



# Raman Spectroscopy of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ Ceramics Revisited

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**Abstract:** The  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO) ceramic has been prepared by Solid State Reaction method in excess oxygen. It possesses a well-defined double-perovskite type crystalline structure and exhibits a colossal dielectric constant of around 50000 at room temperature. This paper revises the imprints of Raman spectroscopy of this compound to validate its structural characteristics and optical behaviors. A special attention is paid on the account of optical phonons which show a recognizable agreement with the other results recently reported.

**Keywords:** CCTO, structure, optical phonon, ceramic method.

## 1. Introduction

The double-perovskite type compound of the stoichiometric content  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (abbreviated as CCTO) is known to possess a colossal dielectric constant  $\epsilon$  at room temperature ( $\sim 50000$  for monocrystals and 30000 for polycrystallites [1, 2]) which can be tuned in a wide range by mean of doping of other element or by variation of preparation conditions. The larger is  $\epsilon$  the wider is application range of the compound. Among the advantages of this compound belongs its high temperature stable dielectric constant from 100 to 600 K. Therefore, it is a valuable material for various device applications. The CCTO inherits its structure from perovskites and is usually crystalized in the  $\text{Im}\bar{3}$  space group ( $T_h$ ) with large unit cell containing 20 atoms. The  $\text{Im}\bar{3}$  space group has a mirror symmetry, therefore it prohibits a formation of spontaneous polarization. The inset in Fig. 1 shows two unit cells, where four perovskite units  $\text{CaTiO}_3$  are showed. As seen, the cations  $\text{Cu}^{2+}$  replace three cations  $\text{Ca}^{2+}$ . The octaheders  $\text{TiO}_6$  are rotating with respect to their own axis and six oxygen atoms surrounding the Ti cations are equally spaced by a same bond length  $\text{Ti-O} = 0.194$  nm. Similarly, each  $\text{Ca}^{2+}$  cation falls inside a cavity formed by 12 oxygen atoms and the  $\text{Ca}^{2+}$  are also equally spaced by  $\text{Ca-O} = 0.255$  nm. The different orientations of the  $\text{TiO}_6$  octaheders lead to the

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different Coulomb fields above each  $\text{Cu}^{2+}$  sites at a body center and face center positions. Among 12 oxygen atoms that surround each  $\text{Cu}^{2+}$  cation, four are equally distanced by 0.192 nm and other eight are lying further. Many studies have been reporting on the origin of the colossal dielectric constant of CCTO but a clear explanation has not been achieved. The polycrystallite CCTO is usually the *n*-type semiconductor which consists of complicated system of grain boundaries, so they exhibit a microstructure typical of a model of an internal barrier layer capacitor (IBLC). The achievement of a colossal dielectric constant within a IBLC system can be considered as arised from the Maxwell-Wagner contribution from all vacuum spaces between the grain boundaries [3, 4]. Several authors argued that the IBLC effects seemed to follow from the twin boundaries inside the monocrystallites [5]. Besides, in many perovskite-based dielectric materials like  $\text{CaTiO}_3$ , the main contribution to dielectric constant originates from the lattice susceptibility associated with phonons. Therefore, we present here both structure characterization and phonons study using the Raman scattering measurements.

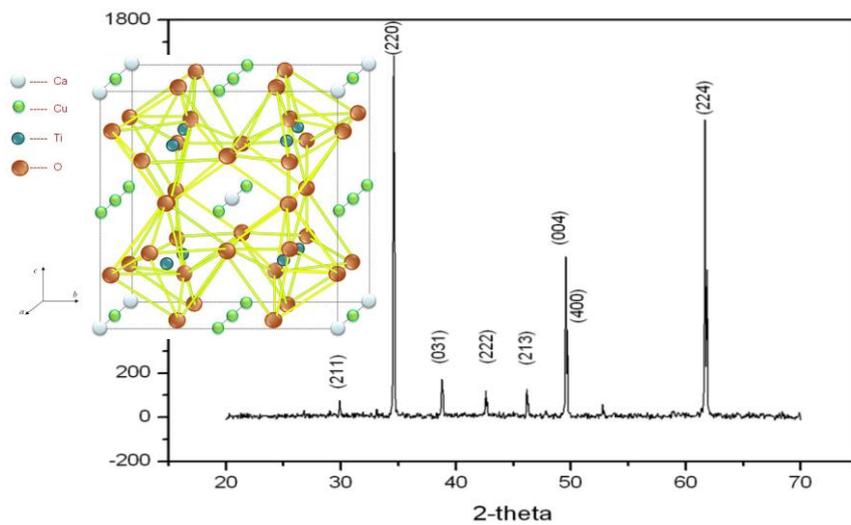


Fig. 1. X-Ray diffraction patterns for  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  with  $(hkl)$  indices given in a standard  $(abc)$  orientation of  $\text{Im}\bar{3}$  space group. Inset: illustration for two unit cells of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ .

