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Structurally frustrated relaxor ferroelectric behavior in $CaCu_3Ti_4O_{12}$

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Direct diffraction evidence for structurally frustrated relaxor ferroelectric behavior in the form of one-dimensionally correlated, off-center displacements of Ti ions within the TiO_6 octahedra of $CaCu_3Ti_4O_{12}$ (CCTO) has been obtained. When coupled with the observation of a ferroelectric effect, important implications for the understanding of the extraordinary dielectric properties of CCTO arise. That the incipient ferroelectric behavior is correlated only along one-dimensional $\langle 001 \rangle$ columns of TiO_6 octahedra in the absence of an applied electric field offers a crucial insight into the underlying nature of CCTO and suggests the existence of a unique class of structurally frustrated, ferroelectric relaxors.

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I. INTRODUCTION

Conventional displacive ferroelectricity arises from correlated displacive shifts of ions away from originally nonpolar, typically high-symmetry positions into lower-symmetry positions, giving rise to an asymmetric and polar resultant structure at a well defined para/ferroelectric transition temperature (known as the Curie temperature). The inherent susceptibility to polar displacements ensures that the dielectric permittivity of such materials (e.g., $BaTiO_3$) is typically high, peaks sharply at the Curie temperature, and is strongly temperature dependent.[1] For capacitor applications, the high permittivity of such ferroelectric materials is highly desirable. For practical applications, however, it is also necessary for this high permittivity to be maintained over as wide a temperature range as possible around room temperature.

This latter requirement led to systematic doping studies of displacive ferroelectrics, in particular $BaTiO_3$, in order to broaden out its maximum in permittivity and to increase the temperature stability of the high-permittivity state.[1] Studies of this type led to the discovery and development of a class of compositionally disordered, structurally frustrated incipient ferroelectrics known as relaxor ferroelectrics (RFs).[2] Such RF materials, e.g., $PbMg_{1/3}Nb_{2/3}O_3$ or Sr-doped $BaTiO_3$, are characterized by high permittivities that vary rather less over a somewhat wider temperature range, as well as by the existence of an underlying polar nanostructure that sometimes gives rise to observable structured diffuse scattering.[3] Both ferroelectric and RF materials have been the traditional target systems for materials scientists looking for higher performance (particularly high dielectric constant) dielectric materials (see e.g., Refs. 4 and 5).

Ever since centrosymmetric (space group $Im\bar{3}$) $CaCu_3Ti_4O_{12}$ (CCTO; see Fig. 1) was reported in 2000 (see Ref. 6) to have a dielectric constant at 1 kHz of ~12 000 that was nearly constant from room temperature up to 600 K but which dropped rapidly to less than 100 below 100 K, a huge amount of work[1,6–14] has been carried out in an attempt to understand the origin of these remarkable dielectric properties. Both extrinsic (microstructural) as well as intrinsic mechanisms for the observed dielectric properties have been proposed. Extrinsic mechanisms such as an internal barrier layer capacitance (IBLC) mechanism are strongly supported by impedance spectroscopic results[1,14] as well as by the dependence of measured dielectric properties upon processing conditions and grain size.[1] Consensus as to the nature of the proposed insulating barrier layers, however, has yet to be reached nor has direct imaging evidence for the existence of such barrier layers been found.

Dielectric constants greater than 1000 have traditionally been associated with intrinsic ferroelectric or RF properties.

