

New Electrical Field-tunable Dielectric Materials – Structurally Frustrated Ferroelectric Relaxors

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Dielectric ceramics which have high relative permittivities, low dielectric losses as well as low temperature coefficients of permittivity are of great interest for use as microwave dielectric resonators, oscillators and filters. Materials of this type whose dielectric properties are furthermore tuneable under the action of an applied electric or magnetic field are of even greater interest. $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) is one such material. A characteristic, highly structured diffuse intensity distribution observed via electron diffraction is used to show that CCTO is an example of a unique new class of structurally frustrated ferroelectric relaxor in which spontaneous polarization is only correlated along one-dimensional $\langle 001 \rangle$ columns by virtue of off-center displacement of Ti ions within TiO_6 octahedra. This unique local structural characteristic partially explains the origin of the giant dielectric constant observed for this compound. It also helps explain the observed electric field tuneability of the dielectric properties of CCTO. This work suggests the potential application of this structurally frustrated ferroelectric relaxor as a smart dielectric material.

1. Introduction

A significant issue for the next generation of information and communication technology is the need for novel nonlinear dielectric materials capable of satisfying the requirements for electronic devices to be of small size, high-density, low cost and to be environmentally-friendly. Doped BaTiO_3 is one such potentially useful class of material. Partial substitution for either the Ba or Ti site ions can significantly improve the dielectric properties of BaTiO_3 [1,2]. $(\text{Ba},\text{La})\text{TiO}_3$ (BLT) for instance, has good dielectric properties coupled with 60 % DC-voltage tuneability [3]. The disadvantages of doped BaTiO_3 -based ceramics are the complicated multi-sintering processes involved as well as the polymorphic phase transitions of such materials. A further candidate material, as a result of its very low dielectric loss and dielectric constant tuneability [4], is the pyrochlore type ceramic $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ (BZN). Its dielectric constant, however, is much lower than that of the BaTiO_3 based materials. As a result, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) instantaneously attracted strong attention when it was recently first reported to have a “giant dielectric constant” [5] achievable via a simple one-step synthesis process.

2. Sample preparation

CCTO samples were prepared via solid state reaction using highly pure CaO , CuO and TiO_2 . The raw materials were homogeneously mixed by grinding for one hour in a mortar, and then heat treated at 800°C for 24 h. The resultant powders were then re-ground, pelleted to a diameter of 15 mm under 8 kPa, and finally annealed in air at 1000°C for 72 h. Both sides of the resultant pellet were then brushed with silver conductive paste and further heat-treated at 550°C for 30 min to achieve excellent electrical contacts for dielectric measurements. The dielectric properties under a DC bias were measured using a high precision LCR meter

(HP4284A) while the pressure-dependance was carried out using a home-made automatic hydrostatic pressure-dielectric measuring system.

3. Results and discussion

Figure 1 shows the measured dielectric permittivity of CCTO under a DC bias at 35°C. The measured dielectric constant for our sample is over 10^3 but less than the 10^5 reported for CCTO single crystals [6], and similar to the result of Jha *et al* [7]. Reviewing the published literature, there is a large diversity in reported dielectric constant - all the way from 478 to 10^5 [3,5-7]. That is one reason why people are in doubt as to the *intrinsic* origin of this unusual giant dielectric constant. From Fig.1, the dielectric constant of CCTO can be adjusted ~ 15 % if an electric field of 8 KV/cm is applied. By comparison, the dielectric constant of (Ba,La)TiO₃, a well-known tuneable dielectric material, changes by 44.8% under a 100 KV/cm bias [8] - corresponding to a tunability of 3.6 % under an 8 KV/cm field. Obviously, CCTO has a relatively higher tuneability than BLT. The sensitivity to such a low bias field suggests that CCTO has considerable potential for application in next generation RF/microwave wireless communication technology.

