Relaxor behavior in CaCu$_3$Ti$_4$O$_{12}$ ceramics

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The dielectric properties of CaCu$_3$Ti$_4$O$_{12}$ (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 ε’(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 ε”(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 Im3) CaCu$_3$Ti$_4$O$_{12}$ (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, a huge amount of work has 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 relaxation modes or to the slowing down of dipolar fluctuations in nanosized domains. 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 as well as by the dependence of dielectric properties on processing history.

Generally, dielectric constants greater than 1000 are associated with intrinsic ferroelectric or relaxor ferroelectric properties. 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. 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 (Keithley 6517) was employed for the I-V measurement.

Figure 1 shows the temperature dependence of the real part of dielectric constant ε’(T) and the real part of conductivity σ’(T) under various measuring frequencies. At temperatures below 300 K, similar to earlier reports, ε’(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 σ’(T). An Arrhenius relationship f ∼ 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.
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 the low-temperature side of \( T_m \) is associated with the slowing down of dipolar fluctuations within the polar nanoclusters.

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

\[
\frac{1}{\epsilon} = \frac{1}{\epsilon_m} + \frac{(T - T_m)^\alpha}{C},
\]

where \( \epsilon \) and \( \epsilon_m \) are the dielectric constant and its maximum value, respectively. It is believed that a power factor \( \alpha \) 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 \( \alpha \) values of the CCTO sample are between 1.68 and 1.78. It is indicative that CCTO is a relaxor ferroelectric.

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
from an off-center displacement of the Cr ions. In CCTO, it et al. transmission electron microscopy relaxor ferroelectric behavior indeed exists in CCTO. Recent features. The contribution from polar nanoclusters could not be

displacement along the ions in CCTO show a one-dimensional correlated off-center frustrated ferroelectric relaxor. They concluded that the Ti

crystallographic direction. As 1 significant tilting of the crystallographic direction,1

The author suggests that ferroelectricity in CdCr2S4 results CdCr2S4,14 which is a pure compound without any disorder. In summary, we have investigated the temperature and frequency dependence of dielectric spectra of polycrystalline CaCu3Ti4O12. 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 (001) column but without any correlation between neighboring columns.

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