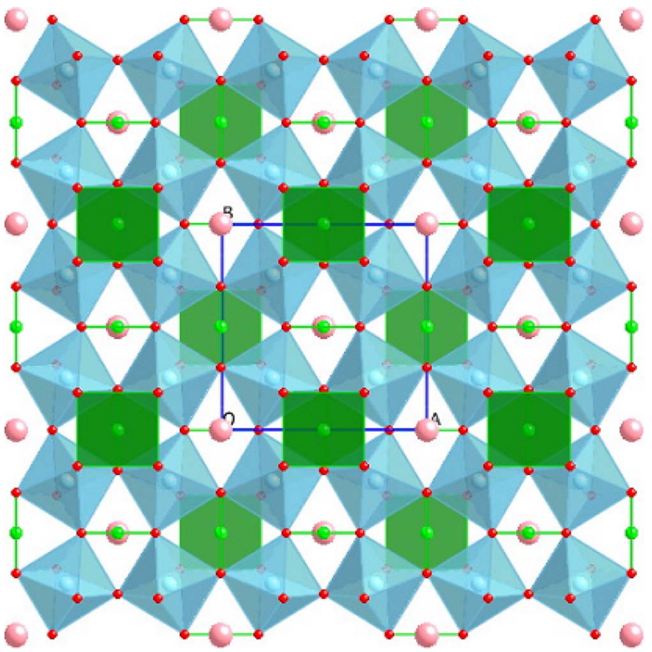

FIG. 1. (Color online) The $Im\bar{3}$ average crystal structure of $CaCu_3Ti_4O_{12}$ in projection along $\langle 001 \rangle$ showing the tilted TiO_6 octahedral network as well as the CuO_4 square planar coordination of the Cu ions.

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Experimentally, however, no evidence for a ferroelectric phase transition in CCTO has been found via either diffraction or spectroscopic techniques right down to very low temperatures.[6,7,9,13] In addition, the refined atomic displacement parameters have been reported to be "…normal over a wide temperature range … and … inconsistent with random local polar displacements of the magnitude typical in ferroelectrics or their disordered paraelectric phases …" while evidence for "… nano-domain or disorder effects, common to relaxor materials, are notably absent: neither superstructure peaks nor strong diffuse scattering are observed …."[13]

In view of the above and given the known ability of electron diffraction to pick up weak features of reciprocal space often initially missed by x-ray or neutron diffraction techniques,[15,16] we have carefully reinvestigated the reciprocal space of CCTO looking for evidence of a polar nanostructure that might provide insight into its dielectric properties. Permittivity versus electric field data have also been collected using the same sample investigated by electron diffraction.

II. EXPERIMENT

A. Sample fabrication and average structural analysis

The CCTO samples used here were synthesized via solid state reaction using high purity CaO (Aldrich 4N), CuO (Aldrich, 4N), and TiO_2 (Aldrich, 3N). The raw materials were initially ground together in the appropriate proportions for 1 h in a mortar followed by heat treatment at 800 °C for 24 h. The resultant powders were again ground, pelleted to a diameter of 15 mm under 8 kPa pressure, and finally annealed in air at 1000 °C for 72 h with intermediate grinding and investigation via x-ray powder diffraction (XRPD). Powdered samples of the resultant fired pellets were analyzed via XRPD using a Guinier-Hagg camera with a Cu $K_{\alpha 1}$ radiation source. Silicon (NBS No 640) was added as an internal standard for accurate determination of the unit cell dimensions, refined using the UNITCELL software package. The resultant sample was determined to be single phase with a lattice paremeter of 7.3810(5) Å, very close to that reported in Ref. 7 [of 7.3798(1) Å].

B. Electron diffraction

Electron diffraction was carried out in a Philips EM 430 transmission electron microscope on crushed grains of the single-phase sample dispersed onto holey carbon coated copper grids.

C. Dielectric property measurement

Silver conductive paste was coated onto both sides of pellets and heat-treated at 550 °C for 30 min to obtain good electrical contact. The sample pellets were 10 mm in diameter and about 1 mm in thickness. The dependence of the dielectric properties on bias electric field was then investigated using a computer controlled system,[17] consisting of an SRS 350 high voltage source (Stanford Research System Inc.), TH2816 LCR (Tonghui Electronic Instrument Inc.), Delta Design 9023 envioronmental box (Delta Design Inc.) and an in-house voltage protection circuit. The frequency used was 10 kHz, and the measurement was carried out at 35 °C.

