Chinese Science Bulletin 2004 Vol. 49 No. 1 1—3

Structural phase transition of edge-sharing copper oxide $Ca_{0.85}CuO_2$ under high pressure

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Abstract **The perovskite-like structure compound $Ca_{0.85}CuO_2$ has interesting structural properties: it has infinite one-dimensional edge-sharing copper-oxygen chains as well as partial occupancy of the Ca sites resulting in an incommensurate superstructure. *In situ* high-pressure energy dispersive X-ray diffraction measurements on polycrystalline powder $Ca_{0.85}CuO_2$ have been performed by using diamond anvil cell (DAC) instrument with synchrotron radiation. The results for the first time show that edge-sharing copper oxide $Ca_{0.85}CuO_2$ undergoes a structural transition at 14.5GPa, and furthermore the structural transition is reversible.**

Keywords: **edge-sharing copper-oxygen chain, $Ca_{0.85}CuO_2$, synchrotron radiation, high pressure X-ray diffraction.**

DOI: 10.1360/03ww0085

In high-temperature copper-oxide superconductors (HTSC), the most common non-copper metal elements are alkali-earth metal elements (A): Ca, Sr and Ba. In order to seek new high-temperature superconductors with simple structures and to understand the fundamental structural properties of the copper-oxide superconductors, the study on the A-Cu-O seems especially important[1].

In Ca-Cu-O system, there are two kinds of infinite 1-D copper-oxygen chains made from $[CuO_4]$ squares: one is a corner-sharing chain as in Ca_2CuO_3; the other is an edge-sharing chain as in $Ca_{0.85}CuO_2$ which are studied in present work. The different copper-oxygen chains result in the different magnitudes in the Cu-O-Cu superexchange interaction. The different superexchange interaction causes different kinds of magnetic phenomena [2]. Even to the similar edge-sharing chain compounds, their properties are sensitive to the Cu-O-Cu angle θ. The nearest Cu-Cu interaction J_1 changes from the anti-ferromagnetism (AFM) to ferromagnetism (FM) when the angle θ is closer from 180° to 90°. For example, the nearest interaction J_1 is AFM for $CuGeO_3$ ($\theta=99°$), while it is FM for Li_2CuO_2 ($\theta=94°$) and $La_8Ca_6Cu_{24}O_{41}$ ($\theta=91°$)[3].

1-D copper-oxygen chains are widely regarded as a key to understand the mechanism of superconductivity of the CuO_2 planes. It has been earlier known that superconductivity of high-T_c copper-oxide superconductors takes place on the $[CuO_2]$ planes. While not long time ago, new superconductivity was found in the $[Cu_2O_3]$ ladder material under 3—3.5 GPa[4] and in the [CuO] double-chain material[5], suggesting that there is a rich mine of physics on the way from two-dimensional to one-dimensional systems.

In the 1990s, Siegrist et al. firstly found $Ca_{1-x}CuO_2$, that is, $Ca_{0.85}CuO_2$. In fact, it is a low-temperature phase and is structurally related to the $NaCuO_2$-type. It has an orthorhombic substructure with lattice parameters a_0= 0.2807 nm, b_0=0.6351 nm, c_0=1.0597 nm. The copper-oxygen chains are formed from edge-sharing $[CuO_4]$ squares (Fig. 1). Unlike $NaCuO_2$, the vacancies of Ca atoms in $Ca_{1-x}CuO_2$ result in the promotion of the chemical valence of the Cu, which makes a great impact on the electrical and magnetic properties of material. Later, it is found that x is about 0.15 for ambient pressure sample[7—9].

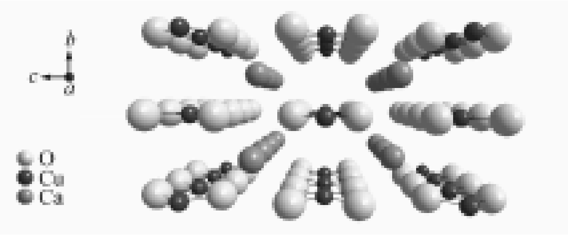

Fig. 1. A schematic representation of the crystal structure of $Ca_{0.85}CuO_2$.

