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Raman spectroscopy of $CaCu_3Ti_4O_{12}$

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The polarized Raman spectra of $CaCu_3Ti_4O_{12}$ (CCTO) single crystals were studied between 10 and 600 K. Five of the eight $(2A_g+2E_g+4F_g)$ Raman active modes expected for the $Im\overline{3}$ structure were observed at 292 (F_g), 445(A_g), 499(E_g), 511(A_g), and 575(F_g) cm^{-1}. The assignment of the Raman lines to modes of definite symmetry and eigenvector was done in close comparison with results of lattice dynamics calculations. The mode frequency vs temperature dependence exhibits no anomalies in the whole temperature range. This is consistent with earlier indications that the high value of the dielectric constants and its strong decrease below 100 K are not related to temperature-dependent atomic displacements. An additional line of A_g symmetry, clearly seen at low temperatures is tentatively assigned to vibrations of distorted TiO_6 octahedra, presumably at twin boundaries.

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$CaCu_3Ti_4O_{12}$ (CCTO) is characterized by unusually high value of its dielectric function (10^5-10^6), which remains constant over wide temperature (100–700 K) and frequency $(0\leqslant f<10^6$ Hz) ranges. The origin of the large polarizability of CCTO is still unclear. As a rule, the large dipole moments in some perovskitelike materials are due to atomic displacements within a non-centrosymmetrical structure. Recent neutron powder diffraction studies,[1] however, have refined the CCTO structure in the centrosymmetric $Im\overline{3}$ space group (No. 204, $Z=2$). No indication of phase transition has been found down to 35 K.[1] Given no structural rearrangement was detected, Subramanian *et al.*[1] suggested that the high value of the dielectric function could be due to creation of barrier layer capacitances, presumably at twin boundaries. The observation of small length scale twinning in the CCTO single crystals[1] is consistent with such a suggestion. In search for additional information, the nonpolarized Raman[2] and infrared[3] spectra and their dependence on temperature have also been measured. The reported Raman spectrum consist of several sharp lines, which exhibit no broadening or splitting at low temperatures that may indicate change of the long-range order and transition to lower symmetry state.[2] Except for the sharp lines, a Raman continuum scattering, most clearly pronounced between 220 and 400 cm^{-1}, is present. The origin of this continuum, which decreases sharply below 100 K, is unclear. The complex dielectric function in the phonon energy range has been determined from a Kramers-Kronig analysis of the infrared reflectance.[3] It has been established that the high-frequency infrared-active lattice vibrations (above ~ 300 cm^{-1}) have normal behavior, i.e., harden and narrow, with decreasing temperature. In contrast, the low frequency modes soften and display an anomalous increase of the oscillator strength below ~ 100 K. It has been speculated that the change of the oscillator strength could be due to a redistribution of the formal charge within the TiO_6 octahedra, without associated commensurate structural changes. In the far infrared region $(\omega<20$ $cm^{-1})$ the real part $\epsilon_1(\omega)$ of the dielectric function also increases with decreasing temperature. This is opposite to the dramatic decrease of $\epsilon_1(\omega)$ in the near-zero frequency range $0\leqslant\omega<10^{-4}$ cm^{-1} $(0\leqslant f<10^6$ Hz) and infers the existence of very strong absorption in the microwave frequency range.

Raman spectroscopy allows probing the models of polarizability by analyzing the number and symmetry of Raman modes and searching for anomalies in variations with temperature of the Raman lines corresponding to different types of atomic motions. Indeed, charge redistribution or Ti-shift within the TiO_6 octahedra should strongly affect the frequency of modes involving Ti-O stretching, but to a lesser extent the modes, corresponding to TiO_6 rotations. The latter modes, however, would be more sensitive to changes of the TiO_6 tilts. The existence of domains of different atomic ordering at the twin boundaries would result in appearance of new Raman lines. It is plausible to expect that the degree of twinning will depend on sample technology and, therefore, the twin-boundary-related structures in the Raman spectrum will be sample dependent.

In this paper we report the polarized Raman spectra of oriented microcrystals of CCTO. The symmetry of all observed Raman lines was determined from their polarization properties, whereas the assignment to definite atomic motions was done in close comparison with the calculations of lattice dynamics. The frequency vs temperature dependence for the most pronounced Raman lines corresponding to modes dominated by either TiO_6 tilts or Ti-O stretching was studied between 20 and 600 K. The observation of additional line of A_g is discussed in terms of coexistence of domains of different atomic arrangement, presumably at the twin boundaries.