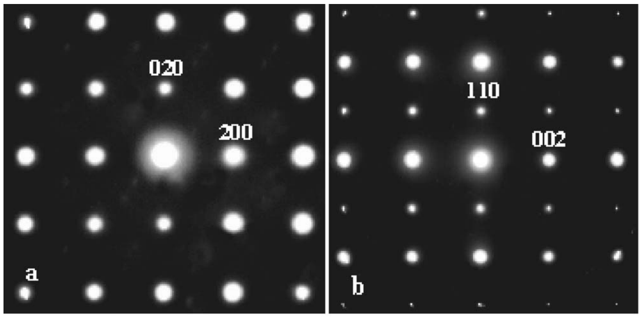

FIG. 2. Typical (a) ⟨001⟩ and (b) ⟨110⟩ zone axis EDPs of CCTO.

III. RESULTS AND DISCUSSION

Both ⟨001⟩ and ⟨110⟩ zone axis electron diffraction patterns (EDPs) of CCTO are entirely unremarkable and quite compatible with the reported $Im\bar{3}$ average structure space group symmetry for CCTO as shown in Fig. 2. On tilting away from such exact zone axis orientations, however, keeping an $\langle 002\rangle^*$ systematic row excited and choosing rather longer exposure times, a weak, but quite reproducible, highly structured diffuse intensity distribution becomes apparent. Figure 3, for example, shows (a) ⟨140⟩ and (b) ⟨130⟩ zone axis EDPs of CCTO. Note the characteristic diffuse streaking running perpendicular to $\mathbf{c}^*$ through the hkl, l even Bragg reflections in both (a) and (b) as well as the diffuse streaking running perpendicular to $\mathbf{a}^*$ through the hkl, h even Bragg reflections in both (a) and (b). Note also the strong azimuthal intensity variation of this diffuse streaking. Such diffuse streaking continues to exist no matter how far we tilt around the $\langle 002\rangle^*$ systematic row, showing that the diffuse distribution takes the form of quite sharp $\{001\}^*$ sheets of transverse polarized diffuse intensity, perpendicular to each of the three ⟨001⟩ real space directions. It is important to note that a very similar structured diffuse distribution is also characteristic of the high-temperature, cubic paraelectric phases of the well known ferroelectric perovskites $BaTiO_3$ and $KNbO_3$.[18–20]

Such $\langle 001\rangle^*$ sheets of diffuse intensity require the existence of one-dimensional ⟨001⟩ columns of atoms exhibiting displacements away from their $Im\bar{3}$ average structure positions that are correlated along the ⟨001⟩ column direction but with no correlation from one such column to the next in the transverse direction (see Fig. 1). The transverse polarized character of this observed diffuse distribution, i.e., the fact that the diffuse streaking is always strongest when observed perpendicular to the direction of the streaking and absent when viewed along the direction of the streaking itself (see Fig. 3), requires that the atomic displacements responsible must be along the ⟨001⟩ column direction. Furthermore, the hkl, l even extinction condition associated with the $(001)^*$ diffuse distribution requires the existence of two identical

