Chem. Mater. **2006,** *18,* 3257−3260

Structural Model of Planar Defects in $CaCu_3Ti_4O_{12}$ Exhibiting a Giant Dielectric Constant

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Received February 8, 2006. Revised Manuscript Received May 4, 2006

It is known that the unusually large dielectric constant in single crystals of $CaCu_3Ti_4O_{12}$ (CCTO) requires the existence of barrier layers in the form of twin boundaries or planar defects within the crystals, and even the high dielectric constant of ceramic CCTO samples requires one to consider domain boundaries within the crystallites. As a probable origin of such domain boundaries, we proposed a structural model of plane defect that can result from a twinning parallel to the (100), (010), and (001) planes and examined its local electronic structures. This plane defect model provides a plausible microscopic explanation for the origin of gigantic dielectric constants in CCTO.

1. Introduction

The existence of $CaCu_3Ti_4O_{12}$ (CCTO) with a perovskite-related structure was reported in 1967.[1] The recent discovery of giant dielectric constants ($\geq 10^4$) in ceramics, single crystals, and thin films of nonferroelectric CCTO has received lots of attention because the calculated dielectric constant of CCTO from polarizabilities of its constituent atoms using the Clausius−Mossotti relation is only about 50.[2−7] Although an internal barrier layer capacitor mechanism can satisfactorily explain the high dielectric constant in ceramic specimens, the large dielectric constant in single crystals of CCTO indicated that the barriers to conductivity should exist within the crystals in the form of defects. It has been shown that the crystals of CCTO are twinned on a microscopic level with essentially the same amount of twins in different orientations, and the associated twin boundaries might become insulating barriers.[2,7] On a macroscopic level, scanning electron microscopy, high-resolution transmission electron microscopy, and selected area electron diffraction measurements of polycrystalline CCTO showed that internal domain boundary structures are present inside the grains of CCTO.[8,9] So far, however, no plausible structural model has been put forward concerning how a twinning might produce insulating barrier layers within the crystals.

Recent impedance measurements[7] for a crystal of CCTO at temperatures between 289 and 456 K showed the presence of the bulk and the barrier phases with widely different activated conductivities (i.e., $E_a = 0.087$ between 289 and 417 K for the bulk phase, and 0.24 eV between 289 and 456 K for the barrier phase). Above 417 K, the bulk conductivity deviates from an activated behavior; that is, it does not increase with increasing temperature. The difference in the temperature dependence of the bulk phase conductivity below and above 417 K suggested that the defects originate from a trace amount of Ti atoms at the Cu sites as well as that of Cu^+ and Ti^{3+} ions.[7] Seebeck voltage measurements showed n-type conduction in both ceramic and single-crystal specimens, indicating that the majority charge carriers are electrons. So far, no microscopic model is known as to how such ions can be accommodated in a CCTO crystal.

In a perfect crystal of CCTO, the CuO_4 square planes containing Cu^{2+} ions share corners with the TiO_6 octahedra containing Ti^{4+} ions (Figure 1). Such an ideal arrangement might be disrupted in a plane defect that results from a twinning in a crystal of CCTO, so that the plane defect may create Cu and Ti environments conducive for accommodating Cu^+ and Ti^{3+} ions. The charge balance associated with the latter would require oxygen vacancies in the plane defect. As a consequence, the resulting plane defect may become an insulating barrier. In the present work, we explore this possibility by analyzing the coordination environments of Cu and Ti in a plane defect that is likely produced by a twinning in a crystal of CCTO.

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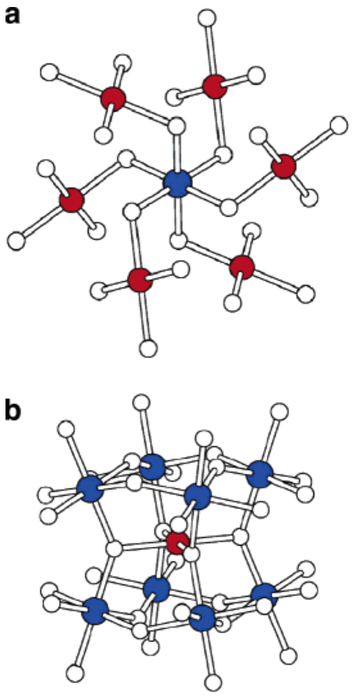

Figure 1. Coordination environments of the Ti^{4+} and Cu^{2+} ions in CCTO: (a) a TiO_6 octahedra corner-sharing with six CuO_4 square planes and (b) a CuO_4 square plane corner-sharing with eight TiO_6 octahedra. The red, blue, and white circles represent the Cu, Ti, and O atoms, respectively.

