



Communication

Evidence of iso-structural phase transition in high pressure Raman spectroscopic studies of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$

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A B S T R A C T

High pressure Raman spectroscopic studies on Polycrystalline $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ and $\text{SrCu}_3\text{Ti}_4\text{O}_{12}$ compounds are carried out in order to validate the theoretical predictions of a structural transformation near 3–4 GPa and an insulator to metal transition above 7 GPa [S. B. Fagan et al., Phys. Rev. B **72**, 014106 (2005)]. Our studies showed normal hardening and broadening of peaks with increasing pressure up to 20 GPa besides a discontinuity between 8 and 9 GPa which is attributed to an isostructural phase transition. The $\text{Ag}(1)$ peak occurring at 442 cm^{-1} showed asymmetric Fano lineshape and the lineshape parameter ' q ' shows an increase with increasing pressure. This is completely against the theoretical predictions of an insulator to metal transition above 7 GPa.

1. Introduction

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) is a giant dielectric constant material with value $\sim 10^5$ in bulk form over a wide range of temperatures [1]. Amazingly, it stabilizes in cubic perovskite structure having a centre of symmetry. Normally, high dielectric constants are observed in ferroelectrics that are non-centro-symmetric by definition. CCTO does not fit in the standard definition of a relaxor either. It shows a three orders of magnitude increase in dielectric constant when heated above 100 K, which remains constant till 700 K [2–6] and is nearly independent of frequency. Neutron diffraction studies [1] resulted in a centro-symmetric space group Im-3 which remains unchanged down to 35 K indicating towards the absence of structural rearrangement. The theoretical studies (DFT calculations) also failed to provide proper explanation for large dielectric constant [7], suggesting that an intrinsic mechanism may not be responsible for this phenomena. Extrinsic mechanism such as formation of “internal barrier layer capacitance” (IBLC) consisting of semiconducting grains and insulating grain boundaries was proposed [8] to explain this enormously high dielectric constant. Zhu et al. [9] from their local structure studies showed a considerable substitutional disorder at the Ca/Cu sites at nano scale and they attributed the high dielectric constant of CCTO to the changes of local electronic structure associated with this substitutional disorder. In our recent Raman scattering studies [10–12], we showed the existence of an orbital order disorder transition around 100 K leading to the conductivity changes required in the internal barrier layer capacitance model. Our conclusions were based on the changes in

intensity of a broad hump at high wave numbers and the changes in Fano line shape around 100 K. These studies even ruled out domain mis-orientation as the cause for observed changes. In an ab initio study using total-energy first-principles methods a pressure-induced structural phase transition between 3 and 4 GPa with the crystalline structure changing from (Im-3) cubic to $(R-3)$ rhombohedral is predicted along with a pressure induced semiconductor-metallic transition between 6 and 7 GPa [13]. Experimentally pressure dependent Raman spectroscopic work is carried out on $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ upto 6 GPa [14]. In this work no anomaly was observed up to 6 GPa, however, they observed a negative slope for the pressure dependence of Raman mode positioned at 761 cm^{-1} , implying a possibility of a structural transition at higher pressures. In order to validate these predictions, Raman spectroscopy is employed as it is an ideal tool that can probe the structural transition as well as the onset of metallicity in this compound as shown in our previous studies [10,11]. As such, the onset of local metallic regions in a matrix of insulating phase can only be detected by very few techniques and Raman spectroscopy is one of them. In case a local metallic region is present, electronic and phononic scattering processes interact strongly resulting in a Fano line shape in Raman spectra. The inception of metallicity has been described as the reason behind the appearance of Fano resonance effect in many other compounds [15,16].

Therefore, local structural and electronic properties of CCTO are studied using pressure dependent (20 GPa) Raman scattering in search of changes in phonon structure and Fano resonance effect. For comparison and better understanding studies are also carried out on

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an isostructural compound $\text{SrCu}_3\text{Ti}_4\text{O}_{12}$ (SCTO). To the best of our knowledge there is no high pressure Raman studies on CCTO up to 20 GPa and no pressure dependent Raman studies on SCTO.