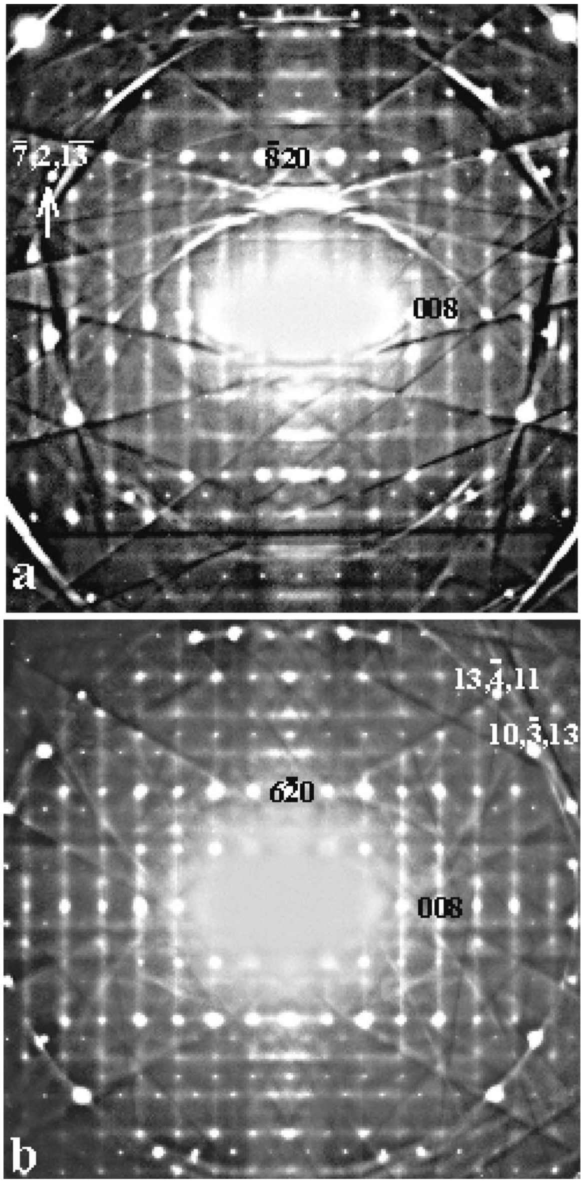

FIG. 3. Typical (a) ⟨140⟩ and (b) ⟨130⟩ zone axis EDPs of CCTO. Note the characteristic transverse polarized diffuse streaking running perpendicular to the $\langle 001\rangle^*$ directions of reciprocal space.

atoms separated by $\frac{1}{2}[001]$ in each [001] column, which displace the same amount along the [001] direction. The only possible candidate ions that can fulfill all these requirements are the Ti ions (see Fig. 1).

The observed structured diffuse intensity distribution then requires ⟨001⟩ columns of Ti ions displaced along ⟨001⟩, but which are not correlated from one such column to the next. If such displacements are taking place along all three ⟨001⟩ directions simultaneously on the local scale (not necessarily the case), then each Ti ion will locally be displaced along a ⟨111⟩ direction. The refined atomic displacement parameters for Ti[6,7,9] suggest that the magnitude of these local displacements of the Ti ions along ⟨111⟩ is ~0.07 Å, while the individual displacements along the ⟨001⟩ directions are ~0.04 Å at room temperature in the absence of an applied electric field. It is thus not surprising that the observed $\{001\}^*$ sheets of diffuse intensity should be quite weak. Nonetheless, given that the cubic-to-tetragonal ferroelectric phase transition in $BaTiO_3$ itself is caused by the correlated displacements of Ti ions off the center of their octahedral cage by only ~0.10 Å,[1] this evidence for one-dimensionally correlated, off-center displacements of the Ti ions in CCTO is obviously of great potential significance. It provides direct evidence for intrinsic incipient ferroelectric behavior in CCTO.

The difference between CCTO and the ferroelectrics $BaTiO_3$ or $KNbO_3$ (see Refs. 18–20) 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. It is suggested, as originally proposed by Subramanian *et al.*,[6] that the significant tilting of the TiO_6 octahedra required to accommodate the square planar Cu ions (see Fig. 1) and the resultant enhanced rigidity of the octahedral framework, frustrates the incipient tendency towards a long-range ordered ferroelectric state. It is interesting in this context to note the conclusion of Zalar *et al.*[20] when considering the cubic paraelectric-to-tetragonal ferroelectric transition in $BaTiO_3$ that "… in addition to the dynamic Ti disorder the 'displacive' soft mode induced deformation of the (local) unit cell shape (also needs to be) taken into account …." A significantly more rigid framework in the case of CCTO might well also play a role in suppressing long-range ferroelectric order.

