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Raman scattering and x-ray diffraction studies of polycrystalline $CaCu_3Ti_4O_{12}$ under high-pressure

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We report Raman scattering and x-ray diffraction studies of polycrystalline $CaCu_3Ti_4O_{12}$ (CCTO) under high pressures. The pressure dependence of several Raman modes was investigated. No anomalies have been observed on the phonon spectra thereby indicating that the T_h $(Im\overline{3})$ structure remains stable up to the maximum pressure (5.3 GPa) we reached in this experiment. The pressure coefficients for the observed Raman modes were determined. This set of parameters was used for evaluating the stress developed in CCTO thin films. The high-pressure x-ray studies were extended up to 46 GPa and the data confirmed that the T_h structure remains stable up to this pressure. The pressure-volume data are well described by the Birch's equation of state. The experimental value of the zero pressure bulk modulus is $B_0 = 212 \pm 2$ GPa. Grüneisen parameters of CCTO were also determined.

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I. INTRODUCTION

The complex perovskite $CaCu_3Ti_4O_{12}$ (CCTO) has been recently reported as a material having the largest dielectric constant (16000–18000) ever measured in the laboratory.[1–3] In addition to this striking property, the dielectric constant is nearly constant over a wide temperature range (from 100 to 600 K). Explaining the anomalous dielectric constant has been an intriguing issue and many models have been proposed. Some authors have attributed the high values to extrinsic factors such as defects and grain boundaries.[4,5] By performing first principle calculations, the Vanderbilt's group has suggested that the source of such giant dielectric constant should be related to extrinsic effects since the contribution of the lattice effects was estimated to be about 60.[6,7] This value is extremely smaller than what has been found in the experiments (10^5). Recently, homogeneous CCTO thin films epitaxially grown were found to exhibit a low-frequency permittivity of ≈ 100.[8] This experimental result supports the hypothesis that the giant dielectric constant obtained for bulk CCTO comes from extrinsic effects. Owing to these remarkable properties, CCTO is being considered as a very promising material for application in microelectronics, mainly in capacitive elements. With the miniaturization of the devices and having in view the large and prompt integration with the current technology, CCTO thin films are the most likely systems to be used in CCTO-based devices. Such systems have been investigated and several reports on growth,[9–11] dielectrics,[8,12,13] dc and ac electrical resistivity,[14] and optical properties[15] have already been published.

Thin films are expected to exhibit built-in stress due to the grain boundary, reduced dimensionality, and the lattice mismatch with the various substrate used for growing them. The residual stress affects the mechanical, electrical and optical properties of the films. Therefore, it is important to investigate the stress developed in the films in order to improve the growth methods and to tailor desired physical properties. Raman spectroscopy has been established as a powerful and versatile technique (nondestructive, contactless, and noninvasive) for investigating the stress in films by monitoring the phonon frequency shifts of the films relative to their bulk counterparts. For carrying out such analysis, the knowledge of the pressure dependence of the Raman spectra of polycrystalline CCTO can be the basis for probing and interpreting built-in stress in CCTO films.

So far, the Raman modes of CCTO have been measured in ceramics,[16] single crystals,[17,18] and thin films.[15] These investigations have been devoted to study the polarization and temperature dependence of the Raman spectra.[17,18] The effects of pressure on vibrational properties have not yet been reported. Furthermore, to best of our knowledge, there are no structural data of CCTO under high pressure. This investigation is important because it allows one to study the structural stability and to determine the bulk modulus value by fitting of the pressure-volume data to the appropriated equation of state.

In this work we report the effects of pressure on the vibrational (Raman spectrum) and structural (x-ray pattern) properties of polycrystalline CCTO. We found that the Raman modes are sensitive to the applied pressure and their frequencies exhibit a linear behavior. No anomalies in the frequency vs pressure plots have been observed from ambient pressure up to 5.3 GPa thus indicating the absence of structural instabilities (phase transitions) in this pressure range. We used our set of pressure coefficients along with the Raman data available in the literature[15] for evaluating the stress in CCTO thin films. The high-pressure x-ray energy-dispersive patterns have confirmed the absence of any struc-

tural phase transformation in the 0–46 GPa pressure range. The bulk modulus B_0 has been determined by fitting the pressure-volume data to the Birch's equation of state. Finally, the pressure coefficients $\alpha = \partial\omega/\partial P$ along with the Bulk modulus were used for determining the Grüneisen parameters.