2. Experimental procedure

The samples used in the present study are well characterized single phase ceramic samples free of any secondary phase. The samples were characterized using detailed x-ray diffraction, Raman scattering, specific heat and dielectric studies as reported before [10,11]. A diamond anvil cell {cryoDAC-ST} procured from easy Lab Technology, UK with 500 μm diameter culet and stainless steel gasket was used to generate high pressures up to 20 GPa. The pressure transmitting medium used was methanol–ethanol mixture in the ratio 4:1 which maintains hydrostatic conditions up to ~ 9.8 GPa [17]. Pressure measurement was done by the ruby fluorescence technique [18]. The peak positions of the ruby crystal loaded along with the sample were used to determine the pressure in the sample chamber, which allowed in-situ pressure calibration. Raman spectroscopy measurements were performed in the backscattering geometry by excitation with He–Ne laser beam using 632.8 nm line. Scattered light was analysed using a HR-800 Horiba Jobin Yvon, micro-Raman spectrometer having spectral resolution of $\sim 1\text{ cm}^{-1}$ equipped with an edge filter for Rayleigh line rejection, an 1800 g/mm grating and a CCD detector. Prior to the measurement, the system was calibrated by using the 520 cm^{-1} Raman peak of Single crystal Si.

3. Results and Discussions

Fig. 1(a) shows the Raman spectra collected at different pressures up to 20 GPa on $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ compound. The plots are shifted upwards for clarity. As the pressure is increased, the Raman shift of all the modes show systematic increase along with an increase in line width. For comparison the pressure dependent studies are also carried

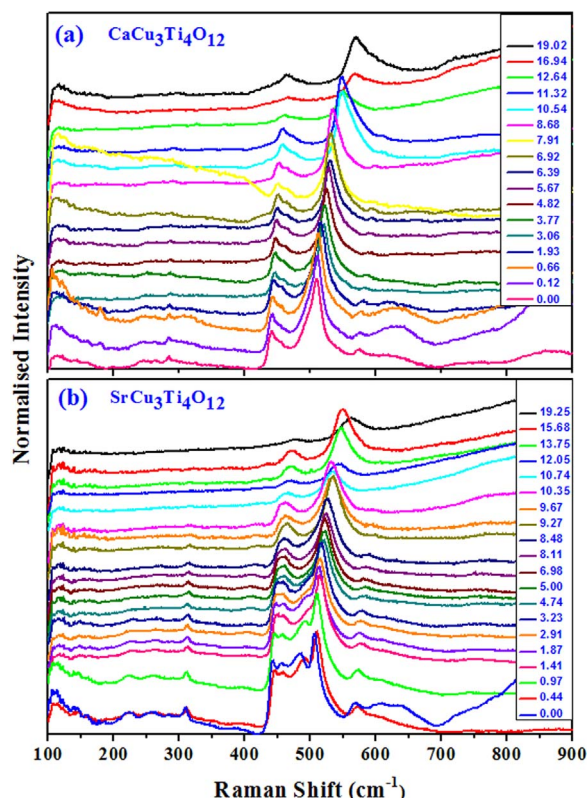


Fig. 1. Raman spectra as a function of increasing pressure up to 20 GPa (bottom to top) for (a) $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ and (b) $\text{SrCu}_3\text{Ti}_4\text{O}_{12}$.

