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Pressure-induced structural changes of the tetragonal Bi_2CuO_4

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Abstract

The tetragonal compound Bi_2CuO_4 was investigated at high pressures by using in situ Raman scattering and X-ray diffraction (XRD) methods. A pressure-induced structural transition started at 20 GPa and completed at ~37 GPa was found. The high pressure phase is in orthorhombic symmetry. Raman and XRD measurements revealed that the above phase transition is reversible.

Keywords: Bi_2CuO_4; High pressure; Raman; X-ray diffraction

1. Introduction

The crystal structure of Bi_2CuO_4 is tetragonal with isolated CuO_4 square-planar units of Cu^{2+} ions that are stacked on the top of each other in a staggered manner along the c-axis and the copper atoms are not bridged by any intervening oxygen ions (Fig. 1). Such a square-planar configuration is common to the majority of copper oxide base high-temperature superconductors. The crystal structure and magnetic properties of Bi_2CuO_4 have been investigated extensively in recent years [1–6]. In the magnetic sense Bi_2CuO_4 is a compensated antiferromagnet with Neel temperature ~45 K. The electronic properties of Bi_2CuO_4 studied by X-ray photoelectron spectroscopy, X-ray Auger electron spectroscopy and electron energy loss spectroscopy, etc. reveal that Bi_2CuO_4 is a charge transfer insulator with a forbidden gap of ~2 eV [7]. The vibrational properties have been studied by polarized IR, Raman and optical measurements [8–11] and magnon light scattering was also found in this compound at low temperature [12].

Thermal stability [13] and temperature dependence of magnetic and transport properties [1–6] have been well established for Bi_2CuO_4. However, pressure effect on the structure and properties of Bi_2CuO_4 is unknown yet and, as far as we know, there is no report on this subject. In this paper, using X-ray diffraction (XRD) and Raman scattering methods, we report on the structural behavior of Bi_2CuO_4 at high pressures and a pressure-induced phase transition was found above 20 GPa for the first time.

2. Experimental

Bulk sample of Bi_2CuO_4 was prepared by solid-state reaction method. Well-mixed Bi_2O_3 (99.5%, Alfa Aser Ltd.) and CuO (Nano Technology, 99%) in a molar ratio of 1:1 was pressed into pellets and then annealed at 800 °C for 3 days in air with intermediate regrinding. The structure of the synthesized sample was checked with a CCD detector, which is installed on a Brucker XRD facility. A pure tetragonal phase of Bi_2CuO_4 was obtained after the above procedure. Pressure was generated with diamond anvil cell (DAC) techniques using stainless steel gasket. Raman spectra were collected by using a high throughput holographic imaging spectrograph with volume transmission grating, holographic notch filter and thermoelectrically cooled CCD detector (Physics Spectra). The light is 783.2 nm in wavelength from an Ar laser. The in situ XRD measurement was performed at Cornell High Energy Synchrotron Source (CHESS). The X-ray beam from synchrotron facility with wavelength of 0.486 Å is focused on the sample with spot size of less than 50 μm. The

