

## HIGH-PRESSURE STRUCTURE STUDY OF CuBa<sub>2</sub>Ca<sub>3</sub>Cu<sub>4</sub>O<sub>10+δ</sub> SUPERCONDUCTOR

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*In-situ* high-pressure energy dispersive X-ray diffraction measurements on CuBa<sub>2</sub>-Ca<sub>3</sub>Cu<sub>4</sub>O<sub>10+δ</sub> (Cu-1234) have been performed by using diamond anvil cell (DAC) device with synchrotron radiation. The results suggest that the crystal structure of Cu-1234 superconductor is stable under pressures up to 34 GPa at room temperature. According to the Birch–Murnaghan equation of state, the bulk modulus is obtained to be  $\sim 150$  GPa.

*Keywords:* Cu-1234 superconductor; synchrotron radiation; high-pressure energy dispersive X-ray diffraction.

### 1. Introduction

Cu-based superconducting homologous series have attracted much interest since they were discovered by using high pressure synthesis.<sup>1</sup> Because of their relatively high  $T_c$ , high  $J_c$  and high irreversible magnetic field  $H_{irr}$ ,<sup>2</sup> absence of toxic and volatile elements or rare and rare earth metals, they are more beneficial to the potential large-scale application of HTSC.

High pressure has been employed extensively in the study of high-temperature superconductivity, not only in synthesizing new superconducting materials like Cu-12( $n - 1$ )<sub>n</sub> superconductors and chlorine-contained superconductors (Sr,Ca)<sub>3</sub>Cu<sub>2</sub>O<sub>4+δ</sub>Cl<sub>2-y</sub>,<sup>3</sup> but also in improving  $T_c$ . In order to understand the physical origin of pressure-induced  $T_c$  increase, it is necessary to investigate the structure aspects for these superconductors under high pressure, such as to identify whether the crystal is stable.

In present work, we report the study on the structural stability of Cu-1234 superconductor under high pressures up to 34 GPa.

### 2. Experimental

The CuBa<sub>2</sub>Ca<sub>3</sub>Cu<sub>4</sub>O<sub>10+δ</sub> sample was synthesized by means of high-temperature and high-pressure synthesis as described in Ref. 1. First, the precursors BaCuO<sub>2.5</sub>

and  $\text{Ca}_2\text{CuO}_3$  were prepared by the standard solid-state reaction method. The starting materials  $\text{BaCuO}_{2.5}$ ,  $\text{Ca}_2\text{CuO}_3$ ,  $\text{CuO}$  with nominal composition  $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{10+\delta}$  and additional  $\text{BaO}_2$  (as oxidizing agent) were completely mixed in the agate mortar. Mixtures were pressed into pellets and sealed in a gold capsule, each being surrounded by a  $\text{NaCl}$  separator and a graphite-tube heater. Finally, the sample was loaded and sintered in a six-anvil type high-pressure apparatus at 5 GPa and  $1100^\circ\text{C}$  for 30 minutes. The sample was then quenched to room temperature before releasing the pressure. The superconducting critical temperature  $T_c$  of the sample was measured resistively by the standard four-probe technique and magnetically by a Quantum Design SQUID magnetometer in the field-cooling mode with an external field of 20 Oe. *In situ* high-pressure energy-dispersive X-ray diffraction experiment on  $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{10+\delta}$  was carried out in DAC with the synchrotron white-radiation at the Beijing Synchrotron Radiation Facility. The size of X-ray spot was  $120\ \mu\text{m} \times 120\ \mu\text{m}$ . The culet of the DAC was  $500\ \mu\text{m}$ . The powder of the sample was loaded, together with a suitable amount of Pt powder for the inner pressure calibration, into a  $300\ \mu\text{m}$ -diameter hole in a T301 stainless steel gasket. The internal pressure of DAC was calculated according to the equation of state of Pt.

### 3. Results and Discussion

Figure 1 shows the temperature dependence of dc magnetic susceptibility and resistance. It indicates clearly the single superconducting transition and large Meissner volume fraction, which can be attributed to the Cu-1234 phase. The  $T_c^0$  value for as-prepared sample of around 116 K was obtained.

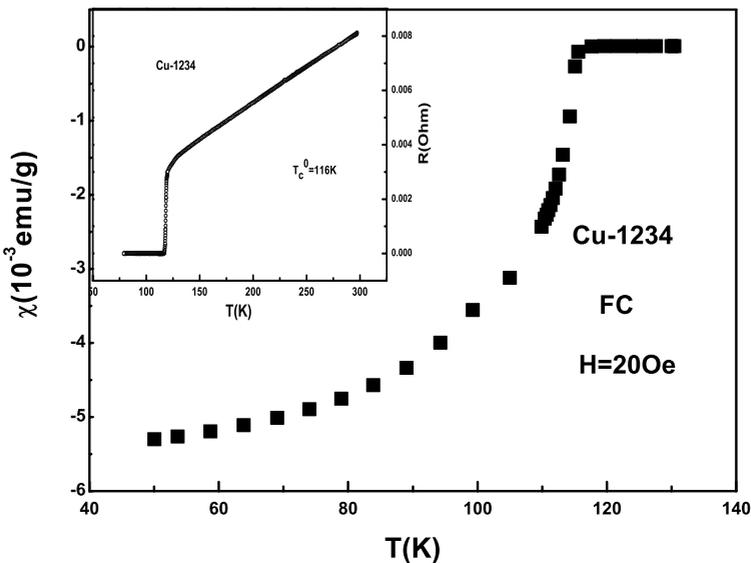


Fig. 1. The dc susceptibility of Cu-1234 superconductor (inset: resistance of Cu-1234).