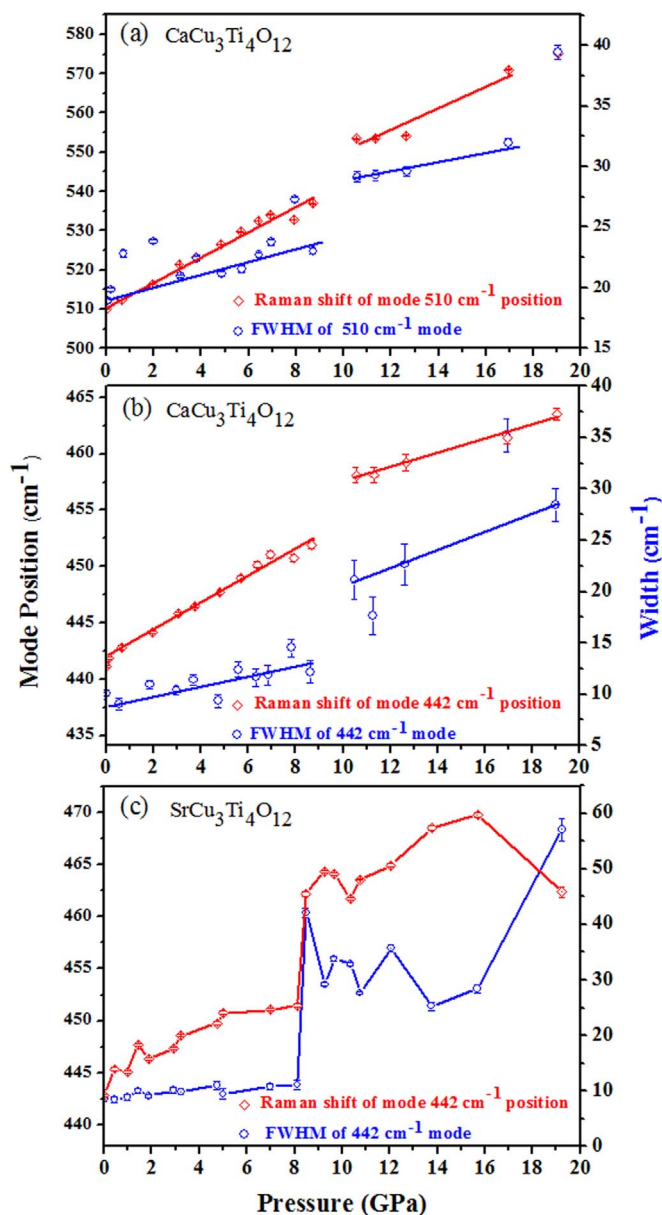


Fig. 2. The evolution of Raman peak position and width with increasing pressure up to 20 GPa for (a) $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$: Ag(2) mode; Ag(1) mode and (b) $\text{SrCu}_3\text{Ti}_4\text{O}_{12}$: Ag(1) mode.

out on iso-structural $\text{SrCu}_3\text{Ti}_4\text{O}_{12}$ and is plotted in Fig. 1(b). The Raman modes are fitted by Lorentzian line shape for all the peaks except the 442 cm^{-1} Ag(1) mode which showed an asymmetric line shape and thus is fitted using a Fano line shape as reported before [11]. The Raman mode peak position and width thus resulted for the 510 cm^{-1} {Ag(2)+Eg(2)} and 442 cm^{-1} Ag(1) modes are shown in Fig. 2(a) and (b) respectively, for the $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ compound. For comparison the mode peak position and width of the $A_g(1)$ peak of the $\text{SrCu}_3\text{Ti}_4\text{O}_{12}$ is plotted in Fig. 2(c). In both the compounds the mode position and width showed a dramatic increase around 8.5 GPa. This indicates a structural rearrangement, however, it can also be due to crossing the hydrostatic limit. As mentioned in experimental section, we have used methanol and ethanol combination liquid during experiment that maintains the hydrostatic condition up to 9.8 GPa. The changes observed are below this limit. The peak at 574 cm^{-1} $\{F_g(3)\}$ also showed suppression above 8.5 GPa and the peak is absent in all the spectra collected above this pressure for both the compounds. This shows that the dramatic change in peak position and width observed in

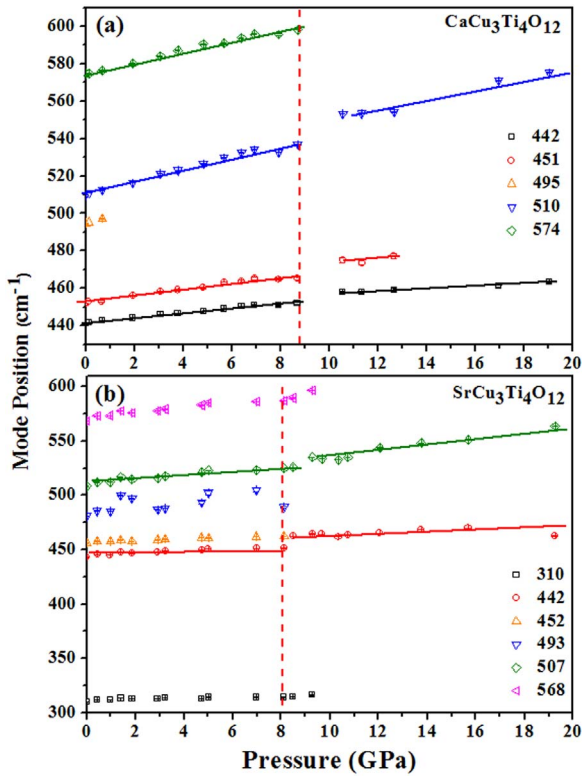


Fig. 3. The Raman mode position versus pressure for (a) $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ and (b) $\text{SrCu}_3\text{Ti}_4\text{O}_{12}$.

