Relaxor behavior in $CaCu_3Ti_4O_{12}$ ceramics

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The dielectric properties of $CaCu_3Ti_4O_{12}$ (CCTO) ceramics have been investigated in a temperature range of 143–573 K and a frequency range of 1 Hz–10 MHz. A dielectric anomaly has been observed between 350 and 600 K. The broad dielectric peaks in $\varepsilon'(T)$ can be well fitted by a modified Curie-Weiss law and a Vogel-Fulcher relationship, which is indicative of a relaxor ferroelectric behavior. A slim *I-V* loop as well as the *P-E* hysteresis loop and broad maxima in $\varepsilon''(f)$ also suggest the existence of a relaxor ferroelectric behavior in CCTO ceramics. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2374682]

Since the perovskite-based oxide (space group *Im*3) $CaCu_3Ti_4O_{12}$ (CCTO) was reported to have a colossal dielectric constant (CDC) in the order of 10^5 which is nearly constant from 100 up to 400 K but drops rapidly to less than 100 below 100 K,[1] a huge amount of work[2–10] have been carried out in an attempt to understand the origin of these remarkable dielectric properties. It has been found that the temperature at which the steplike decrease in dielectric constant takes place strongly depends on the measuring frequency and roughly follows an Arrhenius behavior. This relaxational behavior was ascribed to the slowing down of highly polarizable relaxational modes[2] or to the slowing down of dipolar fluctuations in nanosized domains.[3] Although the high dielectric constant may arise from local dipole moments associated with off-center displacement of Ti ions, it is gradually realized that extrinsic effects such as the polarizations of the electrode/sample interface and grain boundaries in polycrystalline materials or twin boundaries in single crystals should be the sources of the giant dielectric constants (see, for example, Ref. 4 and references therein). Among the extrinsic effects, an internal barrier layer capacitance mechanism has been proposed and is widely accepted. It is supported by impedance spectroscopy results[5,6] as well as by the dependence of dielectric properties on processing history.[7]

Generally, dielectric constants greater than 1000 are associated with intrinsic ferroelectric or relaxor ferroelectric properties.[8] But up to now, no direct evidence for a ferroelectric phase transition in CCTO has been found by high-resolution x-ray, neutron powder diffractions or Raman-phonon measurement. However, it should be noted that weak features of reciprocal space are often missed by x-ray or neutron diffraction techniques. By employing the electron diffraction technique, Liu *et al.* have observed the evidence of a polar nanostructure in CCTO.[8] They pointed out that the incipient ferroelectric behavior is correlated only along one-dimensional ⟨001⟩ columns of TiO_6 octahedra. Moreover, almost all the previous structure studies were conducted at room temperature or below. The dielectric properties at higher temperature are rarely reported. In this letter, we report the dielectric properties on CCTO from 143 to 573 K and show that a relaxor ferroelectric behavior occurs at high temperatures in CCTO ceramics.

Single phase CCTO powders were prepared through a conventional mixed oxide route by mixing appropriate amount of high purity $CaCO_3$, TiO_2, and CuO raw powders. The starting materials were mixed and ball milled overnight in acetone and followed by calcination at 950 °C for 8 h. The x-ray diffraction showed that the calcined powders were single phase. The calcined CCTO powders were then compacted into pellets by cold isostatic pressing and were sintered in air at 1050 °C for 4 h. Silver paint was coated on both surfaces of the sintered disks and fired at 650 °C for 20 min. The sample pellets were 12 mm in diameter and about 1 mm in thickness. The dielectric properties and electric conductivity were measured by using a frequency-response analyzer (Novocontrol Alpha analyzer) over a broad frequency range (1 Hz–10 MHz) at various temperatures down to 143 K. A high resistance meter (Keithly 6517) was employed for the *I-V* measurement.

Figure 1 shows the temperature dependence of the real part of dielectric constant $\varepsilon'(T)$ and the real part of conductivity $\sigma'(T)$ under various measuring frequencies. At temperatures below 300 K, similar to earlier reports,[4] $\varepsilon'(T)$ exhibits a steplike increase from a lower temperature plateau value of the order of 100 towards a higher temperature plateau value of 10^4. The position where the dielectric step takes place shifts to higher temperatures with increasing frequencies and it is accompanied by a peak in $\sigma'(T)$. An Arrhenius relationship $f \sim \exp(-U_0/kT)$ could be used to fit this relaxation results roughly. Homes *et al.* is the first to attribute this relaxational behavior to a freezing dipolar glass model.[3]