Samples of $CaCu_3Ti_4O_{12}$ were prepared by a conventional ceramic method from $CaCO_3$, CuO and TiO_2 starting materials. A stoichiometric mixture of the reagents was initially

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TABLE I. Wyckoff notations, atomic site symmetries, fractional atomic coordinates, and irreducible representations (Γ-point phonon modes) for $CaCu_3Ti_4O_{12}$ (space group $Im\overline{3}$, No. 204, $Z=2$). The corresponding Raman tensors and expected intensities in the four available exact scattering configurations are also given.

Atom	Wickoff notation	Site symmetry	x	y	z	Γ-point phonon modes
Ca	$2a$	T_h	0.000	0.000	0.000	F_u
Cu	$6b$	D_{2h}	0.000	0.500	0.500	$3F_u$
Ti	$8c$	S_6	0.250	0.250	0.250	$A_u+E_u+3F_u$
O	$24g$	C_s	0.303	0.179	0.000	$2A_g+A_u+2E_g+E_u+4F_g+5F_u$

Modes classification

$$\Gamma_{\text{Raman}}=2A_g+2E_g+4F_g \quad \Gamma_{\text{IR}}=11F_u \quad \Gamma_{\text{acoustic}}=F_u \quad \Gamma_{\text{silent}}=2A_u+2E_u$$

Raman tensors

$$A_g \rightarrow \begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{bmatrix} \quad E_g \rightarrow \begin{bmatrix} b & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & -2b \end{bmatrix}, \begin{bmatrix} -\sqrt{3}b & 0 & 0 \\ 0 & \sqrt{3}b & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad F_g \rightarrow \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & d \\ 0 & d & 0 \end{bmatrix}, \begin{bmatrix} 0 & 0 & d \\ 0 & 0 & 0 \\ d & 0 & 0 \end{bmatrix}, \begin{bmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

Scattering configuration	Expected Raman intensities A_g	E_g	F_g
xx	a^2	$4b^2$	0
xy	0	0	d^2
$x'x'$	a^2	b^2	d^2
$x'y'$	0	$3b^2$	0

heated in air at 800 °C to decompose the calcium carbonate. The product was then pressed into pellets and re-fired to a final temperature of 1050 °C in air. By powder x-ray diffraction, the final product was found to be a single body-centered cubic phase with a lattice parameter of 7.396(4) Å—close to the value reported in the literature.[1] Scanning electron micrograph (JEOL JSM 6400 SEM) showed uniform facelet particles in the size range 5–20 μm and no evidence for presence of additional phases.

The polarized Raman spectra were collected in backward scattering configuration using a single spectrometer equipped with a microscope, notch filters and liquid-nitrogen-cooled CCD detector. It was assumed that the rectangular microcrystal surfaces coincide with the xy planes and the edges are along either $x(y)$ or $x'(y')$ direction, where x, y, x', and y' denote [100], [010], [110], and $[1\overline{1}0]$ crystallographic directions, respectively. The polarization properties of the Raman lines (see also Table I) confirm that the microcrystal edges are along x' (or y') directions.

For low-temperature measurements an optical cryostat (Microstat$^{\text{He}}$, Oxford Instruments), where the temperature could be varied between 10 and 300 K, was used. The measurements at higher temperatures (up to 700 K) were performed in air using a homemade heating attachment.

The site-symmetry analysis[4] of the perovskitelike $CaCu_3Ti_4O_{12}$ shows that its $Im\overline{3}$ structure yields a total of 24 Γ-point phonons (see Table I). Eight of them are Raman active $(2A_g+2E_g+4F_g)$. In the available scattering configurations, the Raman allowed A_g modes are expected to appear in the parallel xx and $x'x'$ and should not be seen in the crossed xy and $x'y'$ polarization. The first and second letters in these notations denote the polarizations of the incident and scattered light, respectively. The E_g modes are allowed in the xx, $x'x'$, and $x'y'$ polarizations with relative intensities of 4, 1, and 3, respectively, and are forbidden in the xy polarization. As to F_g modes, they are expected to appear with the same intensity in the xy and $x'x'$ configurations.

To assign the Raman lines to definite atomic vibrations, we performed lattice dynamical calculations (LDC's), which

TABLE II. Shell model parameters for the LDC of CCTO.