II. EXPERIMENTAL PROCEDURE

Commercial oxides $Ca(OH)_2$ (Vetec, 97% with 3% of $CaCO_3$), $CaCO_3$ (Aldrich, 99%), TiO_2 (Aldrich, 99%), and CuO (Aldrich, 99%) were used for preparing CCTO ceramics. The CCTO samples were prepared by the conventional powder-sintering technique. The starting materials were weighted according to the stoichiometric ratios and mixed thoroughly in an agate mortar. The mixed powder was calcined at 900 °C for 12 h, and the resulting samples were sintered in air at 1050 °C for 24 h. High-pressure Raman experiments were performed using a diamond anvil cell (DAC) with 4:1 methanol: ethanol mixture as the transmitting fluid. The pressure dependent Raman spectra were obtained with a triple-grating spectrometer (Jobin Ivon T64000) equipped with a N_2 cooled charge coupled device (CCD) detection system. The line 514.5 nm of an argon ion laser was used as excitation. An Olympus microscope lens with a focal distance $f = 20.5$ nm and numeric aperture N.A. = 0.35 was employed to focus the laser beam on the sample surface.

High-pressure powder x-ray diffraction patterns were recorded at room temperature using the white-beam method and synchrotron radiation at Station F3 of HASYLAB-DESY in Hamburg, Germany. The diffractometer, working in the energy-dispersive mode, has been described elsewhere.[19] High pressures were obtained in a Syassen-Holzapfel-type diamond-anvil cell. A finely ground powder sample and a ruby chip were placed in a 200 μm diameter hole in an inconel gasket, preindented to a thickness of 60 μm. A 16:3:1 methanol:ethanol:water mixture was used as the pressure-transmitting medium. The Bragg angle of each run was calculated from a zero-pressure spectrum of sodium chloride situated in the diamond-anvil cell. For both Raman and x-ray measurements, the pressure in the cell was determined by measuring the wavelength shift of the ruby R_1 luminescence line and applying the non-linear pressure scale of Mao *et al.*[20] The accuracy in the pressure measurements is ±0.1 GPa.

III. RESULTS AND DISCUSSION

A. Raman scattering results

Before discussing our results we briefly summarize some properties of CCTO. This material has a body-center cubic primitive cell containing 20 atoms and belonging to the centrosymmetric $T_h(Im\overline{3})$ group. Standard group theory analysis predicts that the Raman active modes are distributed among the irreducible representation as $2A_g + 2E_g + 4F_g$.[17] The lower trace in Fig. 1(a) shows the Raman spectrum of CCTO at ambient pressure and room temperature. CCTO is a weak scatter and only five of the eight predicted modes are observed at around 444, 453, 510, 576, and 761 cm^{-1}. Based on lattice dynamics studies[6,7] and polarized Raman measurements,[17] the mode symmetries are identified as $A_g(1)$(444 cm^{-1}), $F_g(2)$(453 cm^{-1}), $A_g(2)$(510 cm^{-1}), $F_g(3)$(576 cm^{-1}), and $F_g(4)$(761 cm^{-1}). Following lattice dynamics calculations the 444, 453, and 510 cm^{-1} are TiO_6 rotationlike modes. The peak at 576 cm^{-1} is assigned to the Ti-O-Ti antistretching mode of the TiO_6 octahedra.[17] The $F_g(4)$ mode has been predicted to be observed at about 710 cm^{-1}. We have assigned the mode 761 cm^{-1} to the symmetric stretching breathing of the TiO_6 octahedra. Its low intensity is typical of the structures containing shared units where the neighbors octahedra underdamp the symmetric vibrations. First-principle calculations[6] predict this breathing mode to be observed at 739 cm^{-1}. This value is much more close to 761 cm^{-1} we have observed than the prediction of classical lattice dynamics.[17]

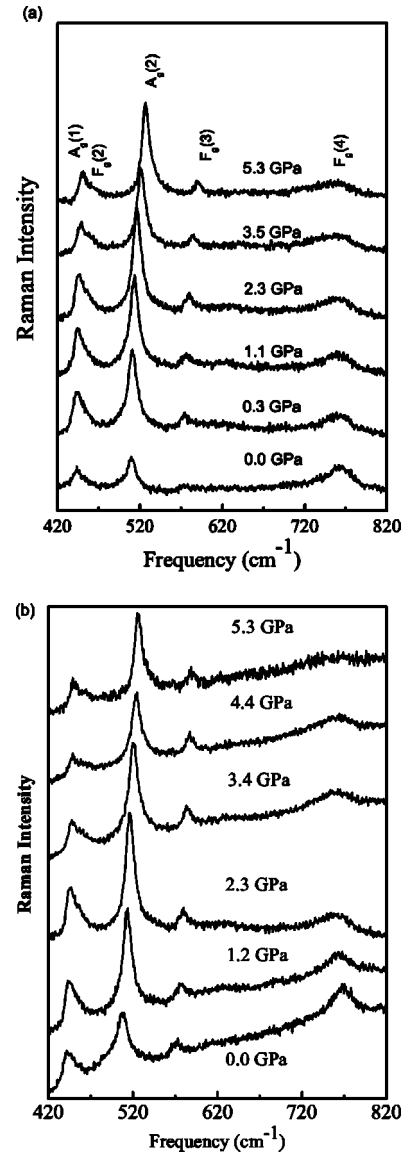

FIG. 1. Pressure dependent Raman spectra of CCTO obtained during (a) compression and (b) decompression runs.