## 2. Experimental

Since the CCTO only requires low sintering temperature (usually below 1300 K) it can be conveniently prepared by ceramic technology without specific conditions, but the enriched oxygen environment is preferred. There are four physical parameters influencing the microstructures and phase properties of the final products prepared by ceramic route: temperature, sintering time, pressure and thermal step speed. For temperature and sintering time, we follow the previous studies which showed the optimal quality may be achieved by sintering at  $1050^\circ\text{C}$  in 24 hours. The obtained products at ambient pressure and atmosphere showed usually a good homogeneity, but to achieve a better phase purity we proceeded the preparation with enriched oxygen content of around 10% surplus. The starting materials are the powders  $\text{CaCO}_3$ ,  $\text{CuO}$  and  $\text{TiO}_2$  (Merck, 99.9%) which were carefully mixed with a stoichiometric cation molar ratio of 1:3:4. The dry milling was for 5 hours and followed by a wet milling in the next 4 hours in ethanol. The mixture was left dried for 12 hours and milled again for 4 hour to ensure the homogeneity. The final powder was pressed into the cylinders of diameter 1 cm and

thickness 1mm under a pressure of 5 tons/cm<sup>2</sup>. The pre-sintering temperature was 950°C in 12 hours and the sintering one was 1050°C in 24 hours in excess oxygen (10% surplus). The X-ray diffraction analysis were taken on a Bruker D5005 diffractometer which is equipped with a monochrome radiation CuK $\alpha$  ( $\lambda=0.15056$  nm). The resistivity was measured by using a standard four probe technique. The Raman scattering spectra were recorded by using the Renishaw Invia Raman-Microscope with the excitation light (3mW) from an Ar laser (514 nm) and He-Ne laser (632.8 nm).

### 3. Results and discussion

Fig. 1 shows the obtained X-ray diffractograms for the samples in a standard (*abc*) axis orientation of the Im3 space group. For Rietveld analysis of phases, the WinMPProf software package was used, which shows an overall agreement of lattice parameters with the values previously reported by the other authors. The refinement procedure was as follows: at first the cell parameters (*a*, *b*, *c*) were refined, then the thermal motions of each atom with their isothermal parameters (*B*<sub>ISO</sub>) were optimized, and at the final stage the oxygen positions (*x*, *y*) were obtained. The results showed that the best lattice belongs to a tetragonal system with constants *a* = *b* = 0.7327, *c* = 0.7356 nm, respectively. This symmetry is lower than the cubic Im3 as for the other cases, and signifies that a certain distortion of lattice occurs in the samples. For comparison, the lattices reported in Refs. [5-8] are 0.7411 [5] (thin films prepared by mean of Pulse Laser Deposition technique), 0.7390 [6] (polycrystallites prepared by the ceramic route) and 0.7384 nm [7, 8] (ceramic route) correspondingly.

Some authors, e.g. Ref. [2], argue that a formulation of the CCTO phase depends on milling time, as a reported cell parameter merely decreases according to milling time. But the reported values (*a* = 0.7414 nm for *t* = 2h, and *a* = 0.7412 nm for *t* = 6h) are so close to each other and their differences fall within a detection error of x-ray scattering technique.