High-pressure technology has been a powerful tool that is widely used in superconductivity research. High-pressure synthesis paves a very important route approaching HTSC and the related compounds. For example, the Cu-homologous series HTSC are synthesized under high pressure[10]. What's more, high pressure has a great impact on superconducting transition temperature. The highest record of T_c was obtained in $HgBa_2Ca_2Cu_3O_8$ under high pressure[11], and the spin ladder material only shows superconductivity when suitable pressure is applied[4]. The vacancies of the Ca atoms in $Ca_{0.85}CuO_2$ will probably increase relative structural instability and cause structural change under high pressure. If this really happens, the bond angle θ of copper-oxygen chains and the related properties of $Ca_{0.85}CuO_2$ should change simultaneously. Singh[12] suggested that the infinite-layer $[CaCuO_2]$ structure, which is the most important to HTSC, might appear when $Ca_{0.85}CuO_2$ is applied under sufficient pressure. The advanced research on $Ca_{0.85}CuO_2$ with high-pressure technique should help to not only understand the complicate properties of the copper-oxygen chain in $Ca_{0.85}CuO_2$, but also seek the mechanism of high-temperature superconductivity and the new HTSC.

We have studied on the stability of $Ca_{0.85}CuO_2$ under high temperature and high pressure, and found that it is relatively stable between the range 890℃—1130℃ and 3.5—5 GPa[13]. In this work, the structural properties of $Ca_{0.85}CuO_2$ under high pressure are studied by using *in situ* high pressure energy dispersive X-ray diffraction experiment.

1 Experiment

The samples of $Ca_{1-x}CuO_2$ were prepared by the standard solid-state reaction method. The high-pure oxides CaO and CuO powders were pre-treated at 950℃ for 10 h, weighed and mixed in the desired proportions 0.85 : 1. Then they were ground in agate mortar for 0.5—1 h, and pressed into pellets. The samples wrapped in Ag foil were calcined in low oxygen pressure atmosphere (about 10 bars) at 750℃ for 24 h followed by a furnace quench. Fig. 2 shows the powder X-ray diffraction pattern (XRD), indicating that the sample is of a single-phase orthorhombic structure of $Ca_{0.85}CuO_2$. The four peaks marked by "*" originate from incommensurate ordering of the Ca^{2+} cations in the Ca channels.

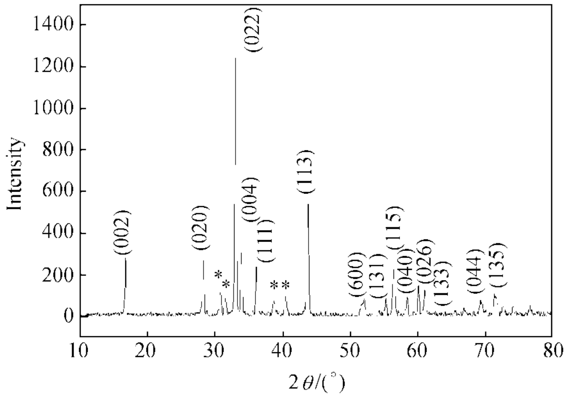

Fig. 2. The profile of XRD for $Ca_{0.85}CuO_2$ (the peaks marked by "*" originate from modulating peaks of the incommensurate superstructure of the sample).

The *in situ* high pressure energy dispersive X-ray diffraction experiment on $Ca_{0.85}CuO_2$ was carried out at room temperature in a diamond anvil cell (DAC) using the white-radiation light from the synchrotron radiation generator at the Beijing Synchrotron Radiation Laboratory (BSRL). The size of the X-ray spot was 120 μm×120 μm. The culet of the DAC was 500 μm. The powder of the sample was loaded, with the Pt powder as an inner pressure standard, into a 500 μm hole in a T301 stainless steel gasket. The internal pressure of the DAC was calculated according to the equation of state of Pt. In our experiments, the relation of energy and channel was $E=0.48611+0.00802\times chn$. According to the formula $\sin\theta=\frac{0.619925}{[d(\text{nm})\times E(\text{keV})]}$, we got the value of $\theta=8°$.