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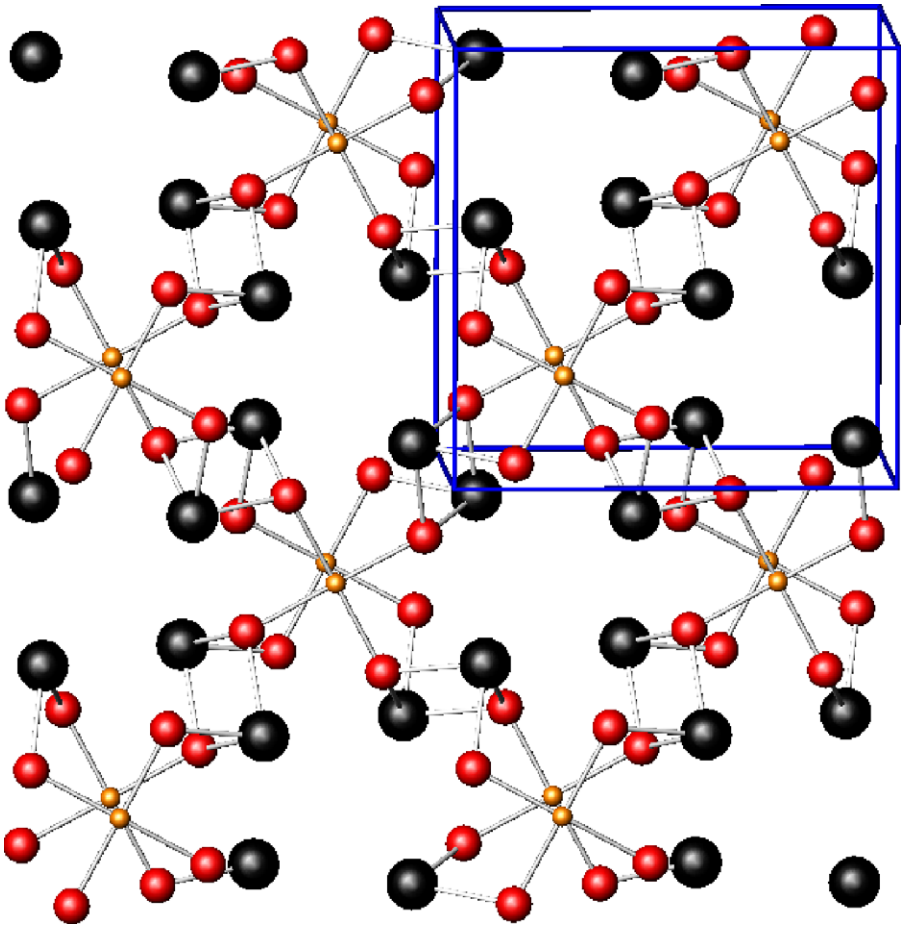

Fig. 1. Schematic crystal structure of tetragonal Bi_2CuO_4, the large balls represent Bi ions and the others are CuO_4 square-planar units.

diffracted X-rays are first collected with an image plate detector (Mar345) and then the patterns are analyzed by integration of images as a function of 2θ using the program FIT2D [14]. The pressure in all the experiments was calibrated with standard ruby luminescence method [15]. A standard methanol/ethanol (4:1) was used as pressure medium for all the experiments. However, the methanol/ethanol pressure medium can not guarantee the hydrostatic condition in our experiments especial in the higher pressure range.

3. Results and discussions

The compound Bi_2CuO_4 crystallizes in a tetragonal space group with four formula units comprising 28 atoms in the unit cell. Fig. 2 shows the observed XRD pattern of the synthesized Bi_2CuO_4 sample taken at room conditions and refined with space group of $P4/ncc$. The observed and calculated XRD patterns fit quite well and the refined lattice parameters are $a = b = 8.475(1)$ Å, $c = 5.806(1)$ Å, which are comparable with those reported in literature [1].

The $P4/ncc$ space group is centrosymmetric and the Bi, Cu and O atoms have C2($8f$), C4($4c$) and C1($16g$) site symmetries, respectively. Factor group analysis results in