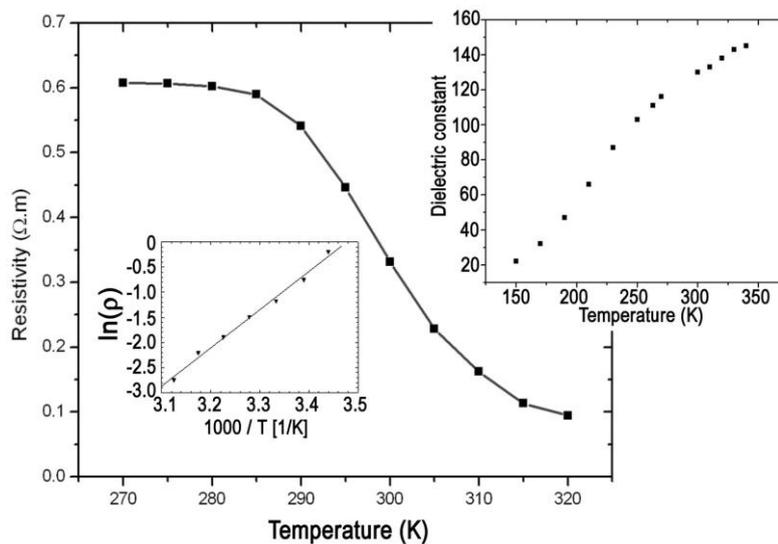


Fig. 2. The temperature dependence of resistivity of CCTO. The small inset shows the linear fit of this curve according to a band gap model:  $\ln \rho = E_a / k_B T + const$ . The attached inset shows the dielectric constant  $\epsilon$  ( $\times 10^{-3}$ ) obtained at room temperature.

Table 1. Phonon modes and site symmetries for CCTO

Atom	Wyckoff symbol	Site symmetry	x	y	z	Modes
Ca	2a	$T_h$	0	0	0	$F_u$
Cu	6b	$D_{2h}$	0	0.5	0.5	$3F_u$
Ti	8c	$S_6$	0.25	0.25	0.25	$A_u+E_u+3F_u$
O	24g	$C_s$	0.303	0.179	0.0	$2A_g+A_u+2E_g+E_u+4F_g+5F_u$

The sintering time may have some effects on the purity of CCTO phase, as the additional phase CaO, CuO may be found. Fig. 2 shows the dependence of resistivity on temperature for a narrow range from 270 to 320 K. In general, the value of resistance was very high, at for T near 340 K the resistance was around  $4.25 \times 10^7 \Omega$ , and for T lower than 250 K the resistance values run up to above  $10^9 \Omega$  which falls out from the measuring range of our equipment.

The increase of resistance according to decreasing temperature suggests that the conduction mechanism is thermally activated. Fig. 2 also shows in the small inset a linear fit for the resistivity according to band-gap model  $\ln \rho \sim E_a/k_B T$  ( $k_B$  stands for a Boltzmann constant). The obtained value for activation energy  $E_a = 0.07$  eV which is very close to the values reported in the previous cases (e.g.  $E_a = 0.08$  eV in Refs. 4 and 9). The activation energy is linked to a gap-width in the band-gap model, and according to it a *dc*-conductivity can be given by a classical Arrhenius law  $\sigma = \sigma_0 \exp(-E_a/k_B T)$  (where  $E_a$  is an activation energy,  $k_B$  is a Boltzmann constant,  $\rho = 1/\sigma$  is resistivity of sample). We have investigated the development of dielectric constant of the samples according to temperature by using the capacitor model. The dielectric constant was evaluated according to a well-known relation  $\epsilon = (Cd)/(\epsilon_0 S)$ , where  $C$  is a capacitance,  $d$  thickness and  $S$  area of sample surface. The obtained typical value is  $\epsilon = 152130$  at 340 K. The attached inset in Fig. 2 shows a dependence of  $\epsilon$  on T with a close linearity well observed.

To investigate the optical properties of the prepared sample, we studied the optical excitations in Raman scattering spectra of CCTO. Table 1 illustrates some information on possible phonon modes as followed from the group theory analysis. The allowed active phonon modes in each regime are:

$$\Gamma_{\text{Raman}} = 2A_g + 2E_g + 4F_g$$

$$\Gamma_{\text{IR}} = 11F_u$$

$$\Gamma_{\text{Acoustic}} = F_u$$

$$\Gamma_{\text{Silent}} = 2A_u + 2E_u$$

Table 2 lists some observed and calculated modes (using LDA/LSDA functionals) for CCTO. As seen, only Raman modes were observed, the IR and other modes were absent.