the two compounds may be representing a structural transition. The transition observed in the Raman line position and widths around 8 GPa and disappearance of 574 cm^{-1} antistretching (O-Ti-O) $F_g(3)$ mode shows that around this pressure the octahedra around Ti atoms becomes more symmetric. According to lattice dynamical calculations [20] all the Raman modes are related to rotation of TiO_6 octahedra barring the antistretching mode observed at 574 cm^{-1} which is again related to Ti-O bonds. It is therefore anticipated from this observation that the sudden change in Raman line position as a function of pressure and disappearance of antistretching mode is a reflection of a sudden change in the oxygen coordinates pushing it towards more symmetric octahedral structure. We further plotted the variation in peak position as a function of pressure in Fig. 3(a) for $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ and (b) for $\text{SrCu}_3\text{Ti}_4\text{O}_{12}$ compound. All the peaks showed a sudden jump in

Raman shift for both the compounds near 8 GPa along with a few peaks getting diminished. The slope of the pressure dependence of mode frequency showed a distinct change before and after the observed sudden jump in Raman shift near 8 GPa. Therefore, this curve is fitted with two linear functions; one up to 7 GPa and the other one from 10 GPa to 20 GPa that is shown in the Fig. 3 as a solid line. From the slopes, pressure coefficient α is extracted and using α , the mode Gruneisen parameter γ is calculated before and after structural transition. The value of the γ up to 7 GPa for $A_g(2)$ mode is found to be 1.44, and for $A_g(1)$ mode is found to be 0.65 which is comparable to that reported in ref. [14]. These values reduce to 1.18 and 0.30 for $A_g(2)$ and $A_g(1)$ modes respectively after structural transition.

We do not see the emergence of a new peak, which is expected for lowering of the symmetry of the system from cubic symmetry. Fagan et al. in their ab initio studies predicted a cubic (space group Im-3) to rhombohedral (space group R-3) transition near 3–4 GPa. Table 1 gives the site symmetry analysis [19] of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ compound in rhombohedral structure with space group R-3. The Wyckoff site symmetry and atomic coordinates for $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ compound at 10 GPa in R-3 space group are adopted from ref. [13]. Table 1 shows that the R-3 structure yields 80 modes for $Z=2$. In order to facilitate comparison with earlier site symmetry analysis [20] in cubic structure where mode analysis is provided for $Z=1$, in the present study also we can consider reduced unit cell with $Z=1$, which gives a total of 40 modes. Out of these, 16 are Raman active ($8A_g+8E_g$) in comparison to 8 Raman active modes ($2A_g+2E_g+4F_g$) in cubic symmetry [20]. According to factor group analysis, the F_g mode in cubic structure splits in A_g and E_g mode in rhombohedral structure. Therefore, in rhombohedral structure a splitting of F_g mode and appearance of extra modes are expected according to site symmetry analysis, which is not observed in present study. Therefore, the structural transition indicated by the sudden changes in mode position and mode width around 8.5 GPa is isostructural in nature. It may be noted that the ab-initio studies [13] predicted a structural transition near 3–4 GPa. However, the predicted transition is with lowering symmetry from cubic Im-3 to rhombohedral R-3. In addition to the lowering in symmetry, the R-3 space group is non-centro-symmetric and hence the LO and TO modes are expected to be separated which is not observed. Thus we can conclude from our Raman studies that there is no symmetry lowering in both the compounds up to 20 GPa.

In order to detect the semiconductor to metal transition around 6–7 GPa predicted by the ab initio studies [13], we fitted the 442 cm^{-1} $A_g(1)$ mode using a Fano asymmetric line shape function. It is known that if free charge carriers are present in the system i.e. in metallic region, then it produces electronic scattering that interferes with adjacent phonon mode centered around 442 cm^{-1} and this composite

Table 1

Wyckoff notations, atomic site symmetries, fractional atomic coordinates, (adopted from ref. [13]) and irreducible representations (Γ -point phonon modes) for $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ in rhombohedral structure (space group R-3, No. 148, $Z=2$).

Atom	Wyckoff notation	site symmetry	x	y	z	Γ -point phonon modes
Ca(1)	1a	S_6	0.000	0.000	0.000	A_u+E_u
Ca(2)	1b	S_6	0.500	0.500	0.500	A_u+E_u
Cu(1)	3d	C_i	0.500	0.000	0.000	$3A_u+3E_u$
Cu(2)	3e	C_i	0.500	0.000	0.500	$3A_u+3E_u$
Ti(1)	2c	C_3	0.000	0.000	0.248	$A_g+A_u+E_g+E_u$
Ti(2)		C_i	0.000	0.500	0.747	$3A_g+3A_u+3E_g+3E_u$
O(1)	6f	C_i	0.141	0.154	0.161	$3A_g+3A_u+3E_g+3E_u$
O(2)	6f	C_i	0.690	0.196	0.001	$3A_g+3A_u+3E_g+3E_u$
O(3)	6f	C_i	0.409	0.296	0.291	$3A_g+3A_u+3E_g+3E_u$
O(4)	6f	C_i	0.109	0.403	0.209	$3A_g+3A_u+3E_g+3E_u$

