

Charge transfer in the high dielectric constant materials $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ and $\text{CdCu}_3\text{Ti}_4\text{O}_{12}$

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The cubic perovskite-related ceramic $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ has a very high static dielectric constant $\epsilon_0 \approx 10\,000$ at room temperature (RT), which drops to about 100 below ≈ 100 K. Substituting Cd for Ca reduces the RT value of ϵ_0 by over an order of magnitude. The origin of the large ϵ_0 is not fully understood, but may be due to an internal barrier layer capacitance (IBLC) effect. Infrared measurements on the Ca and Cd compounds show that low-frequency modes increase dramatically in strength at low temperature, suggesting a change in the effective charges and increasing electronic localization that may lead to a breakdown of the IBLC effect.

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High dielectric constant materials find numerous technological applications. In the case of memory devices based on capacitive components, such as static and dynamic random access memories, the static dielectric constant ϵ_0 will ultimately decide the level of miniaturization. The dielectric constant of a material is related to the polarizability α , in particular, the dipole polarizability (an atomic property), which arises from structures with a permanent electric dipole which can change orientation in an applied electric field. These two quantities are linked through the Clausius-Mossotti relation. In insulators $\epsilon_0 > 0$; materials with a dielectric constant greater than that of silicon nitride ($\epsilon_0 > 7$) are classified as “high dielectric constant” materials. In general, a value of ϵ_0 above 1000 is related to either a ferroelectric which exhibits a dipole moment in the absence of an external electric field, or a relaxor characterized by a ferroelectric response under high electric fields at low temperature, but no macroscopic spontaneous polarization. However, both classes of materials show a peak in ϵ_0 as a function of temperature, which is undesirable for many applications. The body-centered cubic perovskite-related material $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ shown in Fig. 1 has recently attracted a great deal of attention due to its extremely high value for the static dielectric constant $\epsilon_0 \sim 10^4$ measured in ceramics in the radio frequency kilohertz region,¹⁻⁴ and was found to be practically constant in the 100–600 K region. Both properties are important for device implementation.^{5,6} However, ϵ_0 displays a 100-fold reduction below ~ 100 K, without any detectable change in of the long-range crystallographic structure when probed by high-resolution x-ray² and neutron powder diffraction.¹ This contrasts with known ferroelectrics, which structurally distort because of soft-mode condensation.^{7,8} The substitution of Ca with Cd results in a material with a similar temperature dependence, but a much

lower dielectric constant, $\epsilon_0 \sim 500$ in a ceramic.¹ Concerns have recently been raised that the large values for ϵ_0 is purely an extrinsic effect due to Maxwell-Wagner-type depletion layers at sample contacts or at grain boundaries.⁹ However, one of us (A.P.R.) has recently succeeded in separating the contacts from the sample through the use of a thin aluminum oxide buffer layer, and has shown that $\epsilon_0 \sim 10^4$ for $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, ruling out contact contributions as the sole source of the large ϵ_0 .¹⁰ Moreover, it is not clear why the substitution of Cd for Ca results in such a dramatically lower value for ϵ_0 . In this report, we present optical results which

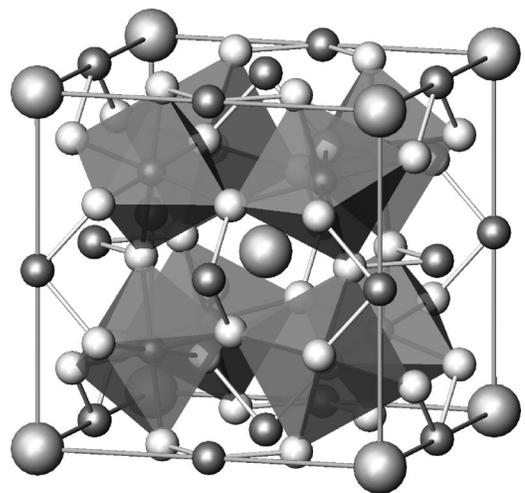


FIG. 1. The unit cell of body-centered cubic $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ in the $Im\bar{3}$ space group, which consists of two formula units. The Ti atoms sit at the center of the canted TiO_6 octahedra (the tilt angle is nominally 141°), with bridging Cu atoms bonded to the oxygens, and large Ca atoms the corners and center of the unit cell.