2. Arrangement of CuO_4 and TiO_6 Polyhedra in CCTO

The crystal structure of CCTO is made up of corner-sharing TiO_6 octahedra and CuO_4 square planes. Every TiO_6 octahedron is corner-shared with six different CuO_4 square planes (Figure 1a), and every CuO_4 square plane with eight different TiO_6 octahedra (Figure 1b). In CCTO, layers of Ti atoms alternate with layers of Cu atoms along the [100], [010], and [001] directions (Figure 2a). Along each of the [100], [010], and [001] directions, there run chains of CuO_4 square planes and Ca atoms (Figure 2b) as well as chains of CuO_4 square planes (Figure 2c). The CuO_4 square planes parallel to a (100) plane are colored in red (Figure 2b), and those perpendicular to a (100) plane are in cyan (Figure 2c).

The most probable twinning planes of CCTO would be parallel to the (100), (010), and (001) planes. As illustrated in Figure 2a, a twinning of CCTO parallel to a (100), (010), or (001) plane requires the cutting of the Ti−O and Cu−O bonds that pass through the plane. Figure 3a and b shows the top projection views of the two surfaces that result when the three-dimensional lattice of CCTO is sliced into two halves by the (100) plane shown in Figure 2a. The surface containing the topmost Cu atoms is presented in Figure 3a, where each CuO_4 square plane (in red) parallel to the (100) plane lost four O−Ti bonds, and each bent CuO_2 unit (in cyan) perpendicular to the (100) plane two Cu−O bonds. The surface containing the topmost Ti atoms is presented in Figure 3b, where each TiO_5 square pyramid lost one Ti−O bond. The cyan O atoms of Figure 3b, when attached to the cyan bent CuO_2 units of Figure 3a, regenerate the cyan CuO_4 square planes perpendicular to (100). The red O atoms of the CuO_4 square planes, when attached to the TiO_5 square pyramids of Figure 3b, regenerate the TiO_6 octahedra.

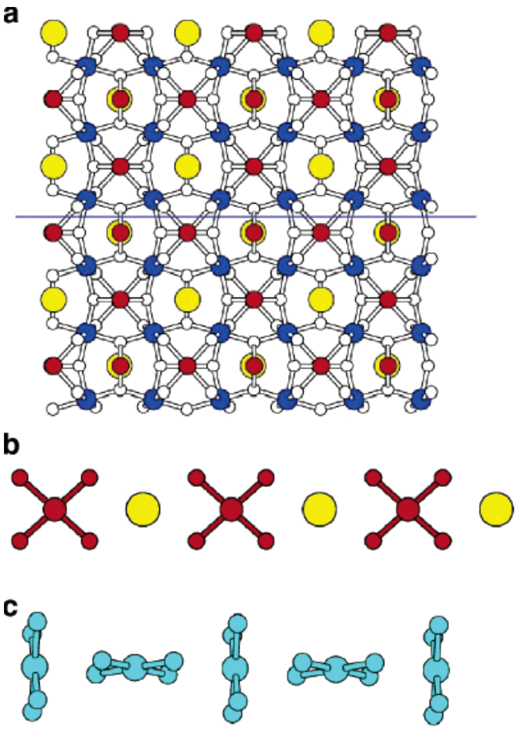

Figure 2. (a) Projection view of the crystal structure of CCTO along one crystallographic direction, where the red, yellow, blue, and white circles represent the Cu, Ca, Ti, and O atoms, respectively. The horizontal blue line represents a (100) plane by which to cut the crystal and introduce a twinning. (b) A chain of Ca atoms and CuO_4 square planes parallel to the (100) plane. (c) A chain of CuO_4 square planes perpendicular to the (100) plane.

3. Plane Defect, Charge Balance, and Oxygen Vacancy

The simplest plane defect resulting from a twinning parallel to (100) is obtained when the two surfaces of Figure 3a and b are reattached after one surface is rotated by 90°, with respect to the other surface, around a rotational axis perpendicular to the surface. The surface of Figure 4a is the same as that in Figure 3a, but has the bent CuO_2 units of the surface divided into two groups (cyan and green). The surface of Figure 4b is the same as that in Figure 3b, but is rotated by 90° with respect to the surface of Figure 3b. The surface O atoms of Figure 4b are divided into two groups (cyan and red), while the CuO_4 units lying below the surface and perpendicular to the (100) plane are colored in green.