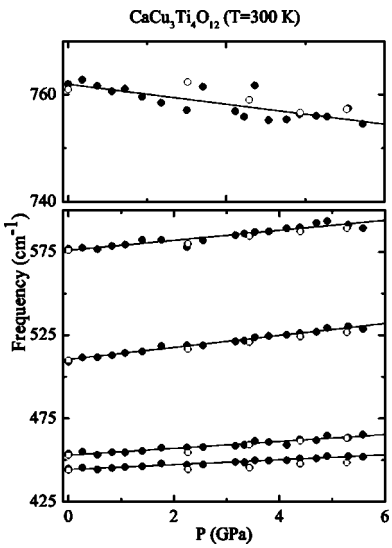

FIG. 2. Frequency vs pressure plots for CCTO Raman modes. The solid and open circles stand for compression and decompression runs, respectively. The error bar for both frequency (± 1.5 cm^{-1}) and pressure (± 0.1 GPa) are smaller than the symbols. The solid lines are fit to the experimental data using $\omega(P)=\omega_0+\alpha P$.

Upon increasing pressure, it is evident from the spectra [see Fig. 1(a)], that the material remains in its initial configuration up to the maximum pressure we have reached in our Raman experiments. We also record the data during decompression runs [see Fig. 1(b)] and we observed that the high pressure behavior of CCTO is reversible. In order to discuss in detail the pressure effects on CCTO phonon frequencies we have constructed the frequency (ω) vs pressure (P) plots. The results for both compression (solid circles) and decompression (open circles) experiments are shown in Fig. 2. All peaks exhibit a linear behavior $\omega(P)=\omega_0+\alpha P$ and both frequency intercepts (ω_0) and pressure coefficients (α) are listed in Table I. Note, that all modes are sensitive to pressure and large α values were observed. For the breathing mode $\partial\omega/\partial P<0$, indicating a possible structural instability that might lead to a structural phase transition at much higher pressures. Finally, the pressure-dependent data also reveal that the linewidths change slightly with pressure. This result suggests that the pressure does not induce any significant disorder in CCTO.

Provided the pressure coefficients we have the ground knowledge for discussing the Raman scattering results in CCTO thin films. Litvinchuk *et al.*[15] report the Raman scattering studies of CCTO thin films prepared by pulsed laser deposition on a (001) $LaAlO_3$ substrate. When compared with bulk CCTO, these authors have observed the Raman modes in the film are shifted toward higher frequency by an amount of 4–7 cm^{-1}. Similarly to the spectra of bulk CCTO, the $A_g(2)$ mode is the most intense mode measured in CCTO films. It was observed at 517 cm^{-1} which is 7 cm^{-1} higher than in CCTO bulk. We attribute this upshift to the stress developed during the growth process. The pressure behavior of the $A_2(2)$ mode has been determined as $\omega(P)=510+3.6P$, being ω and P in units of cm^{-1} and GPa, respectively. By using this equation and the value of ω measured in the CCTO film we calculate that the stress developed in the CCTO film reported in Ref. 15 is 1.9 ± 0.3 GPa.

TABLE I. Frequency intercepts ω_0, pressure coefficients α, and Grüneisen parameters γ_i of CCTO.

Mode	ω_0 (cm^{-1})	α (cm^{-1} GPa^{-1})	γ_i
$A_g(1)$	444	1.5 ± 0.1	0.70
$F_g(2)$	453	2.1 ± 0.1	0.96
$A_g(2)$	510	3.6 ± 0.1	1.49
$F_g(3)$	576	3.0 ± 0.2	1.10
$F_g(4)$	761	-1.2 ± 0.2	-0.33