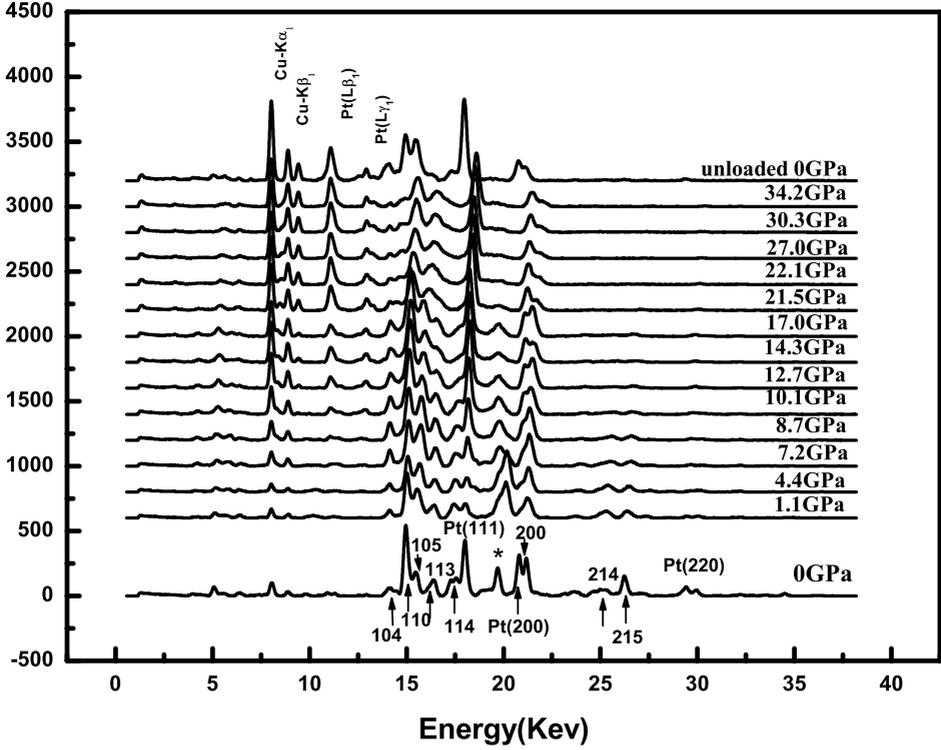


Fig. 2. The spectra of energy-dispersive XRD of Cu-1234 superconductor under various pressures. (\* is for  $\text{Ca}_{0.85}\text{CuO}_2$ .)

The patterns of energy-dispersive X-ray diffraction of  $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{10+\delta}$  under different pressures at room temperature are shown in Fig. 2. All diffraction peaks except the fluorescence peaks shift with increasing pressure. While pressure returns to ambient, the peaks almost recover to the original sites. From Fig. 2, it is also seen that some diffraction peaks are overlapped at a pressure, and then separated at another pressure. It can be induced by assuming that the shifting rate is variant among the diffraction peaks under pressure. But no new diffraction peaks are found in the whole energy spectra. So it is reasonably inferred that no structural phase transition in crystal takes place in the pressure range of 0–34 GPa.

The relationships of the volume compressibility versus pressure for  $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{10+\delta}$  are shown in Fig. 3. We analyze the data of volume compressibility versus pressure of  $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{10+\delta}$ , using the Birch–Murnaghan equation,

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

Assuming pressure derivative  $B'_0 = 4$ , the bulk modulus  $B_0 = 152 \pm 10$  (GPa) is

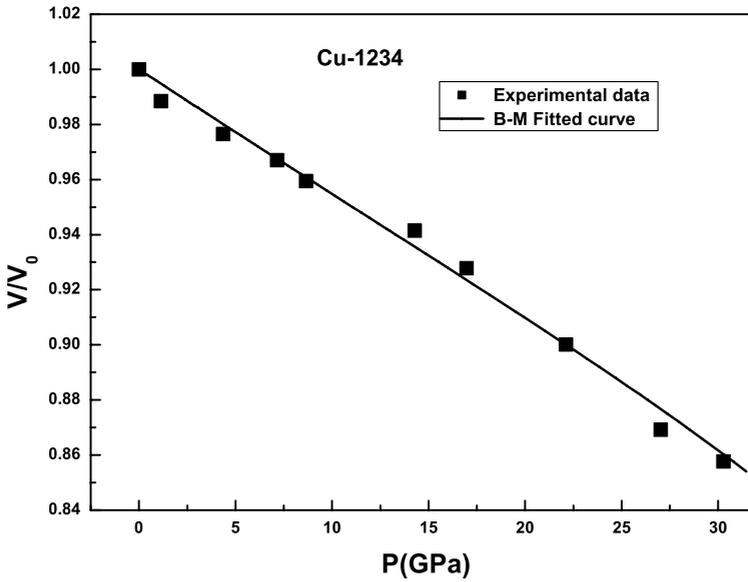


Fig. 3. The relationship of volume change versus pressure for Cu-1234 superconductor.

obtained. This value is comparable to other high  $T_c$  superconductors. These results will provide qualitatively understanding on the physical origin of the  $T_c$  increasing under pressure for cuprate superconductors.

### Acknowledgments

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