The displacements required by the observed diffuse distribution could, from the diffraction point of view, be either static or dynamic in nature. Given the unusual RF-like, frequency-dependent dielectric properties of CCTO,[6,8,9] we propose that they are, in fact, dynamic, with a strongly temperature-dependent characteristic frequency [see e.g., Fig. 2b of Ref. 8]. It is further proposed that this strongly temperature-dependent characteristic frequency is slow relative to infrared frequencies as a result of the fact that whole ⟨001⟩ columns of Ti ions have to simultaneously flip the sign of their Ti shifts. The observed Ti "disorder" implied by the diffuse distribution coupled with the geometrical frustration and enhanced rigidity[8] induced by the large amplitude tilting of the TiO_6 octahedra means that CCTO has many of the characteristics of a structurally frustrated relaxor ferroelectric (as suggested by Homes *et al.*[8]) and hence does not transform into a ferroelectric even at the lowest temperatures. Under the action of an applied electric field, however, one would expect a ferroelectric state to be induced.

The dielectric properties of synthesized pelleted samples were therefore also investigated. A small but reproducible dielectric hysteresis loop was observed showing ferroelectric-like nonlinear behavior in CCTO, as shown in Fig. 4. The measured permittivity was found to be tuneable by up to ~15% via the application of an electric field. (Note that the somewhat lower than usual measured permittivity of 1500 relative to 10 000 may reflect some minor Cu deficiency (see, e.g., Ref. 6). It is known that processing conditions can have a strong effect upon permittivity (see, e.g., Ref. 1). The $Im\bar{3}$ average structure of CCTO has an inversion center and hence precludes the observed macroscopic spontaneous polarization. We believe the observed macroscopic spontaneous polarization arises from the transverse correla-

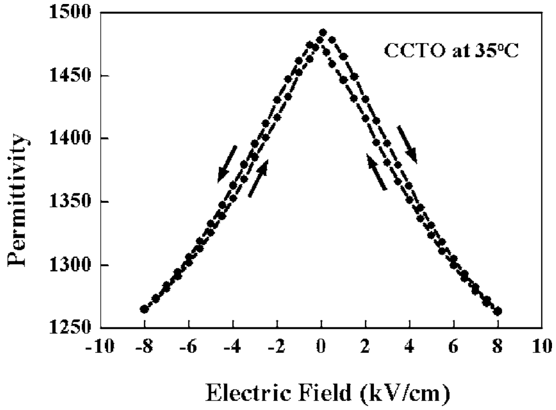

FIG. 4. Dependence of the dielectric constant of CCTO on bias electric field at 35 °C (at 10 kHz).

tion of the inherent ⟨001⟩ Ti shifts induced by the applied electric field.

In the case of $BaTiO_3$, the observed macroscopic spontaneous polarization in the ferroelectric tetragonal state arises from the three-dimensional correlated shifts of Ti ions off the centers of their octahedral O_6 cages by $\sim$0.1 Å along a specific ⟨001⟩ direction. In CCTO, one would expect that the originally only one-dimensionally correlated off-center displacements of Ti ions should align under the action of an applied electric field giving rise to observable macroscopic spontaneous polarization and to hysteresis effects such as we have observed experimentally (see Fig. 4). (According to the experimental formula of Abrahams *et al.*,[21] correlated Ti shifts of 0.04 Å along an ⟨001⟩ direction would give rise to a local spontaneous polarization of $\sim 0.4(\mu\mathrm{C/cm^2})$.

IV. CONCLUSIONS

In conclusion, it is proposed that the structurally frustrated relaxor ferroelectric behavior of CCTO plays a significant role in the measured high dielectric permittivity. By comparison with conventional compositionally disordered relaxor ferroelectrics, the disorder of CCTO is displacive in character and is correlated in one dimension only. In conjunction with 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, this greatly reduces its sensitivity to temperature variation. We cannot rule out the IBLC mechanism for high permittivity. Nonetheless, based on the above experimental evidence, we believe that the displacement of Ti ions plays the dominant role in the intrisic contribution to high dielectric permittivity. This work suggests that a new class of structurally frustrated RF materials with localized incipient relaxor ferroelectric behavior exists and can be used in high-performance dielectric device development.

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