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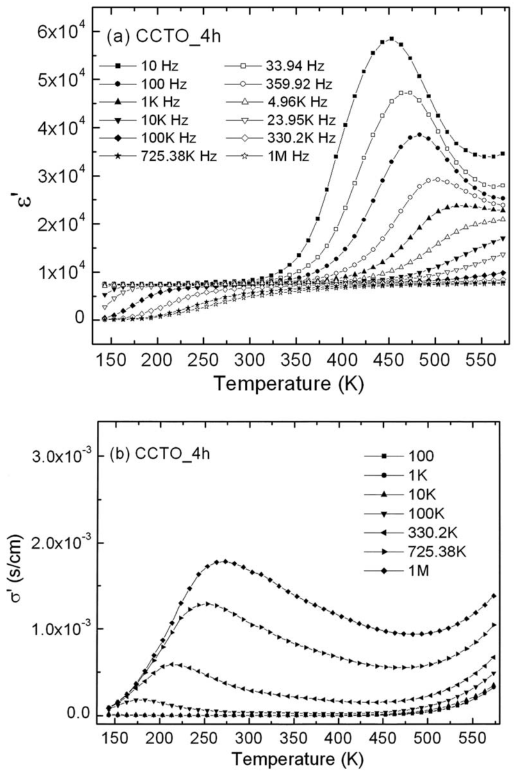

FIG. 1. Temperature dependence of dielectric constant (a) and conductivity (b) of CCTO sintered at 1050 °C for 4 h under different frequencies.

Above room temperature, a broad dielectric peak appears between 350 and 600 K which also shifts to higher temperatures and decreases in amplitude with increasing frequencies. Compared to the low temperature relaxation, this high temperature one exhibits more of the characteristic behaviors of a ferroelectric relaxor which is usually characterized by a diffuse phase transition, and a strong relaxational dispersion in dielectric constant and dielectric loss. The dielectric maximum defines a dynamic freezing or glasslike transition temperature, T_m. The strong frequency dispersion in $\varepsilon'(T)$ on the low-temperature side of T_m is associated with the slowing down of dipolar fluctuations within the polar nanoclusters.[9]

Uchino and Nomura[10] suggested a variable power law to describe the paraelectric dielectric constant of ferroelectrics with diffuse phase transitions,

$$\frac{1}{\varepsilon} = \frac{1}{\varepsilon_m} + \frac{(T - T_m)^{\alpha}}{C}, \tag{1}$$

where ε and ε_m are the dielectric constant and its maximum value, respectively. It is believed that a power factor α close to 1 suggests normal ferroelectrics, while a value close to 2 suggests relaxor ferroelectrics. Curve fitting results for the dielectric constants of a CCTO sample under different frequencies are summarized in Table I. The α values of the CCTO sample are between 1.68 and 1.78. It is indicative that CCTO is a relaxor ferroelectric.

TABLE I. Curve fitting results for CCTO.

Frequency	T_m (K)	$1/\varepsilon_m(10^{-5})$	α
10 Hz	451	1.71	1.78
33.94 Hz	469	2.12	1.68
100 Hz	483	2.60	1.76

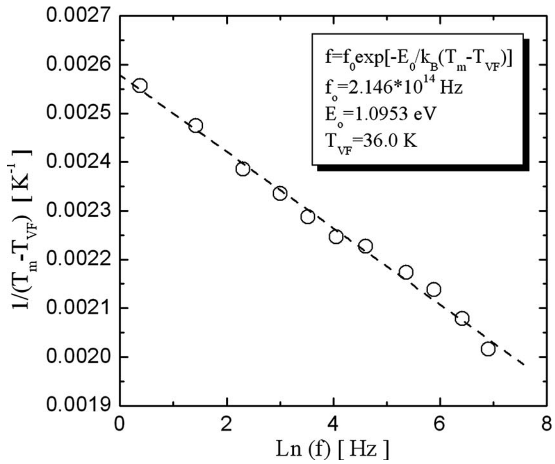

FIG. 2. Vogel-Fulcher fit of the frequency dependence of the dynamic freezing transition temperatures T_m for CCTO ceramics.

The slowing down of the relaxation process is commonly attributed to the evolution of an exponentially wide spectrum of the relaxation time. Glazounov and Tagantsev proved that the Vogel-Fulcher (VF) law corresponds to the freezing of the spectrum and can be used to well describe the relation between the ac frequency f of the measuring electric field and the T_m,[11,12]

$$f = f_0 \exp\{-E/[k_B(T_m - T_{\mathrm{VF}})]\}, \tag{2}$$

where f_0 is the preexponential term, E is the hindering barrier, k_B is the Boltzmann constant, and T_{VF} is the Vogel-Fulcher temperature of dipole. T_{VF} can be viewed as the "static" dipolar freezing temperature at which the distribution of relaxation time becomes infinitely broad. Figure 2 plots the results according to the VF equation. The curve fitting result gives $f_0 = 2.15 \times 10^{14}$ Hz (lower than that of the PMN-PT system) and $T_{\mathrm{VF}} = 36.0$ K.