Modes classification

$$\text{Total}=16A_g+24A_u+16E_g+24E_u \text{ for } Z=2$$

$$\Gamma_{\text{Raman}}=8A_g+8E_g \quad \Gamma_{\text{IR}}=11A_u+11E_u \quad \Gamma_{\text{acoustic}}=A_u+E_u \text{ for } Z=1$$

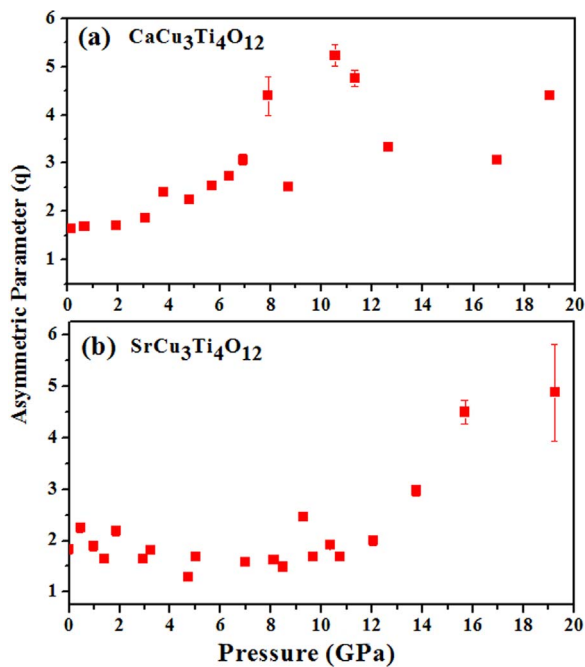


Fig. 4. Variation of the lineshape parameter (q) as a function of pressure. Here the dots are experimental values of ' q ' obtained from the fitting of the Fano profile function to the $\text{Ag}(1)$ mode for (a) $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ and (b) $\text{SrCu}_3\text{Ti}_4\text{O}_{12}$.

scattering reflects in asymmetric line shape [11], commonly known as “fano resonance” effect [21]. An understanding has been developed about the state of the $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ at room temperature. It shows a phase separated state consisting of orbitally ordered highly insulating region coexisting with orbitally disordered metallic region [10,11]. The metallic regions are smaller in area forcing the macroscopic behaviour of the system to remain highly insulating. This metallic fraction (regions) possesses free charge carriers that interact with the phonons giving rise to asymmetric (Fano) line shape of the $\text{A}_1(\text{g})$ mode. Therefore this mode is fitted with fano function $I(\omega) = I_c \frac{1/q + \epsilon^2}{1 + \epsilon^2} + I_b(\omega)$, having characteristic anti-resonance at lower energy side. Where q is the asymmetry parameter, $\epsilon = (\omega - \omega_p)/\Gamma$, ω_p is renormalized phonon frequency, and Γ is the line width. As the peak becomes more asymmetric ' q ' decreases and inverse of the Fano lineshape parameter ($1/q$) is the measure of metallicity in the system [11,16,21].

The ' q ' parameter thus resulted is presented in Fig. 4(a) for $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ and (b) for $\text{SrCu}_3\text{Ti}_4\text{O}_{12}$ as a function of pressure. It showed a linear increase up to 6.92 GPa for $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ and near constant behaviour up to 11 GPa for $\text{SrCu}_3\text{Ti}_4\text{O}_{12}$ and then showed marked fluctuations. However, the lineshape parameter q still showed a continuous increasing trend for both the compounds. The fluctua-

tions at high pressures may be due to the isostructural transition as discussed before. The continuously increasing trend of q parameter shows that the system remains insulating with increase in pressure, there by ruling out the possibility of development of metallic regions above 7 GPa as predicted theoretically [13].

In conclusion, pressure dependent Raman spectroscopic studies on polycrystalline $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ and $\text{SrCu}_3\text{Ti}_4\text{O}_{12}$ is performed up to 20 GPa. The mode positions and line widths showed sudden changes above ~ 8.5 GPa, which is attributed to the isostructural transition. The asymmetry parameter ' $1/q$ ' representing metallicity in the system showed continuous decrease with increasing pressure suggesting that the system remains highly insulating and thus negates the possibility of emergence of metallic phase at higher pressures. These observations completely differ from the ab initio calculations [13] which predicted a lowering of symmetry and occurrence of metallic regions with increasing pressure.

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