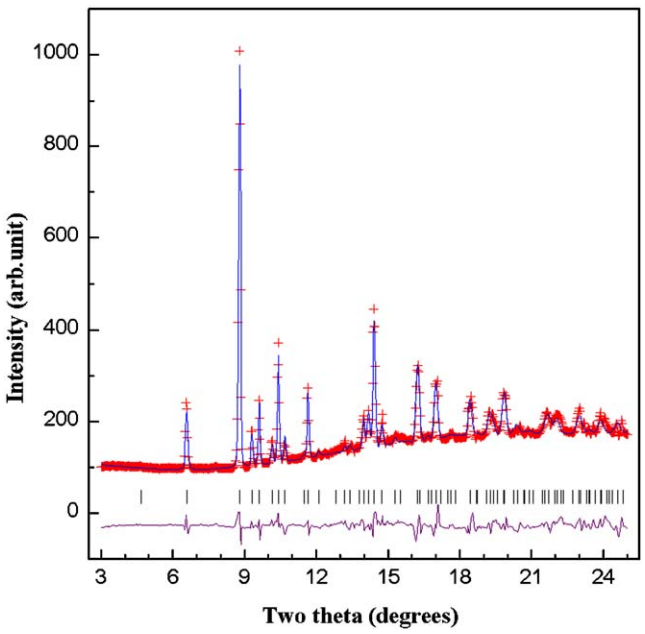

Fig. 2. Observed (symbol), calculated (line) XRD patterns, their differences and Bragg peak positions of Bi_2CuO_4 in tetragonal symmetry with space group of $P4/ncc$ and lattice parameters of $a = b = 8.475$ Å, $c = 5.806$ Å.

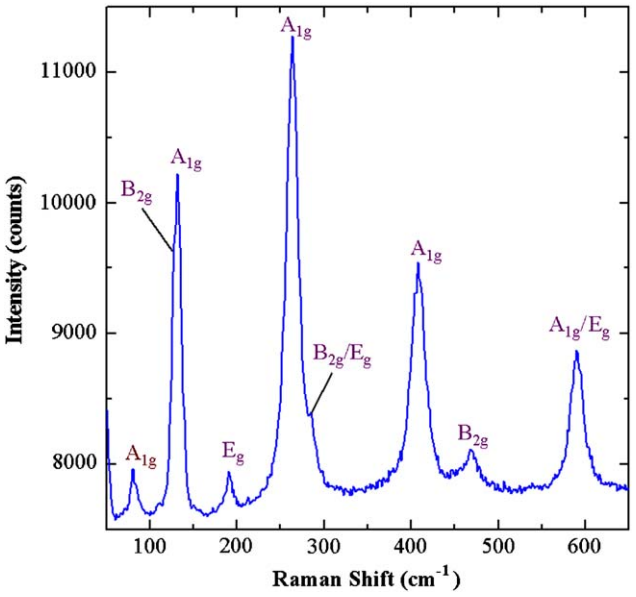

Fig. 3. Raman spectrum of Bi_2CuO_4 measured at room conditions.

25 Raman active modes in Brillouin zone center [8]:

$$\Gamma = 5A_{1g} + 5B_{1g} + 4B_{2g} + 11E_g.$$

Fig. 3 is the unpolarized Raman spectrum of the as-synthesized Bi_2CuO_4 sample measured at room conditions. Eight bands are clearly observed and the band at $\sim$130 cm^{-1}, in fact, composed of two modes with very close frequencies. Our observations are in good agreement with those reported before [8,9]. The peak with frequency of 81.7 cm^{-1} is the B_{2g} mode and is attributed to the in-plane bond bending vibration of the Bi rhombohedra. Another B_{2g} mode at 128 cm^{-1} (very close to the 131.8 cm^{-1} A_{1g} mode) is a bond-bending oxygen mode (deformation of the CuO_4 squares). The strong peak at 131.8 cm^{-1} is the A_{1g} mode, which originates from translational vibrations of the CuO_4 planes along the z-axis. The peak centered at 190.9 cm^{-1} is the E_g mode and attributed to Cu–Cu motion. The strongest band observed at 264 cm^{-1} corresponds to the rotation of two stacked CuO_4 squares in opposite directions. If one considers the Bi environment, this mode is described as a O–Bi–O bending and another A_{1g} mode at 408 cm^{-1} corresponds to Bi–O stretching. The mode at 284.9 cm^{-1} is either B_{2g} or E_g mode and may correspond to the CuO_4 deformation with oxygen motion along the z direction, while the peak at 468.4 cm^{-1} is an in-plane bond-stretching deformation of the CuO_4 squares. The A_{1g} mode with the highest frequency of 590 cm^{-1} is mainly an in-plane "breathing" of the CuO_4 squares—oxygen atoms shrinkage or expand simultaneously.

