

## HIGH PRESSURE SYNTHESIS AND SUPERCONDUCTIVITY OF $\text{Sr}_2\text{CuO}_{2+\delta}\text{Cl}_{2-y}$ BY APICAL OXYGEN DOPING

Q. Q. LIU, C. Q. JIN\*, Y. YU, F. Y. LI, Z. X. LIU and R. C. YU

*Institute of Physics, Chinese Academy of Sciences,  
P. O. Box 603, Beijing 100080, China  
\*cqjin@aphy.iphy.ac.cn*

Using the apical oxygen doping mechanism, i.e. a partial substitution of divalence O for the monovalence Cl, a p-type copper oxychloride superconductor,  $\text{Sr}_2\text{CuO}_{2+\delta}\text{Cl}_{2-y}$ , was synthesized at 1050 °C under 6.0 GPa for 1h. The X-ray powder diffractions show that the main phase has a tetragonal structure with  $a=3.93\text{Å}$ ,  $c=15.65\text{Å}$ . The magnetic susceptibility as well as resistance measurements indicated that the bulk superconducting transition temperature of the sample is 30K.

*Keywords:* High-pressure;  $\text{Sr}_2\text{CuO}_{2+\delta}\text{Cl}_{2-y}$  superconductor; apical oxygen doping.

### 1. Introduction

Intensive efforts have been made in studying the apical oxygen of cuprate superconductors.<sup>1</sup> The novel superconducting homologous series  $\text{Cl-02(n-1)n}$  provide an ideal system in which a partial substitution of the divalent  $\text{O}^{2-}$  for the monovalent  $\text{Cl}^{1-}$ , namely by “apical oxygen doping”, could take place under high pressure synthesis.<sup>2</sup> On the other hand, the  $(\text{Sr,Ca})_2\text{CuO}_2\text{Cl}_2$  compounds are single  $[\text{CuO}_2]$  layer cuprates which is more simple to study the role of apical oxygen in HTSC. So investigation of these materials may provide an important clue to understand high  $T_c$  superconducting mechanism.

Here, we report the high pressure synthesis of  $\text{Sr}_2\text{CuO}_{2+\delta}\text{Cl}_{2-y}$  superconductor induced by using the apical oxygen doping mechanism under a high temperature and high pressure condition. Their structure and superconductivity were measured. Superconductivity at  $T_c=30\text{K}$  was observed.

### 2. Experimental Details

The samples were synthesized in two steps. Firstly, the precursors  $\text{Sr}_2\text{CuO}_3$ ,  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$  were prepared by solid-state reaction from the mixture  $\text{SrCO}_3$ ,  $\text{SrCl}_2$  and  $\text{CuO}$  powders (each 99.9% pure). Secondly, the precursors were mixed with  $\text{SrO}_2$  (99.9% pure) and  $\text{CuO}$  with the nominal composition of  $\text{Sr}_2\text{CuO}_{2+\delta}\text{Cl}_{2-y}$  in a dry environment. The materials were then subjected to high pressure synthesis

under 6GPa pressure and at 1050 °C for 1h using a cubic-anvil-type high pressure facility.

The structure of the samples was analyzed using X-ray powder diffraction. The lattice parameters of  $a$  and  $c$  axes were determined using a Rietveld analysis software (Winplotr). DC resistivity was measured by the standard four-probe method. The DC magnetic susceptibility was determined using a SQUID magnetometer at a 20 Oe applied field in both zero-field and field-cooling modes.

### 3. Results and Discussion

Figure 1 shows the XRD pattern for the  $\text{Sr}_2\text{CuO}_{2+\delta}\text{Cl}_{1.2}$  synthesized under high pressure. It was found that most of the peaks can be indexed into the tetragonal structure, essentially the same as that of the parent material  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ . We refined the cell parameters of the sample and yielded the lattice parameters  $a=3.9310(2)$  Å and  $c=15.6531(3)$  Å. As compared with the ambient pressure phase  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$  ( $a=3.9716(2)$  Å,  $c=15.6126(2)$  Å), the observed shrinkage in the  $a$ -axis should be resulted from the hole doping into the  $\text{CuO}_2$  planes. The increase of  $c$ -axis length can be explained by the expansion of the Sr-Cl rock-salt block due to enhanced Coulomb repulsion between the adjacent  $\text{Cl}^-$  layers resulted from the introduction of  $\text{O}^{2-}$ .