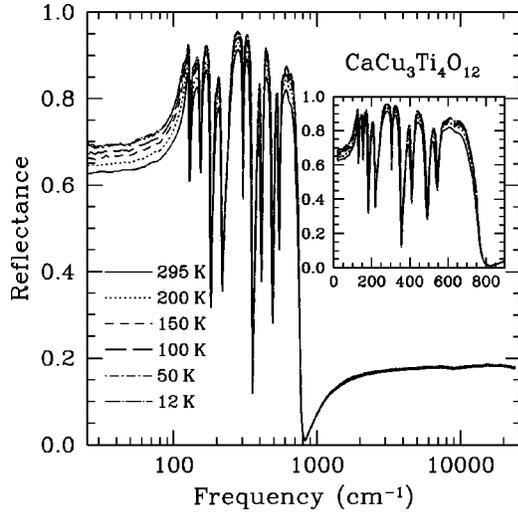


FIG. 2. The temperature dependence of the reflectance of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ from ≈ 20 – $23\,000\text{ cm}^{-1}$. The reflectance is typical for that of an insulator. Above highest longitudinal optic-phonon frequency ($\approx 700\text{ cm}^{-1}$), the reflectance becomes flat and featureless to the highest measured frequency, indicating that the gap edge has not yet been encountered (i.e., $2\Delta \geq 3\text{ eV}$). Inset: The low-frequency reflectance.

provide information as to the origin of the large ϵ_0 in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ and its rapid decrease below $\approx 100\text{ K}$. We reported earlier on the optical spectra of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. Here, we provide optical results on $\text{CdCu}_3\text{Ti}_4\text{O}_{12}$ and compare them with the Ca compound. The results on the two materials offer insights as to the origin of the large value for ϵ_0 and its rapid decrease below 100 K , as well as why ϵ_0 is much smaller in the Cd material.

Single crystals of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ were grown by the traveling-solvent floating-zone method with an image furnace using a technique that has been described in detail elsewhere.³ The ceramic compounds were prepared by conventional solid-state reaction using starting oxides (CaO or CdO, TiO_2 and CuO) with a purity of 99.9% or higher. The mixed powder taken in stoichiometric ratio was calcined at 850°C for 8 h. The calcined powder was reground and pressed into disks and sintered in sealed gold tubes at 1000°C for 20 h. X-ray-diffraction data showed the materials are a single phase. The $\text{ACu}_3\text{Ti}_4\text{O}_{12}$ family of compounds has been known for some time,¹¹ and their structures have been determined (Fig. 1).

The temperature-dependent reflectance of polished $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (crystal) and $\text{CdCu}_3\text{Ti}_4\text{O}_{12}$ (ceramic) have been measured over a wide range (≈ 20 – $23\,000\text{ cm}^{-1}$) using an overcoating technique.¹² In practice, the reflectance of ceramics and crystals is nearly identical. The reflectance of the Ca material shown in Fig. 2 is typical of a nonmetallic system. The sharp features in the reflectance are due to the unscreened infrared-active lattice vibrations; above the highest observed phonon frequency the reflectance is flat and featureless up to the highest measured frequency, suggesting that the optical value for the optical gap $2\Delta \geq 3\text{ eV}$. The optical properties have been determined from a Kramers-Kronig analysis of the reflectance, which requires extrapola-

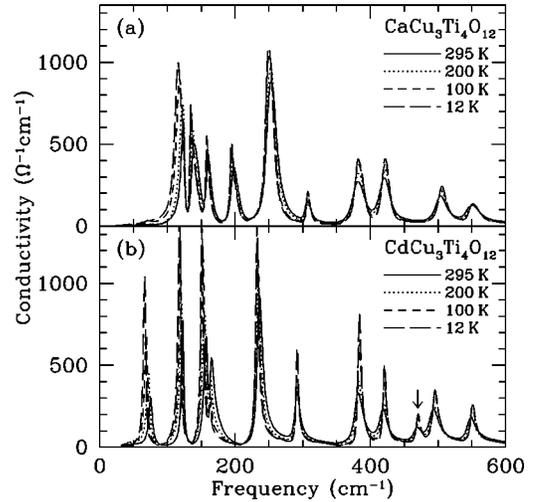


FIG. 3. (a) The temperature-dependent optical conductivity of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. The low-frequency infrared-active lattice modes soften and show an anomalous increase in oscillator strength with decreasing temperature. (b) The temperature-dependent optical conductivity of $\text{CdCu}_3\text{Ti}_4\text{O}_{12}$. The low-frequency modes show the same anomalous increase in strength with decreasing frequency, and in addition, many of the vibrations in this material are narrower at low temperature. Note the unusual appearance of a new mode at $\sim 470\text{ cm}^{-1}$ (arrow) in the Cd material. (The vibrational parameters are tabulated in Table I.)

tions at high and low frequencies. At low frequency, the reflectance was assumed to be constant below the lowest measured frequency for $\omega \rightarrow 0$, while at high frequency the reflectance was assumed to be constant above the highest measured point to $2 \times 10^5\text{ cm}^{-1}$, above which a free-electron approximation ($R \propto \omega^{-4}$) was assumed.

