

High pressure effects on the crystal structure and electric conductivity of perovskite like $(\text{Ca}/\text{Sr})_2\text{CuO}_2\text{Cl}_2$ compounds

LIU QingQing^{1,2}, WANG FuRen¹, LI FengYing², CHEN LiangChen², YU RiCheng^{2†}, JIN ChangQing^{2†}, LI YanChun³ & LIU Jing³

¹ College of Physics, Peking University, Beijing 100871, China;

² Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China;

³ Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China

The crystal structure stability as well as electric conductance of $(\text{Sr}/\text{Ca})_2\text{CuO}_2\text{Cl}_2$ compound with K_2NiF_4 structure was investigated up to 31 GPa using diamond anvil technique. It seems that $(\text{Sr}/\text{Ca})_2\text{CuO}_2\text{Cl}_2$ is quite stable under pressure but with obvious anisotropic compressibility. The equation of state (EOS) obtained shows relative large bulk modulus.

high pressure effects, perovskite type compounds, synchrotron X-ray

High temperature superconductors (HTS) are a focus of study in the condensed matter physics. HTS crystallographically is a kind of perovskite derivation cuprate with CuO_2 plane being the central configuration. High pressure is favorable to stabilization of high density perovskites. Oxychloride cuprates have attracted much attention in recent years as ideal two-dimensional model system materials in the high T_c superconductors. Figure 1 shows the basic crystal structure of perovskite like $(\text{Ca}/\text{Sr})_2\text{CuO}_2\text{Cl}_2$ compound consisting of alternately stacked rock-salt A_2Cl_2 ($\text{A} = \text{Sr}, \text{Ca}$) block and CuO_2 layer. Larger Cl^- radius relative to O^{2-} causes longer c axis, which leads to weak couple between CuO_2 plane and charge reservoir block. The CuO_2 planes in this material become geometrically more two-dimensional due to the larger interlayer distance in the c -axis direction. This is more suitable for angle-resolved photoemission spectroscopy (ARPES) and tunneling scanning microscopy (STM) measurements^[1–3]. In addition, this kind of compound is a crucial precursor in developing novel superconducting materials^[4–8]. For instance, using “apical doping mechanism”, Jin et al. synthesized the oxychloride superconductor with $(\text{Ca}/\text{Sr})_2\text{CuO}_2\text{Cl}_2$ as pre-

cursors under high pressure. Therefore a study on the structure under high pressure is significant for exploring high temperature superconducting mechanism

1 Experimental

The $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ sample was synthesized in two steps. At the first step, the precursor SrCuO_2 was prepared by conventional solid state reaction method from the mixture SrCO_3 and CuO powders with purities higher than 99.9% for each raw material. The powder mixture in an appropriate ratio was ground in an agate mortar and then heated at 930°C in air for 24 h through intermediate grinding. At the second step, the precursor SrCuO_2 was mixed with SrCl_2 (99.9% pure) with a molar ratio of 1:1. These reactants were calcined in air at 950°C for 24 h via intermediate grinding. $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ is prepared by mixing appropriate quantities of CaCl_2 and CuO in agate

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†Corresponding author (email: JIN@aphy.iphy.ac.cn)

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mortar. These reactants were calcined in air at 800°C for 12 h, then reground and heated at 800°C for 24 h followed by furnace cooling to room temperature.