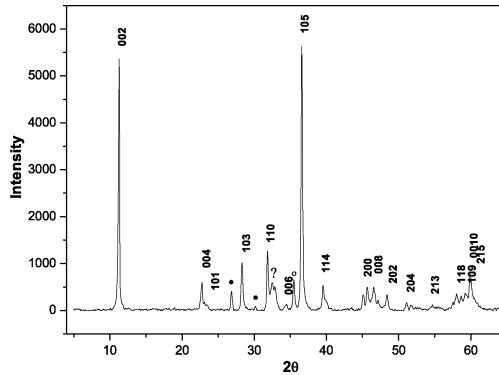


Fig. 1. X-ray powder diffraction pattern for the sample  $\text{Sr}_2\text{CuO}_{2+\delta}\text{Cl}_{1.2}$ . The major phase can be indexed into the Cl-0201 structure with  $a=3.93$  Å,  $c=15.65$  Å. The impurity phases were identified to be CuO (O),  $\text{SrCl}_2\cdot\text{Sr}(\text{OH})_2\cdot\text{H}_2\text{O}$ , and unknown phase(?).

Figure 2 and Fig.2 inset show the temperature dependence of the DC magnetic susceptibility and the electrical resistivity of  $\text{Sr}_2\text{CuO}_{2+\delta}\text{Cl}_{2-y}$ , respectively. A superconducting transition was clearly observed at  $T_c\sim 30$  K as shown in Fig.2 and 3. The FC data revealed a superconducting volume fraction  $\sim 10\%$  at about 10K.

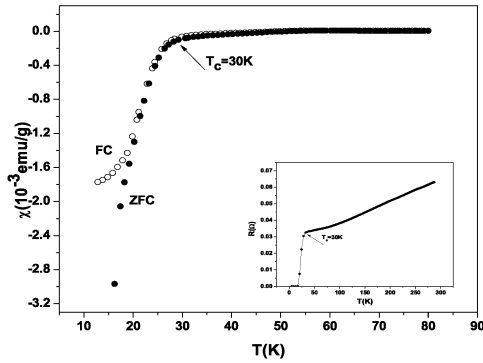


Fig. 2. Temperature dependence of the DC magnetic susceptibility of the sample in an applied external field of 200e. The calculated superconducting volume fraction according to the Meissner signal is  $\sim 10\%$ , indicating the bulk superconducting nature. Inset, resistivity as a function of temperature measured.

It is noted that the  $a$ -axis parameter of the sample is substantially larger than that of those for many hole-doped cuprate superconductors. However, the 0201-type  $Sr_2CuO_{2+\delta}Cl_{2-y}$  contained few oxygen vacancies (less than 5%), suggesting that the  $CuO_2$  sheet is rather perfect.<sup>3</sup> So it is crucial that the proper carriers have to be doped into the  $CuO_2$  sheets in order to induce superconductivity in the  $Sr_2CuO_{2+\delta}Cl_{2-y}$  sample. On the other hand, HRTEM and ED investigation on a large amount of crystals of the sample did not show the trace of other phases with the similar  $K_2NiF_4$  structure (unpublished). So it is likely that the observed 30 K bulk superconductivity is caused by the apical oxygen doped 0201 phase.

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## References

1. S. D. Conradson and I.D. Raistrick, *Science* 243 (1989) 1340
2. C.Q.Jin, X.J.Wu, P.Laffez, T.Tatsuki, T.Tamura, S.Adachi, H.Yamauchi, N.Koshizuka and S.Tanaka, *Nature* (London) 375 (1995) 301
3. T.Tatsuki, S.Adachi, T.Tamura, K.Tanabe, *Physica C* 306(1998) 67-74