2 Results and discussion

The spectra of energy dispersive X-ray diffraction of the $Ca_{0.85}CuO_2$ sample under various pressures at room temperature are shown in Fig. 3. The two peaks of Pt were shown in the ambient pressure spectra, and we choose the stronger peak (111) of Pt to calculate the pressures applied on the sample. Besides the five strongest peaks of the sample (020) (022) (004) (111) (113), three of the four peaks that marked with "*" can also be observed and the undetected one overlaps with the Pt (111). From the spectra we can find that the structure of $Ca_{0.85}CuO_2$ remains stable up to 14.5GPa, and all diffraction peaks shift toward higher value except the three peaks originating from the incommensurate ordering of Ca, which becomes faint under high pressure, meaning that high pressure brings ruin to the incommensurate structure. The shift of (020) is the most obvious, and (022) moves faster than (004), so it catches up and overlaps with (004) at 3.37 GPa, suggesting that *b*-axis is relatively easier to be compressed comparing with *c*-axis.

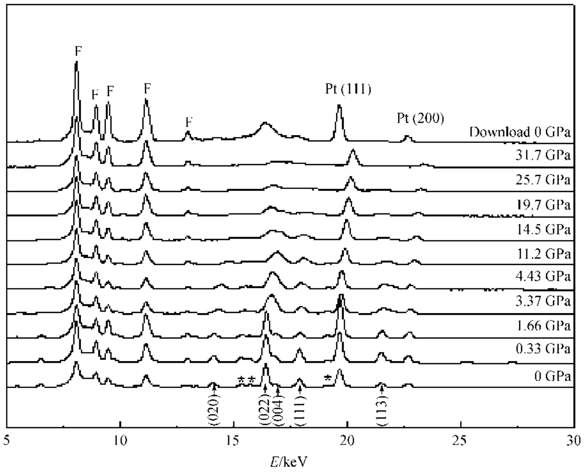

Fig. 3. Spectra of energy dispersive X-ray diffraction of $Ca_{0.85}CuO_2$ under different pressures.

Using the Birch-Murnaghan equation of state,

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

We have analyzed the data of volume compressibility versus pressure for $Ca_{0.85}CuO_2$. Assuming the first order derivative as B_0'=4, we obtain the bulk modulus B_0 =176.8 ±20.2 GPa. This value is comparable to that of ceramic copper oxides.

The main peak (022) splits into two peaks at pressure 14.5 GPa. From the strength, position and the later evolution, we think that there is a new diffraction peak on the low-energy site of (022). At the same time, the two peaks (111) and (113) abnormally shift a little toward the lower value, while the peak (020) continues moving to the higher value. The motions of diffraction peaks seem diverse at this pressure point, indicating a structural transition. When higher pressure is applied, all peaks normally continue to move toward higher values under higher pressure, and the new phase becomes dominant. In order to explain this phenomenon, we suggest that at 14.5 GPa, $Ca_{0.85}CuO_2$ changes into a high-pressure phase, whose lattice parameter "*c*" abnormally extends a little, causing the abnormal motions of (022)(111)(113) peaks.

When the pressure returns to ambient, almost all of the peaks come back to original sites. There is no sign of the high-pressure phase being quenched and it means that this pressure-induced transition is reversible. We did not see any trace of the infinite-layer [$CaCuO_2$] structure in the whole pressure range 0—34 GPa.

The recently joint high-pressure studies on corner-sharing copper-oxygen chain compound Ca_2CuO_3 showed that its structure was quite stable up to 34 GPa[14]. So the difference of structural properties of Ca_2CuO_3 and $Ca_{0.85}CuO_2$ under high pressure is obvious. Yet there is not enough evidence to decide whether the different copper-oxygen chains or the vacancies in Ca sites of $Ca_{0.85}CuO_2$ cause this difference. But we speculate that the structural transition under high pressure will probably reduce the angle θ, inducing the change from AFM to FM in the copper-oxygen chains, and in turn causing the great changes of its electrical and magnetic properties. So more advanced research into the $Ca_{0.85}CuO_2$ will help to understand the properties of the 1-D copper-oxygen chain compounds and the fundamental pictures of HSTC.