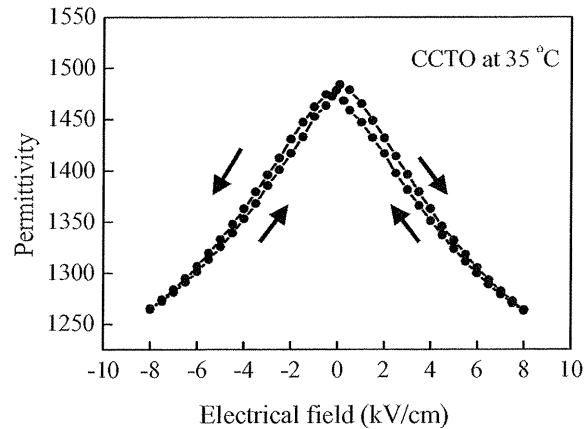


Fig. 1 Dielectric hysteresis loop of CCTO under the action of DC bias.

It is noteworthy that ferroelectric-like behaviour occurs in CCTO as can be seen from Fig.1. Ferroelectric-like hysteresis loop behavior has also been reported by Chung *et al* [9] who observed bias-induced polarization within a single grain of a CCTO sample using Kelvin probe force microscopy. The observed phenomenon was interpreted as implying the existence of a reversible macroscopic dipole moment. It is, however, difficult to believe that this nonlinear dielectric behavior can originate from such a ferroelectric mechanism given that the space group symmetry of the average structure of CCTO is centrosymmetric $Im\bar{3}$. The lack of a four-fold axis in the $Im\bar{3}$ space group for CCTO also apparently eliminates the possibility of a transition to a tetragonal ferroelectric structure [5]. That is why Chung *et al* did not provide any further discussion as to the origin of this dipole moment. Our recent electron diffraction results [10] provide strong support for the existence of this tetragonal ferroelectric kind of dipole moment under the application of an applied electric field. The $\langle 001 \rangle^*$ sheets of diffuse intensity observed (see Fig. 2) require the existence of one-dimensional $\langle 001 \rangle$ columns of atoms exhibiting displacements away from their $Im\bar{3}$ average structure positions

that are correlated along an $\langle 001 \rangle$ column direction but with no correlation from one such column to the next in the transverse direction. Based on careful investigation and analysis of electron diffraction (see the detail in ref. [10]), these displacements can be shown to arise from Ti ion shifts within the TiO_6 octahedra. The difference between CCTO and the ferroelectric BaTiO_3 is that these one-dimensional Ti displacements (in the case of CCTO) never become correlated from column to column and hence never lead to long-range ferroelectric behavior. We believe the significant tilting of the TiO_6 octahedra required to accommodate the square planar Cu ions and the resultant enhanced rigidity of the octahedral framework, frustrates the incipient tendency towards a long range ordered ferroelectric state.

In conclusion, CCTO not only has a giant dielectric constant, but also is tuneable using a relatively low applied electric field.

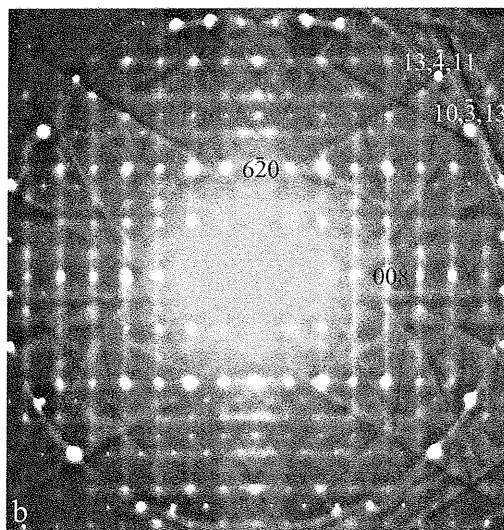


Fig. 2 A typical $\langle 130 \rangle$ zone axis electron diffraction pattern of CCTO .

Acknowledgments

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