The surface of Figure 4a may now be attached to that of Figure 4b, without changing the distance between the two surfaces from the value before cutting, such that each cyan bent CuO_2 unit forms a CuO_4 pseudo-tetrahedron with two cyan O atoms (Figure 5a). Next, each green bent CuO_2 unit would lie on top of each green CuO_4 square plane, but would remain as an isolated CuO_2 unit (Figure 5b) because the shortest Cu···O distances between the bent CuO_2 and the CuO_4 square plane are rather long (approximately 2.6 Å). In addition, as depicted in Figure 6a, a group of four adjacent TiO_5 square pyramids becomes connected to the four O atoms of a red CuO_4 square plane to form four slightly distorted TiO_6 octahedra. Next, every two red O atoms lying on top of each red CuO_4 square plane form a CuO_6 unit (Figure 5c, Figure 6a), which is sterically congested (e.g., the shortest O···O distance is approximately 1.97 Å). It is energetically favorable for such a CuO_6 unit to become a

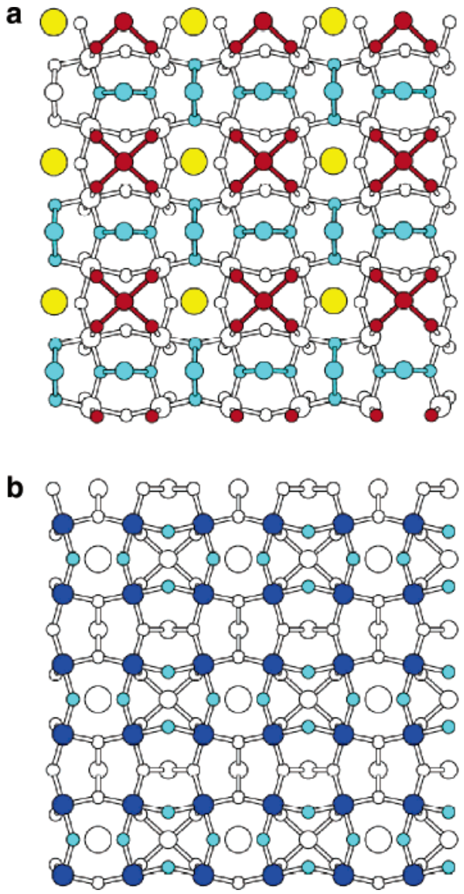

Figure 3. Two surfaces that result when the three-dimensional lattice of CCTO is cut by the (100) plane shown in Figure 2a: (a) the surface containing the topmost Cu atoms and (b) the surface containing the topmost Ti atoms. In (a), each CuO_4 square plane in red is parallel to the (100) plane, and each bent CuO_2 unit in cyan is perpendicular to the (100) plane. In (b), the cyan O atoms, when attached to the cyan bent CuO_2 units of Figure 3a, regenerate the cyan CuO_4 square planes perpendicular to (100), while the blue circles represent the surface Ti atoms. For the clarity of our discussion, only those atoms of the surfaces relevant for the discussion of their reattachments are colored.