3 Conclusion

In summary, through *in situ* high-pressure synchrotron radiation measurements we have found that the edge-sharing copper-oxygen chain compound $Ca_{0.85}CuO_2$ is stable up to 14.5 GPa. According to the Birch-Murnaghan equation of state, assuming B_0'=4, the bulk modulus B_0=176.8±20.2 GPa has been obtained. At higher pressure, $Ca_{0.85}CuO_2$ experiences a structural transition. This transition is reversible, and ambient phase of $Ca_{0.85}CuO_2$ will appear again when the applied pressure is removed. The results are calling for the further study on the corresponding electrical and magnetic properties under high pressure, which will be conductive to understand the physical properties of the 1-D copper-oxygen chain compounds and the fundamental physical pictures of HTSC.

Acknowledgements This work was financially supported by the National Natural Science Foundation of China(Grant No. 50328102)and the State Key Development Project on Fundamental Research(Grant No.2002CB613301).

References

1. Kobayashi, N., Hiroi, Z., Takano, M., Compounds and phase relations in the SrO-CaO-CuO system under high pressure, J. Solid State Chem., 1997,132: 274—283.
2. Hayashi, A., Batlogg, B., Cava, R. J., $Ca_4Cu_5O_{10}$: copper oxide chains highly occupied by Zhang-rice singlets, Phys. Rev. B, 1998, 58: 2678—2683.
3. Mizuno, Y., Tohyama, T., Maekawa, S. et al., Electronic states and magnetic properties of edge-sharing Cu-O chains, Phys. Rev. B, 1998, 57: 5326—5335.
4. Uehara, M., Nagata, T., Akimitsu, J. et al., Superconductivity in the ladder material $Sr_{0.4}Ca_{13.6}Cu_{24}O_{41.84}$, J. Phys. Soc. Jpn., 1996, 65: 2764—2767.
5. Matsukawa, M., Yamada, Y., Chibe, M. et al., Double-chain superconductivity in perovskite copper-oxide with insulating CuO_2 plane, Cond-mat/0302508.
6. Roth, R. S., Rawn, C. J., Ritter, J. J. et al., Phase equilibria of the system SrO-CaO-CuO, J. Am. Ceram. Soc., 1989, 72: 1545—1549.
7. Siegrist, T., Roth, R. S., Rawn, C. J. et al., $Ca_{1-x}CuO$, a $NaCuO_2$-type related structure, Chem. Mater., 1990, 2: 192—194.
8. Babu, T. G. N., Greaves, C., The synthesis and structure of the new phase $Ca_{0.85}CuO_2$, Mat. Res. Bull., 1991, 26: 499—506.
9. Milat, O., van Tendeloo, G., , Amelinckx, S. et al., On the origin of the modulated structure in $Ca_{0.85}CuO_2$: An electron microscopy study, Solid State Comm., 1991, 79: 1059—1061.
10. Jin, C Q., Adachi, S., Wu, X. J. et al., 117 K superconductivity in the Ba-Ca-Cu-O system, Physica C, 1994, 223: 238—242.
11. Gao, L., Xue, Y. Y., Chu, C. W. et al., Superconductivity up to 164 K in $HgBa_2Ca_{m-1}Cu_mO_{2m+2+\delta}$, (*m*=1, 2 and 3) under quasihydrostatic pressures, Phys. Rev. B, 1994, 50:4260—4263.
12. Singh, K. K., Morris, D. E., Sinha, A. P. B., Stability of Ba, Sr and Ca cuprate phases as a function of oxygen pressure, Physica C, 1994, 231: 377—382.
13. Mai, W. J., The fabrication and stability of $Ca_{1-x}CuO_2$ chain structure under high pressure high temperature sintering (In preparation) .
14. Zhang, G. M., Mai,W. J., Li, F. Y. et al., The structure stability and electrical properties of the chain structure Ca_2CuO_3 under high pressure, Phys. Rev. B, 2003, 67: 212102(1-4) .

(Received May 9, 2003; accepted March 31,2004)