# The Very Large Dielectric Constant of $CaCu_3Ti_4O_{12}$: An Inhomogeneous Semiconductor

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**Motivation**—The unusual dielectric properties of $CaCu_3Ti_4O_{12}$ (CCTO) have been of much recent scientific and technical interest. The material has a distorted, complex cubic perovskite ($ABO_3$)-like structure and exhibits a very large (>10,000) and nearly temperature (T)-independent apparent static dielectric constant, ε′, for ceramic samples in the range 200-300K. Such large ε′ values make CCTO an attractive material for ultra high energy density capacitors. Below ~ 200K ε′ exhibits relaxational behavior, ultimately dropping to a value of ~100 at the lowest T with the crystal structure remaining cubic and centrosymmetric down to at least 35K. While dipole relaxation models associated with the complex crystal structure of CCTO have been suggested to explain this dielectric response, it is now generally agreed that the observed behavior is not intrinsic. However, more complete understanding of the physics is still needed.

**Accomplishment**—We have investigated the influences of temperature, pressure, and Nb and Fe doping on the dielectric properties of CCTO. The results have revealed new features and have shed much light on the physics of this material. Highlights of the work are as follows: The unusual dielectric relaxation response of CCTO (Fig. 1) is indeed extrinsic and can be understood essentially quantitatively in terms a capacitive barrier-layer model, as for an inhomogeneous semiconductor, consisting of semiconducting grains and insulating grain boundaries. The energetics and kinetics of the main (low T) relaxation process were determined. Two thermally activated regimes related to different conduction processes in the CCTO grains control the dynamics. It is suggested that these two regimes result from the emission of electrons from two energy levels associated with the processing-induced oxygen vacancy. A higher T relaxation process was also discovered that is determined by grain boundary conduction. Both Nb and Fe doping lead to lower ε′ in the temperature insensitive region and to lower dielectric loss, but Fe doping leads to the more dramatic effects (Fig. 2). In particular 3 at. % Fe makes CCTO an intrinsic very low loss dielectric and removes the anomalous ε′(ω,T) response. It is suggested that the intrinsic behavior is due to carrier compensation in the grains, the Fe-produced holes from $Fe^{3+}$ substituting for $Ti^{4+}$ compensating the conduction electrons attributed to oxygen vacancies. The intrinsic nature of the response for the 3 at.% Fe sample allowed determination of the intrinsic value of ε′ (≈75 at low T) and its temperature dependence. This large ε′ (compared to that of normal dielectrics where ε′≤10) and its decrease with increasing T (unlike normal dielectrics) are largely determined by a low-lying, long wavelength, soft TO phonon – a ferroelectric-like mode. A dielectric anomaly associated with the onset of antiferromagnetic order is observed below the 24 K Neel temperature, providing evidence of coupling between the polarization and sublattice magnetization (Fig. 3).

**Significance**—We have recently observed very large and nearly T-independent ε′ over substantial T ranges and relaxational responses, similar to those for CCTO in studies on doped single crystal perovskites, suggesting that these properties may be general for complex oxides. Thus understanding the physics and controlling the dielectric loss of such materials are essential and could have high payoff in the technology of high energy density capacitors.

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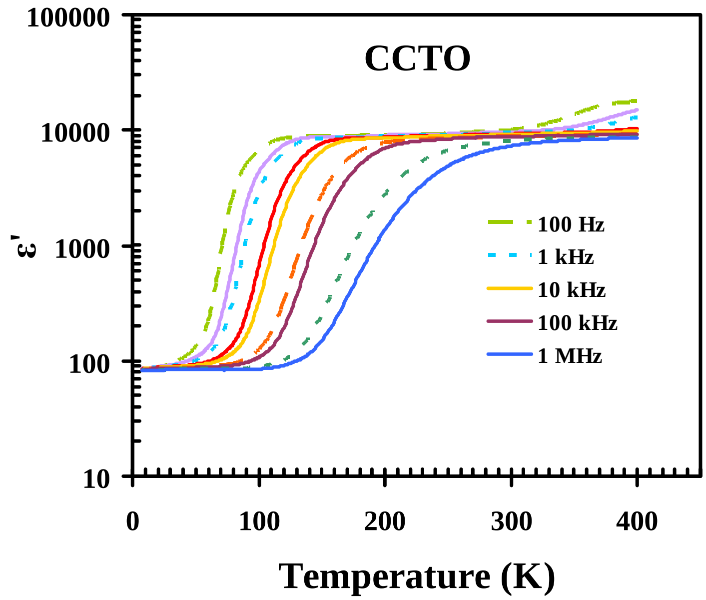