In order to check the pressure effect on the structure of Bi_2CuO_4, in situ Raman scattering measurement was performed up to 50 GPa. Fig. 4a shows the evolution of the Raman spectra with pressure during loading. There are several obvious changes in the Raman spectra during loading pressure. First, a higher-level background appeared clearly in the spectrum starting at 20 GPa associated with the intensity decrease of the Raman active modes. The strong background may be due to either the pressure-induced disorder in the sample or the free electron scattering, which may associate with a transport change in the sample. Second, two new modes between 300 and 500 cm^{-1} were observed in the spectra when pressure is higher than 24 GPa, which indicates a pressure-induced phase transition occurred at this pressure or earlier due to the broadening of the peaks. The two new modes are attributed to the high pressure phase. The first new mode is, in fact, barely observable at pressure larger than 43.2 GPa and it may be due to the pressure effect. Besides peak broadening, the intensity of some Raman active modes is also great reduced at high pressures. The strongest band at 131.8 cm^{-1} at normal conditions is observed in the whole measured pressure range and the other two strong bands lost their intensities until 37 GPa. The pressure dependence of the frequencies of the observed modes for Bi_2CuO_4 is plotted in Fig. 4c. Though the three strongest modes of Bi_2CuO_4 were observed at high pressures, the discontinuity of the frequency change slope with pressure are clearly observed in Fig. 4c in the range of 20–24 GPa. So it can be concluded that the pressure-induced phase transition in Bi_2CuO_4 started at 20 GPa. The transition should be completed between 32.6 and 37 GPa.

During the process of unloading pressure, the spectrum gradually changes back to a pattern similar to that of the starting material (Fig. 4b). So the above phase transition is reversible and the recovered sample from 50 GPa should have the same tetragonal structure at normal conditions.

In order to confirm the above phase transition in Bi_2CuO_4, in situ XRD measurements were performed at high pressures. The evolution of XRD patterns with pressure is shown in Fig. 5. The Bi_2CuO_4 shows a greatly broadening of diffraction peaks at high pressure. The indexed lattice parameters and cell volumes of the tetragonal Bi_2CuO_4 at various pressures are plotted in Figs. 6a and b, respectively. The sample shows anisotropic compression behavior and is easily to be pressed along the c-axis. The c parameter shrinks 10% from room conditions to 32 GPa while a (or b) only shrinks 7%. This is reasonable because of the layer structure and the layers stacking along the c direction have more free space between them. Such a behavior was also found in other compounds with layer structures [16].

In order to describe the pressure effect on the compressibility and mode frequency, the Grueneisen scaling approximation is introduced [17]:

$$\gamma_i = -(V/\omega_i)\mathrm{d}\omega_i/\mathrm{d}V = -\mathrm{d}(\ln\omega_i)/\mathrm{d}(\ln V)$$
$$= \kappa^{-1}\,\mathrm{d}(\ln\omega_i)/\mathrm{d}P,$$

where γ_i is the mode-Grueneisen parameter for phonon i, V the crystal volume, P the pressure, and κ the compressibility.

