

## Giant Dielectric Effect in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ and Its Cd Analogue

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*The perovskite-related material  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  has a very high static dielectric constant  $\epsilon_0 \sim 10^4$  at room temperature, which drops to about 100 at low temperature. Substituting Cd for Ca reduces the room temperature value by over an order of magnitude. The origin of the large  $\epsilon_0$  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 dramatic changes in the nature of the normal modes at low temperature, suggesting that increasing electronic localization may lead to a breakdown of the IBLC effect.*



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Materials with large dielectric constants are highly sought after in the microelectronics industry for use in memory devices; the static dielectric constant  $\epsilon_0$  acts as a scaling factor and ultimately determines the level of miniaturization. One of the most commonly used dielectric materials is silicon nitride with  $\epsilon_0 \sim 7$ ; materials with  $\epsilon_0 > 7$  are generally referred to as high-dielectric constant materials. It was recently noted that the cubic perovskite-related material  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  shown in **Figure 1** had a tremendously high dielectric constant at room temperature,  $\epsilon_0 \sim 10^4$ , which showed little temperature dependence until about 100 K, below which it decreased by nearly two orders of magnitude to  $\epsilon_0 \sim 100$ , shown in **Figure 2a**. The substitution of Cd for Ca results in a large reduction of  $\epsilon_0$ , shown in **Figure 2b**. It was initially suggested that this large value for  $\epsilon_0$  was a purely extrinsic effect due to Maxwell-Wagner-type depletion layers forming between the sample and the metal contacts used in the capacitive measurements of  $\epsilon_0$  in the kHz range. This effect has indeed been observed in a number of different materials. However, the addition of a thin a buffer layer of a dielectric with well-known electrical properties (aluminum oxide) has demonstrated that the large value for  $\epsilon_0$  persists in these materials, and is therefore a property of the bulk. The dramatic drop of  $\epsilon_0$  at low temperature is curious because it is not accompanied by any change in the long-range crystallographic structure when probed by high-resolution x-ray and neutron powder diffraction. In ferroelectric materials, large changes in  $\epsilon_0$  are usually accompanied by a structural distortion and soft-mode condensation.

Infrared (IR) spectroscopy is a powerful tool to study the lattice vibrations in insulators, in particular soft-mode condensation. The large change in  $\epsilon_0$  and the absence of any structural distortion suggested that the normal modes should be examined. The temperature dependence of the reflectance was determined over a wide frequency range using the spectrometer at NSLS beamline U10A and the complex optical properties determined from a Kramers-Kronig analysis. The real part of the dielectric function  $\epsilon_1$  is shown in **Figures 3a and 3b** for  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  and  $\text{CdCu}_3\text{Ti}_4\text{O}_{12}$ , respectively, at a variety of temperatures in the infrared region. The dielectric function is dominated by the infrared ac-

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tive lattice modes. (The units of  $\text{cm}^{-1}$  are commonly used in IR spectroscopy,  $1 \text{ THz} = 30 \text{ cm}^{-1}$ .) While these experiments are done in the THz range, the low-frequency value for  $\epsilon_1$  agrees with the values for  $\epsilon_0$  (kHz) at low temperature. It is clear from **Figure 3** that  $\epsilon_1$  at low frequency is also increasing at low temperature. Fits to simple Lorentzian oscillators describe these features quite well and indicate that many of the vibrational modes are gaining strength at low temperature, a violation of the partial  $f$ -sum rule for oscillators. From this result, it may be inferred that the Born effective charge on the atoms is changing and that the material is becoming more ionic. We (along with others) have speculated that the large value of  $\epsilon_0$  is due to an internal barrier layer capacitance (IBLC) effect due to extensive twinning or grain boundaries. This view is consistent with impedance spectroscopy that indicates these materials may be described as semiconducting regions separated by insulating barriers. The increase in ionicity implies increasing charge localization at low temperatures. This localization may lead to an increase in the size of the insulating regions and a commensurate reduction of  $\epsilon_0$  within the IBLC picture, suggesting that the large value for  $\epsilon_0$  is, at least in part, due to “extrinsic” effects.

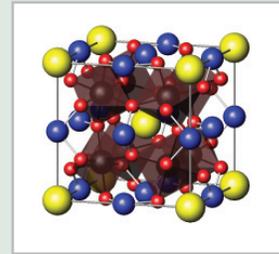


Figure 1. The unit cell of body-centered cubic  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ , which consists of two formula units. The Ti atoms sit at the center of canted  $\text{TiO}_6$  octahedra (the tilt angle is nominally  $141^\circ$ ), with bridging Cu atoms and large Ca atoms sitting at the center and corners of the unit cell.

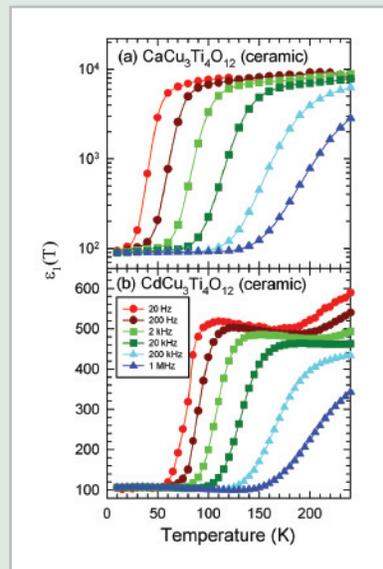


Figure 2. The temperature dependence of the real part of the dielectric constant of (a)  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  and (b)  $\text{CdCu}_3\text{Ti}_4\text{O}_{12}$  ceramics for several fixed frequencies.

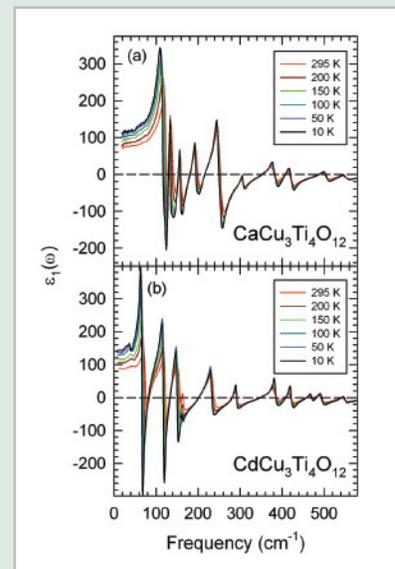


Figure 3. The temperature dependence of the real part of the dielectric function for (a)  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  and (b)  $\text{CdCu}_3\text{Ti}_4\text{O}_{12}$  in the infrared region.