Ion	Z ($\lvert e\rvert$)	Y ($\lvert e\rvert$)	α (Å^3)	Ionic pair	a (eV)	b (Å^{-1})	c (eV Å^6)
Ca	1.90	3.5	1.5	Ca-O	942	2.69	0
Cu	1.90	3.0	1.3	Cu-O	1400	3.55	0
Ti	3.80	2.0	0.2	Ti-O	3050	3.55	0
O	−1.90	−3.0	2.0	O-O	22764	6.710	20.37

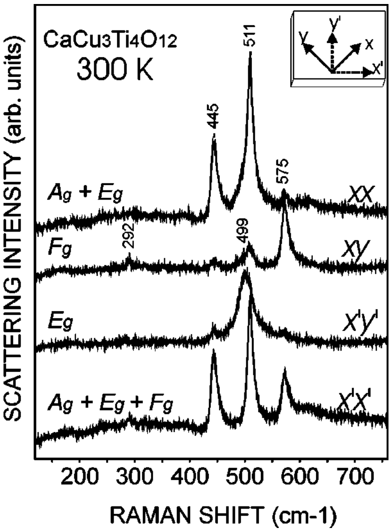

FIG. 1. Polarized Raman spectra of $CaCu_3Ti_4O_{12}$ (CCTO) at room temperature.

predicted both the eigenfrequencies and eigenvectors of the phonon modes. CCTO is mostly ionic and for this reason the LDC were carried out within a shell model.[5] In this model the ions are considered as a three-dimensional periodic array of point charges which interact with each other through long-range interactions modelled by Coulomb potentials. The repulsion of the electron densities of neighboring ions is described by a short-range potential of the Born-Mayer-Buckingham form

$$V = a\exp(-br) - c/r^6, \tag{1}$$

where a, b, and c are parameters and r is the interionic separation. Finally, a simple model of the deformability of the electron shells of the ions is used in which an ion is represented as a point charged core coupled with a force constant k to a charged massless shell with charge Y around it. The free ion polarizability is then given by the formula $\alpha = Y^2/k$. The values of model parameters (see Table II) were taken from Ref. 5. Small changes were required for the values of some of the parameters in order to fulfill the equilibrium conditions. The polarized Raman spectra from single microcrystals of CCTO, as obtained at room temperature with several exact scattering configurations, are shown in Fig. 1. The Raman lines at 445 and 511 cm^{-1} have exact A_g symmetry. One line of E_g symmetry is well pronounced at 499 cm^{-1} in the *xy* spectrum. It is also seen as a shoulder in the *xx* and $x'y'$ spectra. Two lines of F_g symmetry are clearly pronounced at 292 and 575 cm^{-1} in the *xy* and $x'x'$ spectra. The weak steplike continuum scattering above 220 cm^{-1} is observed in only parallel *xx* and $x'x'$ configurations, i.e., it is of A_g symmetry. The positions of the most lines in the Raman spectra are in a good agreement with those predicted by the calculations of lattice dynamics. This allows one to assign unambiguously the experimentally observed lines to definite atomic motions as shown in Table III [see also Fig. 2(a)].

TABLE III. Theoretical and experimental values and the main atomic motions of the Raman active modes in $CaCu_3Ti_4O_{12}$.

Mode	LDC cm^{-1}	Exp cm^{-1}	Main atomic motions
$A_g(1)$	428	445	TiO_6 rotationlike, see Fig. 2
$A_g(2)$	512	511	TiO_6 rotationlike, see Fig. 2
$E_g(1)$	318		TiO_6 rotationlike
$E_g(2)$	548	499	TiO_6 rotationlike
$F_g(1)$	280	292	TiO_6 rotationlike
$F_g(2)$	405	400?	TiO_6 rotationlike
$F_g(3)$	574	575	O-Ti-O antistretching
$F_g(4)$	708		O-Ti-O stretching (breathing)

The temperature variation of the Raman spectra between 20 and 600 K (Fig. 3) does not exhibit any anomalies. Figure 4 shows the temperature dependence of the position of the main peaks in the Raman spectra. The experimental points for the A_g and F_g lines at ≈511 and ≈575 cm^{-1} follow in a good approximation the expected dependence for temperature shift due to anharmonic phonon decay,[6]

$$\omega_{\mathrm{ph}}(T) = \omega_0 - C\left[1 + \frac{2}{e^x - 1}\right], \tag{2}$$

where ω_0 and C for the case of single crystal have the values of 520.5 and 4.9 cm^{-1} (585.8 and 6.4 cm^{-1}), respectively, and $x = \hbar\omega_0/2k_BT$.