Another typical characteristic for relaxor ferroelectrics is a slim *C*-*V* or *I*-*V* or *P*-*E* loops. Figure 3 shows the current density as a function of the applied electric field. A slim *I*-*V* loop is observed. The inset of Fig. 3 shows a slim *P*-*E* hysteresis loop. Both *P*-*E* and *I*-*V* measurements imply that the material is a ferroelectric relaxor. Generally, lattice or

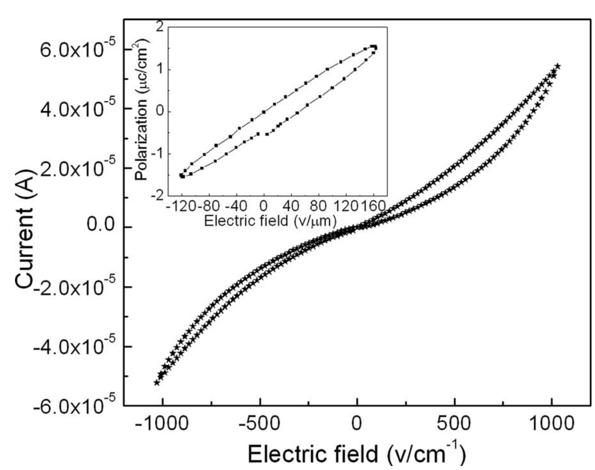

FIG. 3. Current density as a function of the applied electric field. The inset shows a *P*-*E* hysteresis loop. Both measurements were conducted at room temperature.

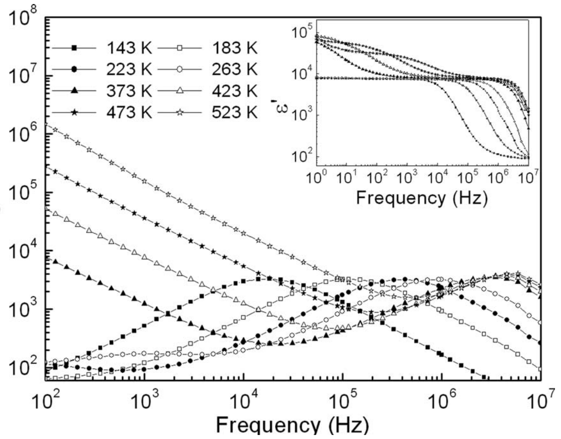

FIG. 4. Frequency dependence of the imaginary part of dielectric permittivity, $\varepsilon''(f)$. The inset shows the corresponding real part of the dielectric permittivity.

electronic ferroelectricity tends to predict a saturation of the *P-E* loop which can be extrapolated to a characteristic bulk spontaneous polarization, while nonferroelectrics give a more or less linear behavior up to the breakdown voltage.[13] The dielectric hysteresis loop and current density hysteresis loop observed in CCTO indeed indicate a nonlinear ferroelectriclike behavior.

Further evidence for relaxor behavior arises from the frequency dependence of the imaginary part of the dielectric permittivity. Figure 4 shows $\varepsilon''(f)$ for a series of temperatures. Broad peak maxima are indicative of typical relaxational behavior. The peak frequency decreases with decreasing temperatures, indicating the freezing in of polar nanoclusters. The half-width of the relaxation peak at 143 K is nearly two decades in frequency, much broader than one decade usually expected for a Debye-type relaxation. Such a broad relaxation peak implies a broad distribution of relaxation times. The insert of Fig. 4 shows the variation in dielectric constant ε' with frequency for different temperatures. The contribution from polar nanoclusters could not be excluded.

Based on the analysis above, it can be concluded that relaxor ferroelectric behavior indeed exists in CCTO. Recent transmission electron microscopy (TEM) studies on CCTO by Liu *et al.*[8] have provided an evidence for this structural frustrated ferroelectric relaxor. They concluded that the Ti ions in CCTO show a one-dimensional correlated off-center displacement along the $\langle 001 \rangle$ crystallographic direction. As proposed by Subramanian *et al.*,[1] significant tilting of the TiO_6 octahedra is required to accommodate the square planar Cu ions, which results in the enhanced rigidity of the octahedral framework and frustrates the incipient tendency to form a long-range ordered ferroelectric state. Similar relaxor ferroelectricity has been observed in spinel compound $CdCr_2S_4$,[14] which is a pure compound without any disorder. The author suggests that ferroelectricity in $CdCr_2S_4$ results from an off-center displacement of the Cr ions. In CCTO, it is the square planar Cu ions that destroy the correlated one-dimensional displacement of Ti atoms from column to column ($\langle 001 \rangle$ direction) and result in a relaxor behavior. In contrast, significant tilting of oxygen octahedron is also observed in lead zirconate titanate.[15,16] But the Ti atoms are in a correlated motion among neighboring columns and therefore normal ferroelectricity results. The atomic displacement of Ti in CCTO is about 0.004 nm along the $\langle 001 \rangle$ direction,[1] according to the calculation by Abrahams and Kebe,[17] this gives rise to a local spontaneous polarization of 0.4 $\mu C/cm^2$, which fits our *P-E* measurement result very well (inset of Fig. 3).

It should be mentioned that the very recent results from Wang and Zhang[18] have shown that a small dielectric peak at around 350 K is due to the competition between *n*- and *p*-type carriers. However, such a peak has not been observed by us and the dielectric peak we observed at around 480 K (under 100 Hz) is completely different from theirs.

In summary, we have investigated the temperature and frequency dependence of dielectric spectra of polycrystalline $CaCu_3Ti_4O_{12}$. Relaxor ferroelectric phase transition was demonstrated in CCTO at a temperature above 400 K. We believe that relaxor ferroelectricity is due to the correlated off-center displacement of Ti ions along each single $\langle 001 \rangle$ column but without any correlation between neighboring columns.

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