The real part of the optical conductivity, derived from the imaginary part of the dielectric function $\sigma_1 = \omega \epsilon_2 / 4\pi$, is shown for $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ in Fig. 3(a) in the low-frequency region. As with the reflectance, the conductivity is characteristic of a semiconductor or insulator [$\sigma_{dc} \equiv \sigma_1(\omega \rightarrow 0) \approx 0$], and is dominated by the lattice modes. The low-frequency modes display an anomalous increase in oscillator strength at low temperature. The optical conductivity of $\text{CdCu}_3\text{Ti}_4\text{O}_{12}$ is shown in Fig. 3(b). The low-frequency vibrations in the Cd material have the same anomalous increase in strength at low temperature. In addition, a new mode is clearly observed at $\approx 470\text{ cm}^{-1}$; this mode is curiously absent in the Ca material,^{3,13} and will be discussed in more detail in a future work. Below $\approx 300\text{ cm}^{-1}$, there are some significant downward frequency shifts with doping with respect to the Ca material, indicating that Cd (Ca) plays a significant role in these vibrations. The infrared-active modes have been fitted using the complex dielectric function $\tilde{\epsilon}(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ for Lorentz oscillators,

$$\tilde{\epsilon}(\omega) = \epsilon_\infty + \sum_j \frac{\omega_{p,j}^2}{\omega_j^2 - \omega^2 - i\omega\gamma_j}, \quad (1)$$

where ω_j , γ_j , and $\omega_{p,j}$ are the frequency, width, and effective plasma frequency of the j th vibration; ϵ_∞ is the core

TABLE I. The phonon parameters for Lorentzian fits to the conductivity of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ and $\text{CdCu}_3\text{Ti}_4\text{O}_{12}$ ceramics at 10 and 295 K, where ω_j , γ_j , and $\omega_{p,j}$ are the frequency, width, and effective plasma frequency of the j th vibration. (All units are in cm^{-1} .)

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$						$\text{CdCu}_3\text{Ti}_4\text{O}_{12}$					
295 K			10 K			295 K			10 K		
ω_j	γ_j	$\omega_{p,j}$	ω_j	γ_j	$\omega_{p,j}$	ω_j	γ_j	$\omega_{p,j}$	ω_j	γ_j	$\omega_{p,j}$
552	27	435	554	18	376	550	26	484	552	13	421
504	19	445	506	14	454	494	20	500	497	13	502
						468	13	250	471	7.1	277
421	19	553	422	11	529	419	17	450	421	6.1	421
382	18	535	383	13	560	383	15	533	384	6.0	534
308	8.7	255	308	5.2	246	292	13	471	292	4.8	410
254	16	913	251	12	916	237	10	745	233	5.8	681
199	9.9	456	195	7.1	448	166	8.5	495	163	8.0	291
161	7.8	423	159	5.2	388	156	5.6	485	151	4.7	619
141	11	562	136	6.1	453	122	4.0	436	118	4.6	636
122	6.0	464	116	12	851	75	6.9	349	66	4.3	523

^aFor $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, single-crystal and ceramic samples yielded similar results.

contribution to the dielectric function at high frequencies. The results of the fits to the conductivity are shown in Table I at 10 and 295 K for both materials.

As we have previously noted, the anomalous increase in oscillator strength of the low-frequency modes is unusual, and has important consequences. Optical sum rules provide a powerful tool with which to analyze the behavior of free carriers and bound excitations.¹⁴ Briefly, the partial conductivity sum rule for oscillators states that¹⁵

$$\frac{120}{\pi} \int_{\omega_a}^{\omega_b} \sigma_1(\omega) d\omega = \omega_{p,j}^2, \quad (2)$$

where the interval $\omega_a \rightarrow \omega_b$ is chosen so that the full spectral weight of the j th oscillator is captured. In the absence of changes in the bonding or coordination, the mode may narrow with decreasing temperature, but the spectral weight (proportional to area under the peak, or $\omega_{p,j}^2$) should not change. The dramatic increase in the oscillator strength of the low-frequency modes (Fig. 3 and Table I) is a clear violation of this sum rule, which in turn has implications for the distribution of charge within the unit cell. Light couples to the induced dipole moments created by the atomic displacements associated with a normal mode—if the Born effective charge per atom Z^* is increasing, then the size of the induced dipole moment and the optical absorption will also increase. For a material with k atoms in the unit cell, the effective charge per atom can be defined as¹⁶