The position of the lowest A_g mode at ≈445 cm^{-1} is practically independent on temperature with tendency of softening below 100 K. A careful observation of the line profile of the ≈445 cm^{-1} peak at low temperatures (Fig. 3) reveals two superimposed components centered at 20 K at

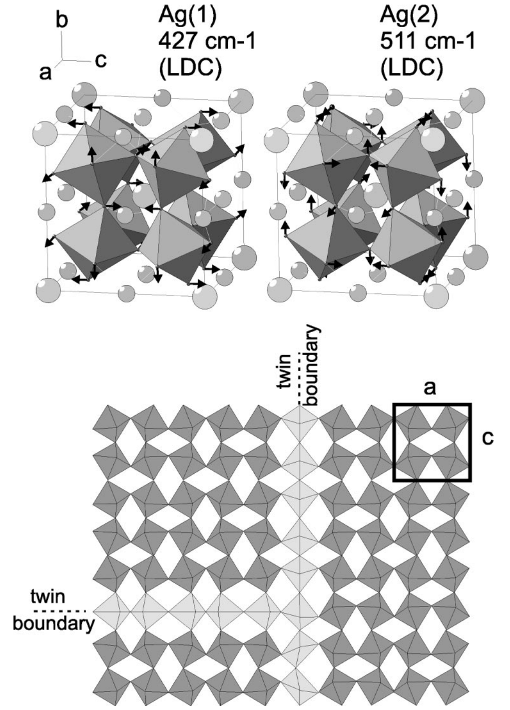

FIG. 2. Oxygen motions in the A_g modes and possible structure of the twin boundaries in CCTO.

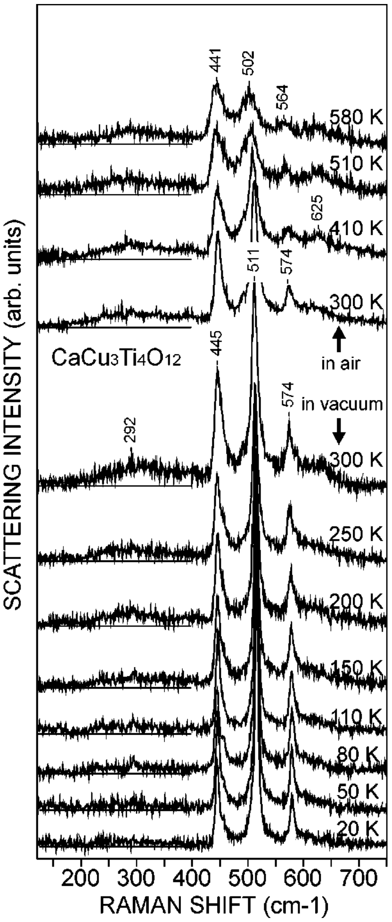

FIG. 3. Variations with temperature of the Raman spectra of CCTO. The scattering configuration is close to $x'x'$. A shoulder of A_g symmetry is clearly seen at low temperatures on the high frequency side of the 445 cm^{-1} peak.

445 ± 1 and 456 ± 2 cm^{-1}. These components become indistinguishable at higher temperatures. It is worth noting here that although similar motions are predicted for the two A_g modes [see Fig. 2(a)], only the low frequency A_g mode exhibits splitting. The relative intensity of the additional A_g component is spot dependent. We tentatively assign this vibration the distorted TiO_6 octahedra constituting the twin boundary layer. It is worth noting that the continuum scattering reported by Ramirez *et al.*[2] is also seen at higher temperatures.

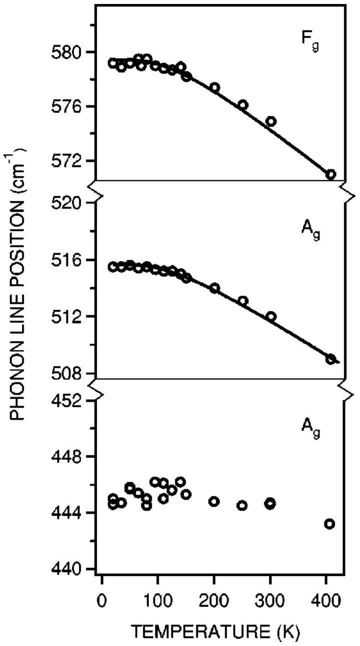

FIG. 4. Variations with temperature of the positions of the main Raman lines. The solid lines fit the experimental points to the dependence expected for anharmonic phonon-phonon scattering [Eq. (1)].

In conclusion, the Raman spectra of CCTO microcrystals were measured in various scattering configurations. The main Raman lines were assigned to definite phonon modes in close comparison with results of lattice dynamical calculations. No evidence for structural phase transition was found in the temperature range between 20 and 600 K. The observation of additional Raman modes of nominally A_g symmetry is consistent with coexistence of domains of different atomic arrangement, presumably at the twin boundaries.

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