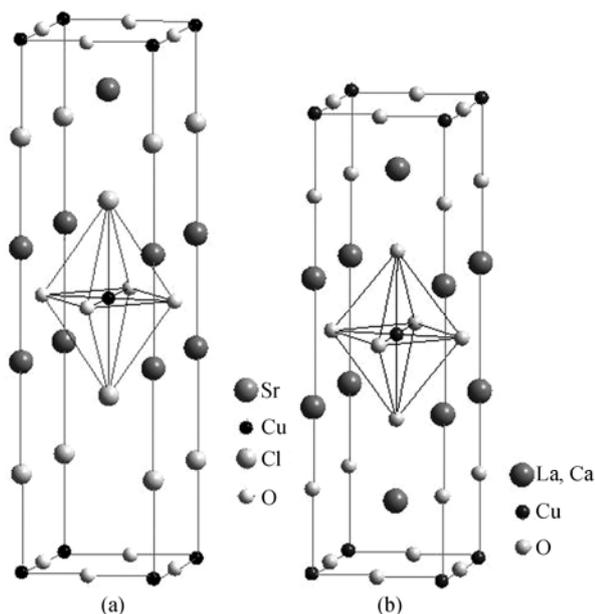


Figure 1 The schematic view of the crystal structure for $(\text{Ca/Sr})_2\text{CuO}_2\text{Cl}_2$ (a) and La_2CuO_4 (b).

The *in situ* high pressure X-ray energy dispersive diffraction experiments on $(\text{Ca/Sr})_2\text{CuO}_2\text{Cl}_2$ samples were carried out at room temperature in a diamond anvil cell at Beijing Synchrotron Radiation Facility (BSRF). The culet of diamond was 500 μm in diameter, and the hole in a T301 stainless steel gasket was 250 μm in diameter. The powder sample was loaded into the hole in the gasket, and platinum powder was covered with the sample

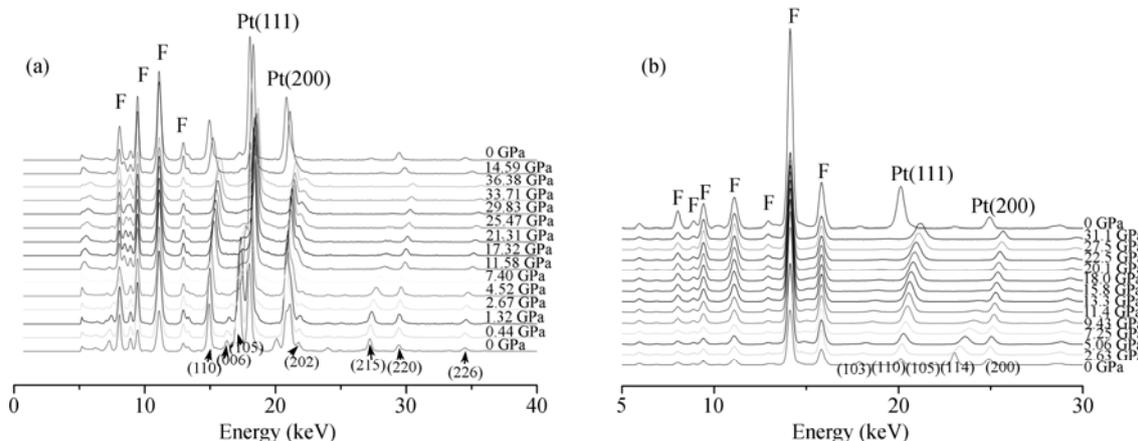


Figure 3 The spectra of energy dispersive X-ray diffraction for the samples of $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ (a) and $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ (b) at various pressures.

as an inner pressure standard. The relationship of electrical resistivity versus pressure was measured by the standard four-probe method.

2 Results and discussion

Figure 2 shows the XRD patterns for $(\text{Ca/Sr})_2\text{CuO}_2\text{Cl}_2$ samples. It is found from the X-ray analysis that the samples are in single-phase and have tetragonal structures with space group $I4/mmm$. The lattice parameters of $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ and $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ are $a=3.8659(1)$ \AA , $c=15.0428(2)$ \AA and $a=3.9728(2)$ \AA , $c=15.6206(4)$ \AA , respectively.