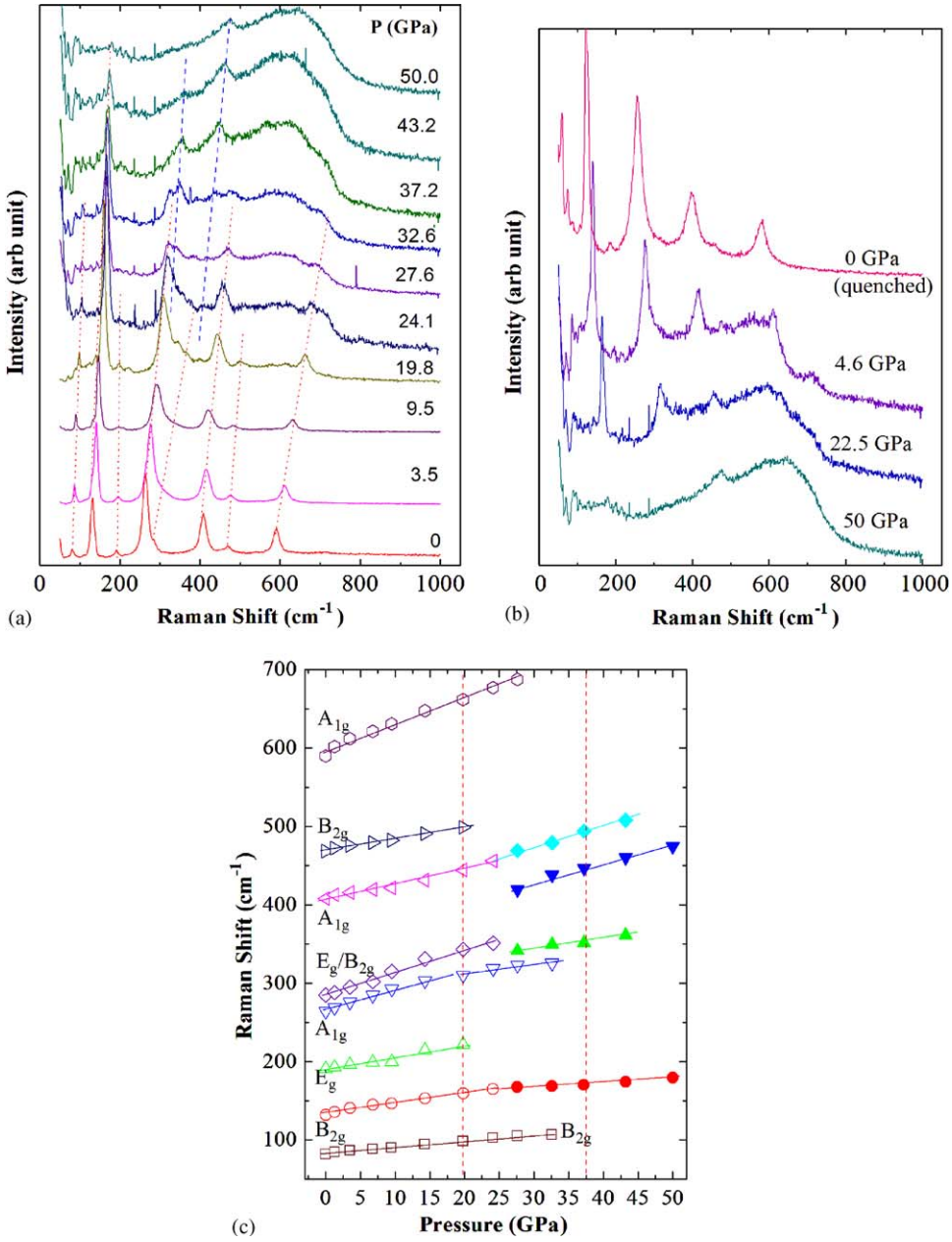

Fig. 4. (a) Raman spectrum evolution of Bi_2CuO_4 from room pressure to 50 GPa. (b) Raman spectra of Bi_2CuO_4 during unloading from 50 GPa to room conditions. (c) Pressure dependence of the shifts of Raman active modes for Bi_2CuO_4.

