Raman studies of polycrystalline CaCu$_3$Ti$_4$O$_{12}$ under high-pressure

D. Valim, A. G. Souza Filho*, P. T. C. Freire, A.P. Ayala, J. Mendes Filho
Laboratório de Espalhamento Raman, Departamento de Física,
Universidade Federal do Ceará, 60455-900 Fortaleza, Ceará, Brazil

A.F.L. Almeida, P.B.A. Fechine, A.S.B. Sombra
Laboratório de Telecomunicações e Ciência e Engenharia de Materiais - LOCEM,
Departamento de Física, Universidade Federal do Ceará, 60455-900 Fortaleza, Ceará, Brazil
(Dated: January 11, 2022)

We report a Raman scattering study of polycrystalline CaCu$_3$Ti$_4$O$_{12}$ (CCTO) under pressure up to 5.32 GPa. The pressure dependence of several Raman modes was investigated. No anomalies have been observed on the phonon spectra thereby indicating that the T$_4$ (Im3) structure remains stable for pressures up to 5.32 GPa. The pressure coefficients for the observed modes were determined. This set of parameters was used for evaluating the stress developed in CCTO thin films.

PACS numbers:

The complex perovskite CaCu$_3$Ti$_4$O$_{12}$ (CCTO) has been recently reported as a material having the largest dielectric constant (16000-18000) ever measured in the laboratory. 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. 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\%\cite{15}. This value is extremely smaller than what has been found in the experiments (10\cite{16}). Recently, homogeneous CCTO thin films epitaxially grown were found to exhibit a low-frequency permittivity of $\approx 100$\cite{16}. 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,\cite{2,10,11} dielectrics,\cite{8,12} dc and ac electrical resistivity,\cite{12} and optical properties,\cite{14} have already been reported.

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 (non-destructive, contact-less and non-invasive) 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,\cite{15}, single crystals,\cite{16,17}, and thin films.\cite{14} These investigations have been devoted to study the polarization and temperature dependence of the Raman spectra.\cite{16,17} In this work we report the effects of pressure on the Raman spectra of polycrystalline CCTO. We found that the mode frequencies exhibit a linear behavior with pressure. No anomalies have been observed from ambient pressure up to 5.32 GPa thus indicating the absence of structural instabilities (phase transitions) in this pressure range. The modes are sensitive to the applied pressure. The pressure coefficients $\alpha = \partial \omega / \partial P$ were determined and these values will be useful for calculating the Grüneisen parameters. Finally, we used our set of pressure coefficients along with the Raman data available in the literature\cite{14} for evaluating the stress in CCTO thin films.

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 calibra-

\*Corresponding author, E-mail: agsf@fisica.ufc.br
tion was achieved by using the well known pressure shift of the ruby luminescence lines. The pressure dependent Raman spectra were obtained with a triple-grating spectrometer (Jobin Ivon T64000) equipped with a N₂ 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 mm and numeric aperture N.A.=0.35 was employed to focus the laser beam on the sample surface.

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 T₆(Im3) group. Standard group theory analysis predicts that the Raman active modes are distributed among the irreducible representation as 2A₉+2E₉+4F₉. The lower trace in Fig. 1 shows the Raman spectrum of CCTO at ambient pressure and room temperature. CCTO is a weak scatter and only five of the eighth predicted modes are observed at around 444, 453, 510, 576 and 761 cm⁻¹. Based on lattice dynamics studies and polarized Raman measurements the mode symmetries are identified as A₉(1)(444 cm⁻¹), F₉(2)(453 cm⁻¹), A₉(2)(510 cm⁻¹), F₉(3)(576 cm⁻¹) and F₉(4)(761 cm⁻¹). Following lattice dynamics calculations the 444, 453, and 510 cm⁻¹ are TiO₆ rotationlike modes. The peak at 576 cm⁻¹ is assigned to the Ti-O-Ti anti-stretching mode of the TiO₆ octahedra. The F₉(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 TiO₆ octahedra. Its low intensity is typical of the structures containing shared units where the neighbors octahedra underdamp

the symmetric vibrations. First-principle calculations 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.