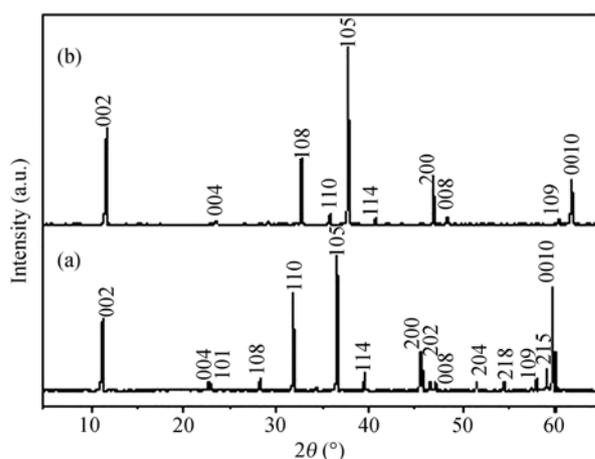


Figure 2 XRD patterns for $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ (a) and $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ (b).

Figure 3 presents the patterns of energy-dispersive of X-ray diffraction of $(\text{Ca/Sr})_2\text{CuO}_2\text{Cl}_2$ under different pressures. All diffraction peaks including two diffraction

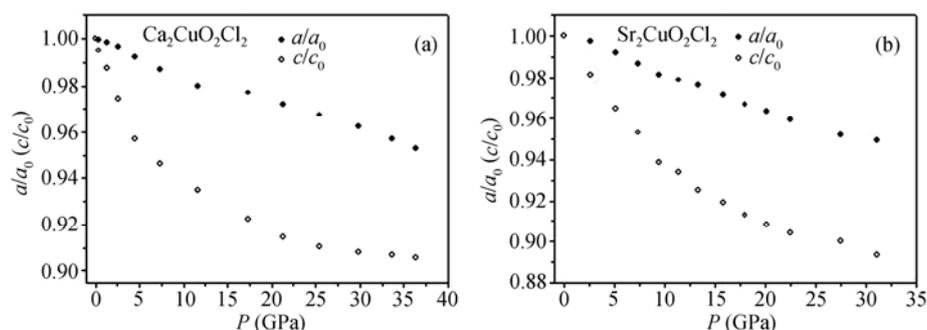


Figure 4 The relationship of lattice parameters a and c versus pressure for $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ (a) and $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ (b).

peaks of Pt and some diffraction peaks of samples, except fluorescence ones from Pt and samples at lower-energy side, shift to higher-energy with increasing pressure as shown in Figure 3. In addition, the intensity of samples peaks becomes weaker with increasing pressure except that the intensity of (110) peak in $(\text{Ca}/\text{Sr})_2\text{CuO}_2\text{Cl}_2$ samples has no obvious change. When pressure returns to ambient, the peaks recover to original sites. No new diffraction peaks appear in the whole energy spectra. Therefore it is inferred that the basic crystal structures of $(\text{Ca}/\text{Sr})_2\text{CuO}_2\text{Cl}_2$ samples keep stable in the whole experimental pressure range.

The lattice parameters and the volumes of $(\text{Ca}/\text{Sr})_2\text{CuO}_2\text{Cl}_2$ samples at different pressures were calculated using a least-squares program based on the main diffraction indices of the samples. The relationship of the lattice parameters a and c versus pressure for $(\text{Ca}/\text{Sr})_2\text{CuO}_2\text{Cl}_2$ samples is shown in Figure 4. It is found from Figure 4 that a and c axes show a distinct decrease with increasing pressure. The decrease of a axis could be caused by the reduction of $\text{Cu}-\text{O}$ bond length in the ab plane, while the decrease of c axis might be caused by the compression of $(\text{Ca}/\text{Sr})_2\text{Cl}_2$ rocksalt layers. However, as is evident in Figure 4, the crystal lattices are anisotropically compressed. Figure 5 shows V/V_0-P curves of $(\text{Ca}/\text{Sr})_2\text{CuO}_2\text{Cl}_2$ samples in the experimental pressure range. In Figure 5 the volumes of the unit cells decrease with increasing pressure. The experimental data are fitted by the Birch-Murnaghan equation:

$$P(\text{GPa}) = \frac{3}{2} \times B_0 \times \left[\left(\frac{V_0}{V} \right)^{\frac{7}{3}} - \left(\frac{V_0}{V} \right)^{\frac{5}{3}} \right] \times \left[1 - \left(3 - \frac{3}{4} \times B'_0 \right) \times \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right] \right]$$

While the first-order derivative $B'_0=4$, the bulk moduli are determined to be $B_0=(116.8 \pm 3.8)$ GPa for $\text{Ca}_2\text{CuO}_2\text{Cl}_2$, and $B_0=(86.5 \pm 1.3)$ GPa for $\text{Sr}_2\text{CuO}_2\text{Cl}_2$.