Numerous experiments revealed that the mode-Grueneisen parameter is frequency independent for three-dimensional network crystals, especially in non-molecular-type semiconductors [18,19]. However, it is strongly and systematically frequency dependent to some molecular crystals, such as in S_8 and As_2S_3 [17], the $\gamma_i(\omega)$ varies by two orders of magnitude when ω is varied from the phonon spectrum [17]. This behavior is a consequence of the coexistence of strong intramolecular and weak intermolecular forces, and should prove characteristic of molecular crystals in general. In order to calculate mode-Grueneisen parameters, we use the average value of $7.15 \times 10^{-3}\,GPa^{-1}$ for the bulk compressibility, which is calculated from the linear fit of the P–V curve. Table 1 lists the pressure dependence and the corresponding mode-Grueneisen parameters of several clear bands in the spectrum. The Grueneisen parameters for the different modes vary around 1 and the maximum deviation is estimated to be less than 0.05. The interaction of CuO_4 squares along the z-direction is relatively weak in the tetragonal Bi_2CuO_4 compound and the Grueneisen parameter for mode B_{2g} (centered at $468\,cm^{-1}$ at room conditions) has thus the largest deviation from 1 because this mode is caused by the in-plane bond-stretching deformation of the CuO_4 squares.

Besides the broadening of the diffractions with pressure, we found several additional peaks appearing at ~7.8°,

10.3°, 13.2° and ~18.5°, respectively, at pressures higher than 22.5 GPa. These peaks should be attributed to the new high pressure phase. According to the Raman measurements, the normal tetragonal Bi_2CuO_4 phase coexists with the high pressure phase till 37.5 GPa. The XRD pattern at 38.6 GPa should be mainly contributed by the new high pressure phase. Phase transition in Bi_2CuO_4 was only reported in the system during long-time ball milling before [20]. The heavy mechanical deformation in Bi_2CuO_4 results in the phase transition and the new phase was indexed with a La_2CuO_4-like tetragonal phase. The diffraction peaks at 38.6 GPa can also be indexed with an orthorhombic unit cell with lattice parameters of $a = 5.45(3)$, $b = 4.91(2)$ and $c = 14.42(9)$ Å (see Table 2). It seems to have the La_2CuO_4-type structure, however, the experimental analysis do not support the La_2CuO_4-type structure for the high pressure phase. First, the orthorhombic La_2CuO_4-type structure should have a complicated Raman spectrum [21] especially at the region of 600–1500 cm^{-1}, while our sample did not show any Raman active modes at frequencies higher than 800 cm^{-1}. Second, the indexed cell volume for the high pressure phase at 38.6 GPa is 385 $Å^3$, which is larger than the low pressure phase at 32 GPa. It is unreasonable unless there are more formula (>4) of Bi_2CuO_4 in the unit cell.

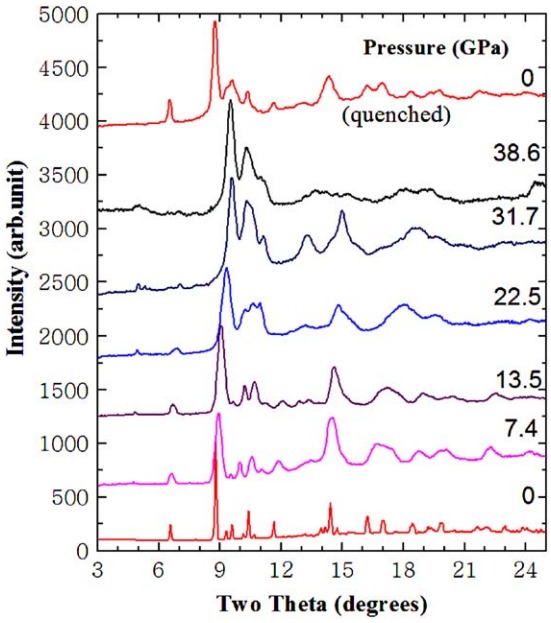

Fig. 5. XRD patterns of Bi_2CuO_4 at various pressures, the diffraction pattern at 38.6 GPa is mainly the new high pressure phase.