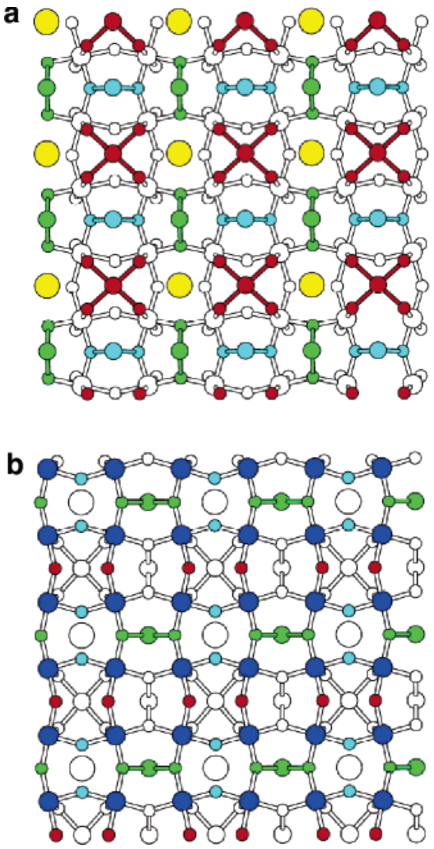

Figure 4. Two surfaces that result when the three-dimensional lattice of CCTO is sliced into two halves by the (100) plane shown in Figure 2a. The surface of (a) is the same as that in Figure 3a, and the surface of (b) is the same as that in Figure 3b except that it is rotated by 90° with respect to the surface of Figure 3b. The bent CuO_2 units of (a) are divided into two groups (cyan and green). The surface O atoms of (b) are divided into two groups (cyan and red), while the CuO_4 units lying below the surface and perpendicular to the (100) plane are colored in green and the blue circles represent the surface Ti atoms. For the clarity of our discussion, only those atoms of the surfaces relevant for the discussion of their reattachments are colored.

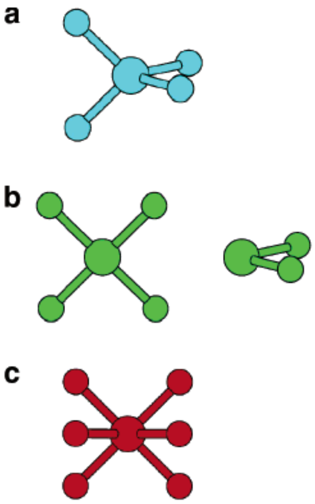

Figure 5. Structural units present in the plane defect: (a) a CuO_4 pseudo-tetrahedron, (b) a neighboring bent CuO_2 in the vicinity of a CuO_4 plane, and (c) a sterically crowded CuO_6 unit.

CuO_4 square plane by removing the two extra O atoms (Figure 6b).

Each CuO_4 pseudo-tetrahedron can accommodate a Cu^+ ion, and so can each bent CuO_2 unit. The charge balance for each $Cu^{2+} \rightarrow Cu^+$ change requires the presence of a half O^{2-} and hence the vacancy of a half O. In the plane defect, every two Cu atoms require one O vacancy. As already pointed out, the O atoms of the plane defect best suited for the vacancy formation are the two red O atoms of Figure 4b. The removal of these two O atoms creates a CuO_4 square plane and four slightly distorted TiO_5 square pyramids (Figure 6b) and leaves four electrons to the plane defect. The latter can be used for

$$2Cu^{2+} + 2e \rightarrow 2Cu^+$$

for the CuO_4 pseudo-tetrahedra and bent CuO_2 units, and

$$2Ti^{4+} + 2e \rightarrow 2Ti^{3+}$$

for the slightly distorted TiO_5 square pyramids.

In summary, the plane defect contains CuO_4 square planes with Cu^{2+} ions, CuO_4 pseudo-tetrahedra and bent CuO_2 units with Cu^+ ions, and TiO_5 square pyramids with Ti^{4+} and Ti^{3+} ions. Note that the plane defect has the chains of CuO_4 square planes and Ca atoms shown in Figure 2b, but not those of CuO_4 square planes shown in Figure 2c. The plane defect discussed so far results from a twinning

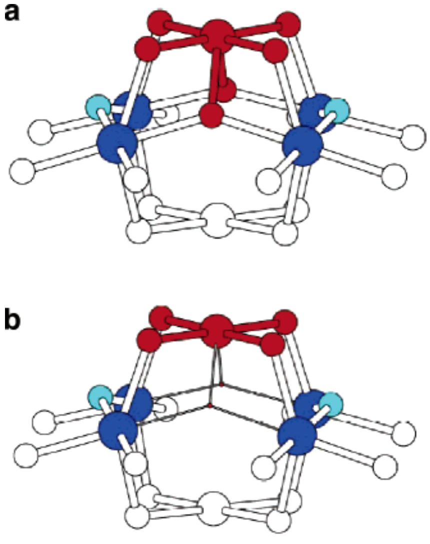

Figure 6. Structural unit in the plane defect that forms when a group of four adjacent TiO_5 square pyramids is connected to the four O atoms of a red CuO_4 square plane: (a) with a sterically crowded CuO_6 and (b) with two oxygen vacancies (indicated by small circles) from the CuO_6 unit.