$$\frac{1}{\epsilon_\infty} \sum_j \omega_{p,j}^2 = \frac{4\pi}{V_c} \sum_k \frac{(Z_k^* e)^2}{M_k}, \quad (3)$$

where $\sum_k Z_k^* = 0$, V_c is the unit-cell volume, and j and k index the lattice modes and the atoms with mass M_k , respectively. The fitted values of $\omega_{p,j}$ in Table I indicate that there is an increase between room temperature and 10 K in the left side of Eq. (3) of $\approx 11\%$ in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, and $\approx 4\%$ in $\text{CdCu}_3\text{Ti}_4\text{O}_{12}$. The increase in the left side of Eq. (3) implies

that the Z_k^* 's are increasing with decreasing temperature. In oxide materials, oxygen is often the lightest element, so that the summation is dropped and the change in the effective charge is associated purely with the oxygen (i.e., $Z_k^* \cong Z_O^*$). While the presence of other light elements in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ may complicate this approach, it is less of a problem in the Cd material. The deduced values for Z_O^* are shown in Fig. 4, and illustrate a noticeably different behavior for the Ca and Cd materials. While Cd is somewhat smaller ($\sim 16\%$) than the Ca cation, the main difference between these two materials is their electronegativity, or the ability of an atom to attract electrons to itself. The Pauling electronegativity for Ca and Cd are 1.0 and 1.7, respectively. It is expected that an atom with a higher electron affinity will result in less charge

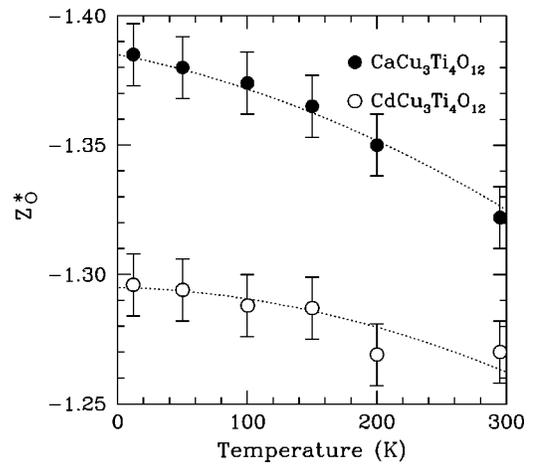


FIG. 4. The temperature dependence of the deduced values Born effective charge per oxygen atom (Z_O^*) in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ and $\text{CdCu}_3\text{Ti}_4\text{O}_{12}$. The dotted lines are drawn as a guide to the eye. Note that the value for Z_O^* in the Cd material is lower for the Ca material, and that the Z_O^* increases by more than 5% in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, compared to an increase of less than 2% in $\text{CdCu}_3\text{Ti}_4\text{O}_{12}$.

transfer to the oxygen atoms, and the reduction in Z_0^* is precisely what is in fact observed in the Cd material.

The large dielectric constant observed in these materials must ultimately be due to either intrinsic effects that arise from the properties of the material (such as lattice vibrations), or extrinsic effects, such as defects¹⁷ or contact problems.⁹ However, the persistence of the large value of ϵ_0 with the addition of a buffer layer between the sample and the contact indicates that contact problems alone are not the source of the large dielectric constant.¹⁰ On the other hand, the absence of a structural transition tends to rule out the possibility that the large ϵ_0 is the result of purely intrinsic effects, such as the displacements of Ca atoms or some distortion that involves the TiO_6 octahedra. A more compelling explanation comes from the observation that $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ single crystals are in fact heavily twinned due to the lack of fourfold symmetry.¹ A possible description of a twin boundary has been described as a mismatch between the tilting angles of the TiO_6 octahedra.^{4,18} The degree of twinning and the domain size may vary from one material to another due to the different chemistry of the cations. This view is consistent with results based on impedance spectroscopy of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics, which indicate that these materials may be understood as being semiconducting regions separated by insulating barriers.¹⁹ This suggests that the giant dielectric constant is, at least in part, an “extrinsic” effect due to an internal barrier layer capacitance (IBLC) effect.^{1,19} The IBLC results in a large ϵ_0 that has the same Debye-like frequency dependence that has been observed in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (Refs. 2 and 3). A puzzling aspect of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, and to a lesser extent $\text{CdCu}_3\text{Ti}_4\text{O}_{12}$, is the rapid suppression of ϵ_0 that occurs at low temperature. The