Both the Raman and XRD results indicate that the above transition is reversible and the tetragonal Bi_2CuO_4 is recovered during unloading pressure. The diffraction peaks of the recovered sample are greatly broadened, which may indicated a pressure-induced distortion exists in the recovered sample. The results also indicated that the compression was highly anisotropic. In fact, methanol/

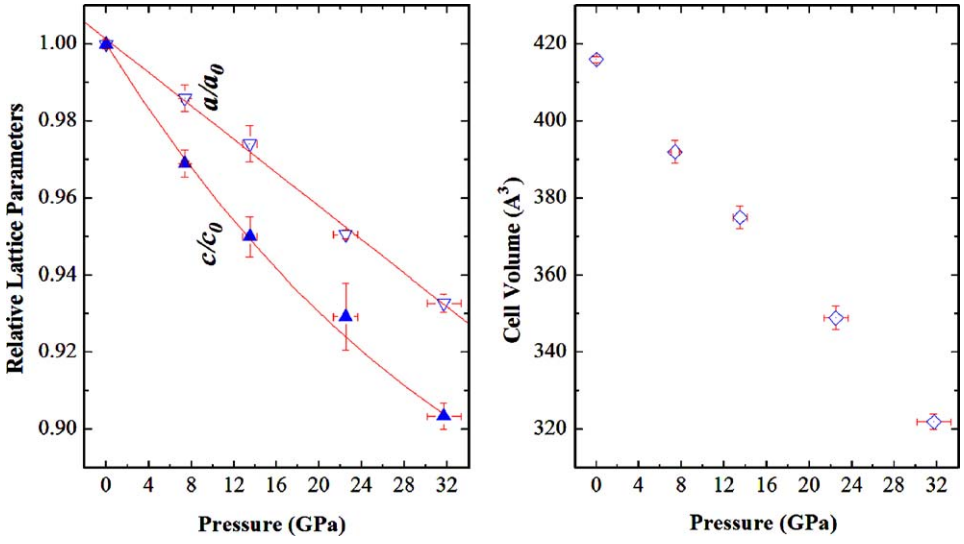

Fig. 6. Cell parameters of the tetragonal Bi_2CuO_4 at different pressures: (a) relative lattice parameters, open symbols are a/a_0 (or b/b_0) and solid ones are c/c_0, (b) cell volume.

Table 1
Pressure coefficient and mode-Grunesien parameters of the vibrational modes for the tetragonal Bi_2CuO_4

Mode	B_{2g}	A_{1g}	E_g	A_{1g}	B_{2g}/E_g	A_{1g}	B_{2g}	A_{1g}/E_g
ω (cm^{-1})	81	132	191	264	285	408	468	584
$d\omega/dP$	0.77	1.29	1.55	1.93	2.88	1.87	1.47	3.34
γ_i	1.31	1.37	1.13	1.02	1.41	0.64	0.44	0.80

Table 2
The diffraction peaks of Bi_2CuO_4 at 38.6 GPa can be indexed with an orthorhombic unit cell and lattice constants of $a = 5.45(3)$, $b = 4.91(2)$ and $c = 14.42(9)$Å

h	k	l	d_{obs} (Å)	d_{calc} (Å)	δd (Å)	I/I_0
0	0	4	3.600	3.606	−0.006	2
1	1	3	2.924	2.907	0.017	100
2	0	0	2.709	2.727	−0.018	59
2	0	2	2.541	2.551	−0.011	32
0	2	4	2.046	2.030	0.016	21
2	2	0	1.836	1.825	0.011	19
0	2	6	1.729	1.718	0.011	14
2	2	4	1.627	1.628	−0.001	16
1	3	1	1.548	1.559	−0.011	21
3	1	5	1.472	1.468	0.004	21
0	2	8	1.444	1.453	−0.009	21

ethanol pressure medium can only keep a hydrostatic condition less than 15 GPa.

4. Conclusions

The vibrational properties of Bi_2CuO_4 have been measured by in situ Raman scattering from atmosphere pressure to 50 GPa. A pressure-induced phase transition occurred at 20 GPa and completed before 37.5 GPa. The XRD results indicated that the new high pressure phase is in orthorhombic symmetry. The reversibility of the phase transition is confirmed by both Raman and XRD measurements.

Acknowledgments

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