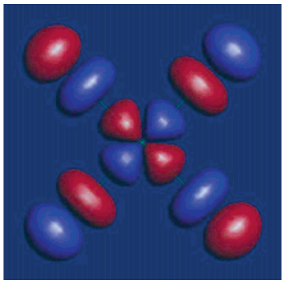

Figure 7. Magnetic orbital of a CuO_4 square plane.

parallel to a (100) plane. Such a plane defect can occur with equal probability from a twinning parallel to a (010) or (001) plane.

4. Discussion

The high conductivity of the bulk CCTO is not expected for a titanate prepared in air. However, it is not surprising because, in general, the activated conductivity of a magnetic semiconductor with localized electrons has a low activation energy and because the conductivity of the bulk CCTO should be dominated by the hopping of the localized electrons at the Cu^{2+} sites. The localized electrons of the bulk CCTO are accommodated in the magnetic orbital of each CuO_4 square plane, in which the Cu x^2-y^2 orbital makes σ antibonding with the 2p orbitals of the surrounding four O atoms (Figure 7). The localized electron at each Cu^{2+} site has a large spatial extension.

The conductivity of a plane defect described in the previous section depends on the hopping of the localized electrons in the TiO_5 square pyramids containing Ti^{3+} ions and the CuO_4 square planes containing Cu^{2+} ions. Each TiO_5 square pyramid has a d^2sp^3 hybrid orbital pointed to the oxygen vacancy site (Figure 6b), which is singly occupied for a Ti^{3+} site, but is empty for a Ti^{4+} site. Each d^2sp^3 hybrid orbital is more localized spatially than is the magnetic orbital of a CuO_4 square plane. Therefore, the d^2sp^3 hybrid orbitals in one cluster of four TiO_5 square pyramids hardly overlap with those in the neighboring clusters of four TiO_5 square pyramids. As was already pointed out, the plane defect has the chains of CuO_4 square planes and Ca atoms shown in Figure 2b, but not those of CuO_4 square planes shown in Figure 2c. Thus, the nearest-neighbor $Cu^{2+}-Cu^{2+}$ distance in the chains of the plane defect is twice longer than that in the bulk. Consequently, the hopping conductivity of the localized electrons in the plane defects should be much lower than that of the localized electrons in the bulk. Furthermore, this plane defect contains Cu^{+} and Ti^{3+} ions as well as oxygen vacancies. The region of the plane defect has disorder that the bulk does not. The random potential[10] associated with the disorder will make the region of the plane defect less conducting than the bulk. In short, the plane defect of CCTO proposed in our work is a natural consequence of twinning parallel to (100), (010), and (001) planes and provides a microscopic explanation for why the plane defect can become a barrier layer with much less conducting than the bulk.

The electrons trapped at the Ti^{3+} sites of the plane defect lie in the d^2sp^3 hybrid levels of the TiO_5 square pyramids. These levels are located below the bottom of the conduction bands of the bulk CCTO, which are essentially the Ti 3d-block bands. At a high temperature, these trapped electrons at the Ti^{3+} sites might be promoted to the conduction bands of the bulk, and hence add metallic conductivity to the bulk. This may be in part responsible for the bulk conductivity above 417 K, which deviates from an activated behavior.

$CaCu_3Ge_4O_{12}$ is isostructural with CCTO, but has a low dielectric constant (i.e., 34) as predicted by the Clausius–Mossotti relation.[2] This means that such a plane defect as proposed for CCTO does not occur in $CaCu_3Ge_4O_{12}$. Indeed, no twinning has been observed for $CaCu_3Ge_4O_{12}$. Furthermore, in an oxide lattice, Ge^{3+} ions are not stable species unlike Ti^{3+} ions.

5. Concluding Remarks

In an attempt to explain the gigantic dielectric constant in crystals of CCTO, we proposed a structural model of plane defect that can result from a twinning parallel to the (100), (010), and (001) planes, and can act as an insulating barrier layer. The comparison of the electron hopping paths of the localized electrons in the plane defect and the bulk as well as the consideration of the random potential associated with the plane defect indicate that the plane defect has a much lower conductivity than does the bulk. Thus, the plane defect model provides a plausible microscopic explanation for the origin of gigantic dielectric constants in CCTO.

Acknowledgment. Work at North Carolina State University was supported by the Office of Basic Energy Sciences, Division of Materials Sciences, U.S. Department of Energy, under Grant DE-FG02-86ER45259.

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