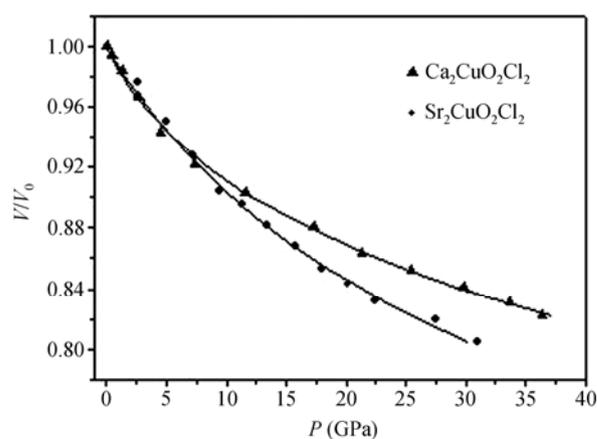


Figure 5 Curves of the volume compression versus pressure of the $(\text{Sr},\text{Ca})_2\text{CuO}_2\text{Cl}_2$.

Figure 6 shows the pressure dependence of resistance of $(\text{Ca}/\text{Sr})_2\text{CuO}_2\text{Cl}_2$ samples at room temperature. The resistance of $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ sample decreases gradually with increasing pressure as shown in Figure 6(a), which is considered as caused by the enhancement of the inter-grain connection. The resistance of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ sample drops steeply at about 2 GPa, then rises slowly in the pressure range up to 13 GPa, and finally decreases gradually at pressures from 13 to 20 GPa. Based on the analysis of the energy-dispersive X-ray diffraction results, the remarkable resistance changes of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ sample come from electronic structure changes which are considered to be caused by the compression of the crystal structure. However, more studies are necessary to further understand the nature physical properties in this kind of materials.

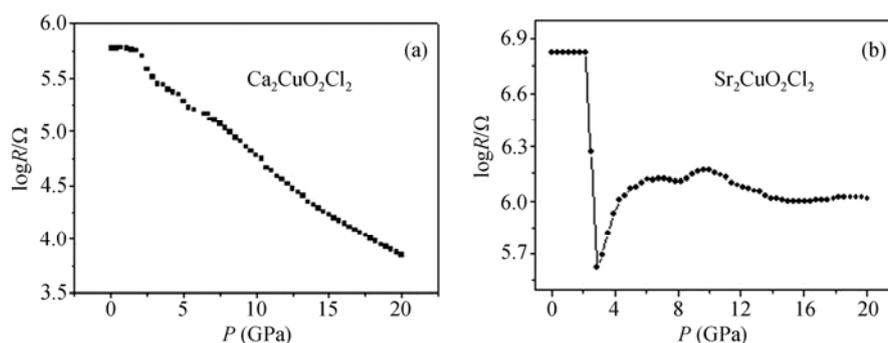


Figure 6 Relationships of the resistance versus pressure for $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ (a) and $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ (b).

3 Conclusion

The experimental results show that the crystal structure of $(\text{Ca}/\text{Sr})_2\text{CuO}_2\text{Cl}_2$ material is stable in the experimental pressure range. Assuming the pressure derivative $B'_0=4$, the bulk modula (116.8 ± 3.8) GPa for $\text{Ca}_2\text{CuO}_2\text{Cl}_2$

and (86.5 ± 1.3) GPa for $\text{Sr}_2\text{CuO}_2\text{Cl}_2$, respectively, are obtained. Abnormal resistance behavior for $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ sample was observed with increasing pressure, suggesting that an electronic structural transition may take place under pressure.

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