Upon increasing pressure, it is evident from the spectra (see Fig. 1), that the material remains in its initial configuration up to the maximum pressure we have reached in our experiments. 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 ω(P)=ω₀+αP and both frequency intercepts (ω₀) 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 ∂ω/∂P<0, indicating a possible structural instability that might lead to a structural phase transition at 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 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 report the Raman scattering studies of CCTO thin films prepared by pulsed laser deposition on a (001) LaAlO₃ substrate. When compared with bulk CCTO, these authors have observed the Raman modes in the film are shifted toward higher pressures.

![FIG. 1: Pressure dependent Raman spectra of CCTO.](image1.png)

![FIG. 2: Frequency vs Pressure plots for CCTO Raman modes. The solid and open circles stand for compression and decompression runs. The solid lines are fit to the experimental data using ω(P)=ω₀+αP.](image2.png)
frequency by an amount of 4-7 cm\(^{-1}\). Similarly to 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 \(A_g(2)\) mode has been determined as \(\omega(P) = 510 + 3.6P\), being \(\omega\) and \(P\) in units of cm\(^{-1}\) and GPa, respectively. By using this equation and the value of \(\omega\) measured in the CCTO film we calculate that the stress developed in the CCTO film reported in ref.\(^{14}\) is 1.94±0.3 GPa.

Summarizing, we studied polycrystalline CCTO under high pressure. No evidence for pressure-induced phase transition was found in the 0-5.32 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 \(\alpha\) values would be also useful for calculating the Grüneisen parameters for CCTO as the Youngs modulus become available. Finally, this work improves the characterization data of CCTO that will be useful for feeding back theoretical models and allowed to improve the understanding of the Raman spectra properties of CCTO thin films.

D.V. and A.G.S.F. acknowledge financial support from the Brazilian agencies CNPq and CAPES (PRODOC grant No. 22001018), respectively. The authors acknowledge Dr. I. Guedes for a critical reading of the manuscript and partial support from Brazilian agencies CNPq, FUNCAP and FAPESP.

---

1 M. Subramanian, D. Li, B. Reisner, and A. Sleight, J. Solid State Chem. 151, 323 (2000).
2 A. Ramirez et al., Solid State Commun. 115, 217 (2000).
3 C. Homes, T. Vogt, S. Shapiro, S. Wakimoto, and A. Ramirez, Science 293, 673 (2001).
4 M. H. Cohen, J. B. Neaton, L. X. He, and D. Vanderbilt, J. Appl. Phys. 94, 3299 (2003).
5 D. Sinclair, T.B. Adams, F. Harrison, and A. West, Appl. Phys. Lett. 80, 2153 (2002).
6 L. He, J. Neaton, D. Vanderbilt, and M. H. Cohen, Phys. Rev. B 65, 214112 (2002).
7 L. He, J. Neaton, D. Vanderbilt, and M. H. Cohen, Phys. Rev. B 67, 012103 (2003).
8 A. Tselev et al., cond-mat/0308057 (2003).
9 Y. Lin et al., Appl. Phys. Lett. 81, 631 (2002).
10 L. Fang and M. Shen, Thin Solid Films 440, 60 (2003).
11 P. Jha, P. Arora, and A. K. Ganguli, Mater. Lett. 57, 2443 (2003).
12 Y. L. Zhao, G. W. P, and Q. B. Ren, Y. G. Cao, L. X. Feng, and Z. K. Jiao, Thin Solid Films 52, 1500 (2003).
13 L. Chen et al., Appl. Phys. Lett. 82, 2317 (2003).
14 A. P. Litvinchuk et al., phys. stat. sol.(a) 195, 453 (2003).
15 A. Almeida et al., Materials Science and Engineering B 96, 275 (2002).
16 N. Kolev et al., Phys. Rev. B 66, 132102 (2002).
17 A. Koistzsch et al., Phys. Rev. B 65, 052406 (2002).