrCuO_2$ first reacted with CO_2 in air to form $SrCO_3$. This reaction should accompany another Cu-enriched phase to keep the balance between strontium and copper in the sample. At ambient pressure, besides SrO and CuO, there are three known phases present in the SrO–CuO system, i.e., orthorhombic $SrCuO_2$, Sr_2CuO_3, and $Sr_{14}Cu_{24}O_{41}$ (10). Considering the effect of CO_2 in air, two new phases, $SrCO_3$ and $Sr_2CuO_2(CO_3)$ (11), may be formed. Among all these known compounds only CuO and $Sr_{14}Cu_{24}O_{41}$ represent Cu-enriched phases. However, it is difficult to identify CuO or $Sr_{14}Cu_{24}O_{41}$ from Fig. 2. We think that the reaction process of $SrCuO_2$ (infinite-layer) + CO_2 = $SrCO_3$ + CuO is the more probable case. The absence of the CuO peaks may indicate that the reaction product CuO was not well crystallized.

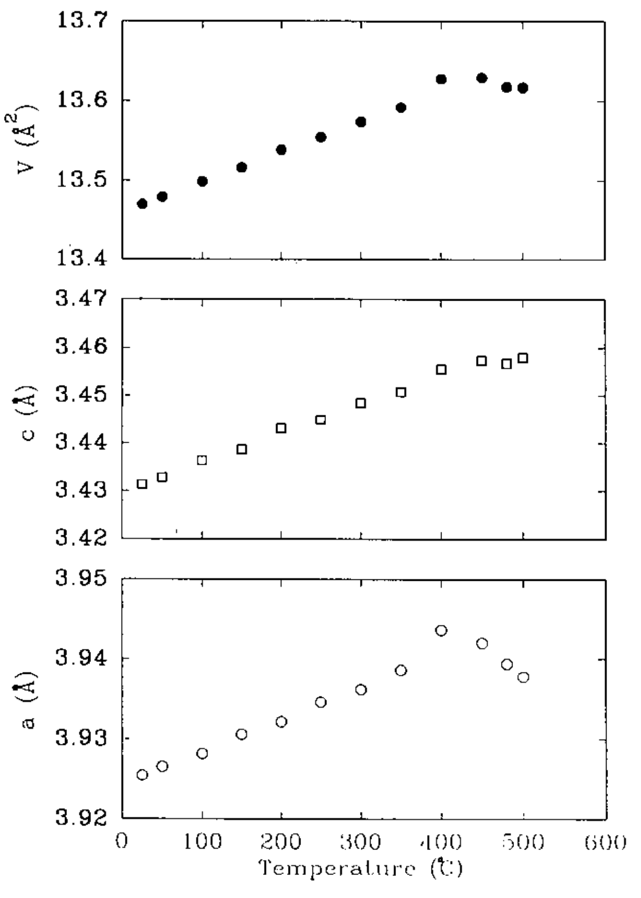

FIG. 3. Variation of the lattice parameters and the cell volume of the infinite-layer $SrCuO_2$ with temperature.

From Fig. 2, the phase transformation of the infinite-layer $SrCuO_2$ to orthorhombic $SrCuO_2$ became remarkable at 400°C. As seen from Fig. 3, the lattice parameter change of the infinite-layer $SrCuO_2$ with temperature also indicated that the infinite-layer structure became unstable at temperatures over 400°C. The infinite-layer structure of $SrCuO_2$ itself would therefore appear to be stable until 400°C if no CO_2 is present around the sample. The existence of air led the infinite-layer $SrCuO_2$ first to react with CO_2 at 300°C before it transformed into the orthorhombic phase at higher temperature.

The DTA result of the infinite-layer $SrCuO_2$, Fig. 1, is clarified by the high-temperature X-ray analysis. The broad exothermic peak between 300 and 423°C represents the reaction of the infinite-layer $SrCuO_2$ with CO_2 in air. The small exothermic peak near 488°C corresponds to the transformation of the infinite-layer $SrCuO_2$ to orthorhombic $SrCuO_2$. The endothermic peak at 1034°C may correspond to the reaction of $SrCO_3$ and CuO in the sample to form orthorhombic $SrCuO_2$. Above 1034°C, the sample would seem to consist of a single orthorhombic $SrCuO_2$ phase because the DTA curves for the infinite-layer $SrCuO_2$ and orthorhombic $SrCuO_2$ at higher temperature become similar.

In summary, at ambient pressure the tetragonal infinite-layer $SrCuO_2$ phase formed at high pressure transforms above 400°C to the orthorhombic $SrCuO_2$ phase. However, in air the infinite-layer $SrCuO_2$ begins to react above 300°C with CO_2 to decompose into $SrCO_3$ and an amorphous copper-rich phase. This reaction appears to broaden the temperature range over which the tetragonal–orthorhombic transition occurs.

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