Table 2. Experimental and theoretical results for the CCTO phonon modes ( $\text{cm}^{-1}$ ) [9-11]

Mode	LDA	Exp.	Mode	LSDA	Exp.
$A_g(1)$	428		$F_g$	277	
$A_g(2)$	512		$E_g$	292	
$E_g(1)$	318		$F_g$	437	
$E_g(2)$	548	499	$A_g$	439	445
$F_g(1)$	280	292	$A_g$	519	513
$F_g(2)$	405	400	$F_g$	552	
$F_g(3)$	574	575	$E_g$	568	577
$F_g(4)$	708		$F_g$	739	

Among the modes, only  $F_u$  is IR-active, and the  $A_u$  and  $E_u$  modes are the silent modes. According to group theory, the Raman spectra of CCTO should possess eight allowed mode: two  $A_g$ , two  $E_g$  and four  $F_g$  modes. As seen in Fig. 3, the experimental data show clearly three strong bands at 445, 512, 576  $\text{cm}^{-1}$ , together with two weaker ones at 292 and 761  $\text{cm}^{-1}$ . This observation agrees well with the results already reported in Refs. [10, 11]. Thus, five allowed modes are present: 292 =  $F_g(1)$ , 445 =  $A_g(1)$ , 512 =  $A_g(2)$ , 576 =  $F_g(2)$ , and 761  $\text{cm}^{-1}$  =  $F_g(3)$  [10, 11]. According to the lattice dynamic calculation, the two modes at 445 and 512  $\text{cm}^{-1}$  are the pseudo-modes originating in the oscillation of the  $\text{TiO}_6$  octaheders. The peak at 576  $\text{cm}^{-1}$  is considered as the Ti-O-Ti anti-stretching vibration of the  $\text{TiO}_6$  octaheders. The mode at 761  $\text{cm}^{-1}$  is probably connected to the symmetric stretching breathing of the same octaheders. A blank area between 210 and 420  $\text{cm}^{-1}$  may be a result of the pairing of two phonons in IR-active regime. The weak features seen after 761  $\text{cm}^{-1}$  were not explained in the previous studies. The reason may lie in the existence of the corrugated phonon modes at the grain boundaries which originate in the bending of the long Cu-O chains and of the bonding Cu-O angles. They may also be caused by the lattice defects.

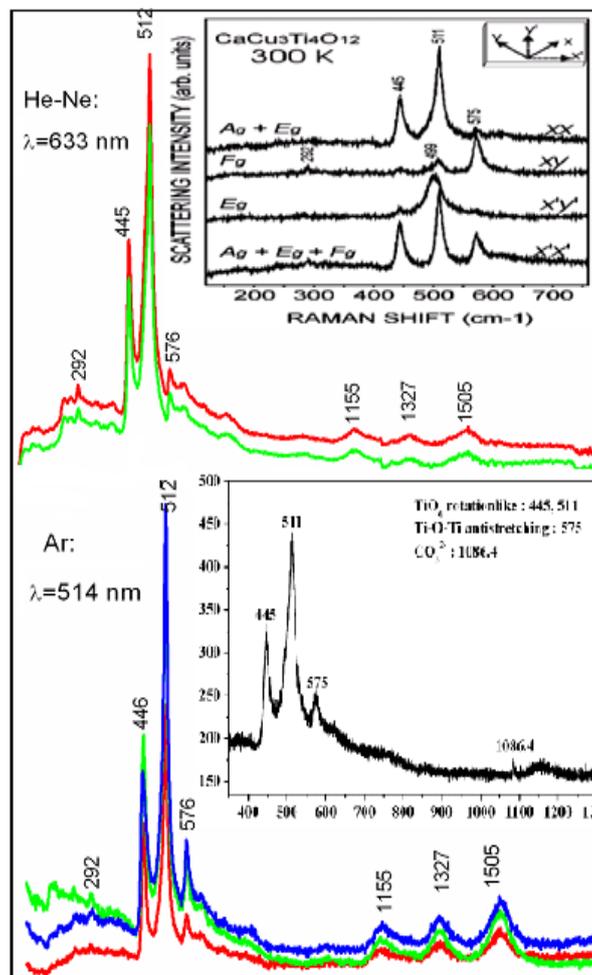


Fig. 3. The Raman scattering spectra of CCTO as obtained using various excitation wave length. Comparisons are given to the results obtained from some previous studies [7, 8].

### 3. Conclusions

We have successfully prepared the  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  materials by a ceramic technology and investigated its electric and optical properties. The sample exhibited a high dielectric constant ( $\sim 52,000$ ) at room temperature and showed almost the same first-order phonon bands as were observed in the previous studies. The results showed that the compound was a semiconductor with the thermally activated conduction regime. The calculated activation energy agreed quite well with the results published by the other groups. The Raman measurement showed that some active modes may be associated with the nanoscale distortion of the grain boundaries.

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