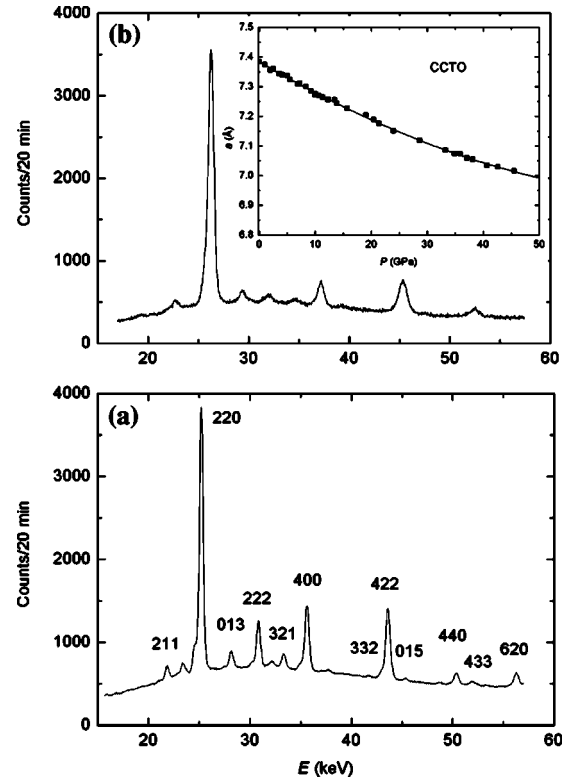

FIG. 3. Energy-dispersive diffraction patterns of $CaCu_3Ti_4O_{12}$ recorded at (a) 4.0 GPa and (b) 24.0 GPa The inset to panel (b) stands for the pressure-volume compression data of $CaCu_3Ti_4O_{12}$. The curve through the experimental points has been calculated from the Birch's equation [see Eq. (1)].

B. X-ray diffraction results

In order to support the Raman scattering results and to experimentally determine the bulk modulus value, we have performed high-pressure x-ray diffraction measurements. The lattice constant of CCTO, as determined from a diffraction pattern at ambient conditions, is 7.385(15) Å, which compares well with values reported in the literature.[1,21] Figures 3(a) and 3(b) show, respectively, the energy-dispersive diffraction spectra recorded at pressures of 4.0 and 24.0 GPa. The diffraction peaks are resolved up to Miller indices 620.

The Bragg angle is $\theta = 5.408°$. A small peak at 23.1 keV in Fig. 3(a) is unidentified. Another two small peaks at about 32.1 and 37.6 keV are diffraction lines of the inconel gasket. By comparing the evolution of the spectra like those in Fig. 3 we can clearly observe that no new diffraction peaks are appearing up to the highest pressure of the present investigation. Thus, there is no evidence for any structural phase transformation of CCTO up to at least 46 GPa.

From the observed diffraction spectra, values for the lattice parameter and the unit-cell volume can be derived and refined. The pressure-volume data for CCTO can then be described by an appropriate equation of state. In the present work, we have used the Birch's equation:[22]

$$P = \tfrac{3}{2}B_0(x^{-7/3} - x^{-5/3})\left[1 - \tfrac{3}{4}(4 - B_0')(x^{-2/3} - 1)\right], \qquad (1)$$

where $x = V/V_0$, V being the volume at pressure P, and V_0 the volume at zero pressure, B_0 is the bulk modulus, and B_0' its pressure derivative, both parameters evaluated at zero pressure. Values of B_0 and B_0' were obtained from a least-squares fit of Eq. (1) to the experimental pressure-volume data points. We obtain $B_0 = 212 \pm 2$ GPa, where the uncertainty is the standard error of the least-squares fit. For the pressure derivative, $B_0' = 4.00$ has been assumed. The fit (solid line) of Eq. (1) to the experimental pressure-volume data is shown in the inset to Fig. 3(b). It is seen that the equation of state in Eq. (1) well describes the experimental data in the whole pressure range up to 46 GPa.

C. Grüneisen parameters

The pressure coefficients $(\partial\omega/\partial P)$ obtained from Raman data along with the bulk modulus B_0 obtained from x-ray measurements are also useful for determining the Grüneisen parameters γ_i. These parameters, for a given mode i with frequency ω_i, are defined as

$$\gamma_i = \frac{B_0}{\omega_i}\left(\frac{\partial\omega}{\partial P}\right)_{P=0}, \qquad (2)$$

where B_0 is the bulk modulus, which is for CCTO 212 GPa as determined by fitting Eq. (1) to the experimental pressure-volume data discussed in the previous section. The Grüneisen parameters of CCTO are listed in Table I.

IV. CONCLUSION

Summarizing, we studied polycrystalline CCTO under high pressure. Both Raman and x-ray results indicated no evidence for pressure-induced phase transition in the 0–46 GPa pressure range. The frequencies of all Raman modes exhibit a linear dependence on pressure. We also determined the pressure coefficients $\alpha = \partial\omega/\partial P$ for all modes. This set of parameters was used for evaluating the built-in stress in CCTO thin films prepared by pulsed laser deposition. The pressure-volume data at room temperature has been well described by the Birch's equation of state. The experimental value of the zero pressure bulk modulus was determined as $B_0 = 212 \pm 2$ GPa. The α values along with the Bulk modulus were used for calculating the Grüneisen parameters for CCTO. Finally, this work improved our knowledge of both vibrational and structural properties of CCTO that will be useful for feeding back theoretical models and allowed to better understanding the Raman spectra properties of CCTO thin films.

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