Clues to the Giant Dielectric Constant of $CaCu_3Ti_4O_{12}$ in the Defect Structure of "$SrCu_3Ti_4O_{12}$"

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The dielectric constant (κ) of $CaCu_3Ti_4O_{12}$ (CCTO) has been found to be 10 000 in sintered pellets and thin films, and 100 000 in single crystals.[1−4] This very high κ remains essentially unchanged from 100 to 500 K. There is not yet a completely satisfactory explanation for this unique and remarkable behavior. However, it is established that this behavior is not related to a ferroelectric transition,[1] and the consensus is that the behavior is not intrinsic.[5] The high κ of CCTO has been interpreted as due to conducting grains with insulating grain boundaries, according to a well-established barrier layer mechanism for high dielectric constant.[6] However, the exceptionally high κ in CCTO crystals[3] dictates that the insulating barriers must be inside the crystals rather than between them. Very high concentrations of twin boundaries seem always to be present in CCTO crystals, and it has been suggested that these somehow become the insulating barriers.[1] An understanding of the dielectric properties of CCTO requires (1) an explanation of how this titanate develops conducting regions and (2) a description of the insulating boundaries between the conducting regions.

The unusual variation of the perovskite structure found for CCTO is shown in Figure 1. The closest analogue to CCTO might be considered to be $SrCu_3Ti_4O_{12}$. Attempts to prepare this compound have failed.[7] These attempts readily give a dominant phase with the CCTO structure, but impurities including $SrTiO_3$ are always present. The purpose of this investigation has been to determine the composition and structure of the CCTO type phase in the Sr/Cu/Ti/O system by combining neutron and synchrotron X-ray diffraction data. The dielectric properties of this phase could then be determined on a phase-pure sample. Furthermore, the defects related to the nonstoichiometry of "$SrCu_3Ti_4O_{12}$" could provide important clues as to the defects that must also be present in CCTO. In fact, a defect we discovered in "$SrCu_3Ti_4O_{12}$" suggests a mechanism to produce conducting titanates under conditions that normally produce insulating titanates.

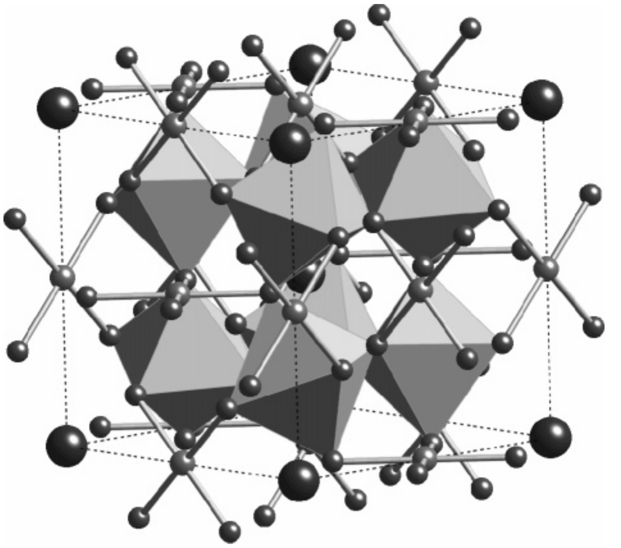

Figure 1. Structure of $ACu_3Ti_4O_{12}$. Large black atoms are A (A = Ca, Sr), medium-size gray atoms are Cu, small gray atoms are O, and atoms in the octahedra centers are Ti.

It was evident from initial refinement of the neutron diffraction data on our sample of overall composition $SrCu_3Ti_4O_{12}$ that the Ti site was completely occupied with Ti and that the oxygen site was completely occupied by oxygen. It was also evident that the Sr site was not completely occupied. This situation leaves only the Cu site as a possibility to attain charge balance. A small substitution of Ti on this site refined to a value that achieved charge balance. The formula was then known to be $A_{0.946}(Cu_{2.946}Ti_{0.054})Ti_4O_{12}$. The amount of Ti on the Cu site is known very precisely due to the large difference in neutron scattering lengths of Ti and Cu (−0.34 for Ti and +0.77 for Cu). However, the neutron data cannot preclude some Cu on the Sr site due to the similarity of the neutron scattering lengths of Sr and Cu (+0.70 for Sr and +0.77 for Cu). Thus, X-ray diffraction data from a synchrotron were used to address this issue. Analysis of these data showed no detectable amount of Cu on the A site. Thus, using both neutron and X-ray data, the formula refines unambiguously to $Sr_{0.946}(Cu_{2.946}Ti_{0.054})Ti_4O_{12}$ (SCTO). Synthesis using this formula leads to a single-phase product. Attempts to vary x in the formula $Sr_{1-x}(Cu_{3-x}Ti_x)Ti_4O_{12}$ failed. The structure and bonding of CCTO and SCTO are compared in Table 1.