increase in Z_0^* (Fig. 4) implies increasing electronic localization with decreasing temperature. This localization may lead to an increase in the size of the insulating regions, which would result in the commensurate reduction of ϵ_0 within the IBLC picture. Within this interpretation, the lower room-temperature (RT) value of ϵ_0 in $\text{CdCu}_3\text{Ti}_4\text{O}_{12}$ suggests that this material is not as heavily twinned, which may in turn be related to the slightly lower values of Z_0^* . It has also been pointed out that a small concentration of defects $\mathcal{O}(10^{-3})$ in a braced structure such as $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ can disrupt the bracing and relax between different equivalent configurations, giving rise to extremely large values for the ϵ_0 above a characteristic temperature.¹⁰ This model provides a useful alternative to the IBLC picture. However, it does not explain why Cd substitution results in a dramatically lower RT value for ϵ_0 ; it may be possible to treat the twin boundaries as “defects” in an attempt to present a unified view.

In summary, the optical properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ and $\text{CdCu}_3\text{Ti}_4\text{O}_{12}$ have been measured at a variety of temperatures. Low-frequency modes are observed to strengthen dramatically at low temperature, indicating that the Born effective charges are increasing in the unit cell. We propose that the large ϵ_0 may be due to extrinsic mechanisms such as the formation of boundary-layer capacitors, and that the rapid reduction of ϵ_0 at low temperature is due to the removal of an IBLC mechanism. The $\text{CdCu}_3\text{Ti}_4\text{O}_{12}$ system has a lower value of ϵ_0 due to a reduced degree of twinning.

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¹M.A. Subramanian, D. Li, N. Duan, B. Reisner, and A.W. Sleight, *J. Solid State Chem.* **151**, 323 (2000).

²A.P. Ramirez, M.A. Subramanian, M. Gardel, G. Blumberg, D. Li, T. Vogt, and S.M. Shapiro, *Solid State Commun.* **115**, 217 (2000).

³C.C. Homes, T. Vogt, S.M. Shapiro, S. Wakimoto, and A.P. Ramirez, *Science* **293**, 673 (2001).

⁴M.A. Subramanian and A.W. Sleight, *Solid State Sci.* **4**, 347 (2002).

⁵R. Singh and R.K. Ulrich, *Electrochem. Soc. Interface* **8**, 26 (1999).

⁶B.-G. Kim, S.M. Cho, T.-Y. Kim, and H.M. Jang, *Phys. Rev. Lett.* **86**, 3404 (2001).

⁷Z. Zeng, M. Greenblatt, M.A. Subramanian, and M. Croft, *Phys. Rev. Lett.* **82**, 3164 (1999).

⁸A.D. Bruce and R.A. Cowley, *Structural Phase Transitions* (Taylor & Francis, London, 1981).

⁹P. Lunkenheimer, V. Bobnar, A.V. Pronin, A.I. Ritus, A.A. Volkov,

and A. Loidl, *Phys. Rev. B* **66**, 052105 (2002).

¹⁰A.P. Ramirez, G.L. and dV. Butko, M.A. Subramanian, and C.M. Varma, cond-mat/0209498 (unpublished).

¹¹B. Bochu, M.N. Deschizeaux, and J.C. Joubert, *J. Solid State Chem.* **29**, 291 (1979).

¹²C.C. Homes, M. Reedyk, D.A. Cradles, and T. Timusk, *Appl. Opt.* **32**, 2976 (1993).

¹³L. He, J.B. Neaton, M.H. Cohen, D. Vanderbilt, and C.C. Homes, *Phys. Rev. B* **65**, 214112 (2002).

¹⁴D.Y. Smith, *Handbook of Optical Constants of Solids* (Academic, New York, 1985).

¹⁵The prefactor in the sum rule assumes that the units of the conductivity are in $\Omega^{-1} \text{cm}^{-1}$, and that the units of the effective plasma frequency for the oscillator are in cm^{-1} .

¹⁶J.F. Scott, *Phys. Rev. B* **4**, 1360 (1971).

¹⁷G.A. Samara and L.A. Boatner, *Phys. Rev. B* **61**, 3889 (2000).

¹⁸N. Kolev, R.P. Bontchev, A.J. Jacobson, V.N. Popov, V.G. Hadjiev, A.P. Litvichuk, and M.N. Iliev, *Phys. Rev. B* **66**, 132102 (2002).

¹⁹D.C. Sinclair, T.B. Adams, F.D. Morrison, and A.R. West, *Appl. Phys. Lett.* **80**, 2153 (2002).