**Figure 1**. Dielectric response of CCTO as a function of temperature for various frequencies from 100 Hz to 1 MHz. Notice the large, temperature insensitive, plateau value of ε′ and the large frequency dispersion at lower temperatures.

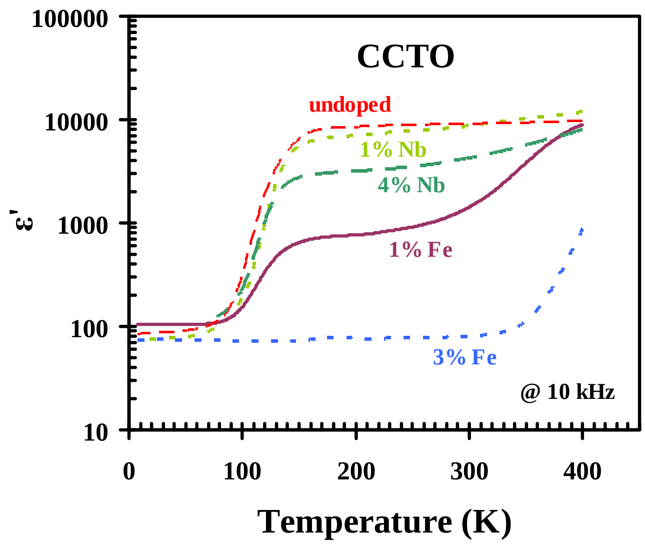


**Figure 2**. Effect of doping on the dielectric response of CCTO at 10 kHz. As doping levels are increased the CCTO dielectric response decreases. Doping CCTO at a concentration of 3 at. % Fe makes the response of CCTO more characteristic of an intrinsic effect.

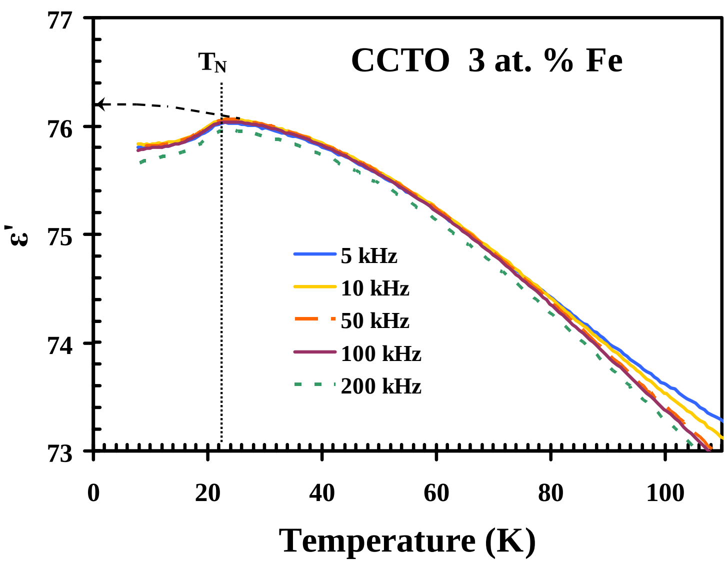


**Figure 3**. Low temperature dielectric behavior of 3 at. % Fe doped CCTO for various frequencies. An intrinsic dielectric constant of 76.2 is extrapolated at T = 0K. Notice the change in the dielectric response at the Neel Temperature, $T_N$ = 23K, indicating antiferromagnetic ordering.