The κ and loss for SCTO from 50 to 575 K are given in Figure 2. The change in κ and the peak in loss at about 100 K are at essentially the same temperature as such features in CCTO.[2] These features are charac-

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Table 1. Bond Lengths (Å), Angles (deg), and Valences[a]

	SCTO	CCTO[c]
A−O[b]	2.6362(6)	2.608(1)
Cu−O	1.9774(5)	1.978(1)
Ti−O	1.9686(2)	1.9625(4)
O−Ti−O	88.41(1)	89.44(4)
O−Ti−O	91.59(1)	90.56(4)
Ti−O−Ti	141.21(3)	141.33(6)
O−Cu−O	94.13(4)	95.32(6)
O−Cu−O	85.87(4)	84.68(6)
BV(A)	2.95	2.12
BV (Cu)	1.78	1.78
BV (Ti)	3.96	4.02
BV (O)	2.01	1.96

[a] Bond valences were calculated by Bond Valence Calculator Version 2.00.[9] [b] A = Sr (SCTO) or Ca (CCTO). [c] Reference 8.

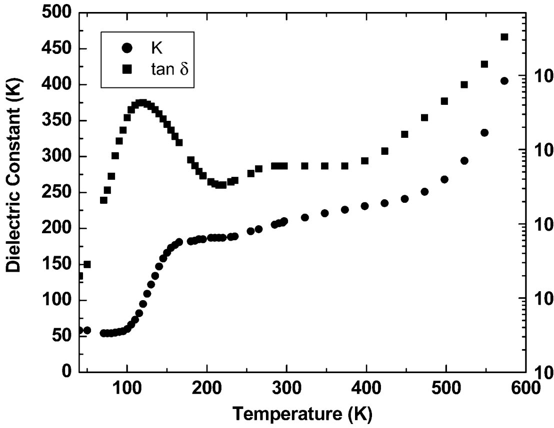

Figure 2. Dielectric constant and loss for $Sr_{0.946}(Cu_{2.946}Ti_{0.054})Ti_4O_{12}$ from 50 to 575 K.

teristic of a barrier layer capacitor when the conducting region is semiconducting with a small activation energy.[5] This same behavior is generally observed for $ACu_3Ti_4O_{12}$ compounds, but only CCTO shows exceptionally high κ.

In the CCTO structure the TiO_6 octahedra of the perovskite framework tilt to form square planar coordination for Cu, and the framework becomes very rigid (Figure 1). The space for the A cation is thus highly restricted. This space is somewhat too small for Ca, but it is much too small for Sr. It is thus understandable that stoichiometric $SrCu_3Ti_4O_{12}$ will not form. The Ca−O distance expected in CCTO based on ionic radii is 2.72 Å, much larger than the 2.61 Å distance observed.[1,8] Thus, Ca is under compression and is overbonded with a calculated bond valence of 2.12 instead of the expected 2.0. The situation is far more extreme in SCTO. The expected Sr−O distance is 2.82 Å compared to the 2.64 Å distance observed. This leads to an extremely overbonded situation with a calculated bond valence of 2.95 for Sr. In the case of CCTO the somewhat too large Ca stretches the weak Cu−O bonds leading to a low bond valence for Cu. In going from CCTO to SCTO, the much too large Sr stretches the Ti−O bonds but does not stretch the Cu−O bonds beyond the values found for CCTO (Table 1). Stretching the Ti−O bonds in SCTO would be expected to increase the polarizability of the TiO_6 octahedra as occurs on going from $SrTiO_3$ to $BaTiO_3$. The fact that SCTO does not show an exceptionally high dielectric constant is further evidence that the very high κ in CCTO is not intrinsic.

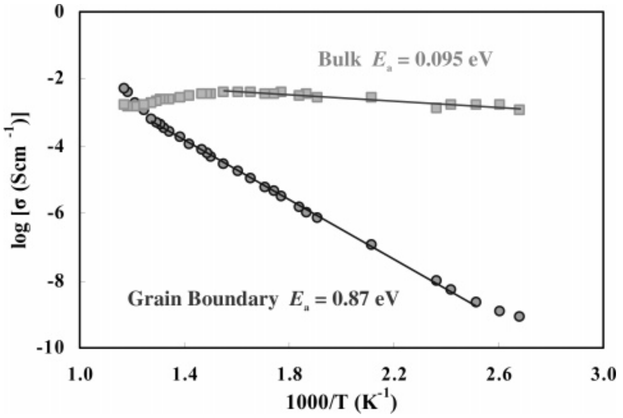

Figure 3. Log conductivity vs 1/*T* for the 2 phases in $Sr_{0.946}(Cu_{2.946}Ti_{0.054})Ti_4O_{12}$.

Vacancies on the A site are well established for the CCTO family. Some examples are phases of the type $A_{2/3}Cu_3Ti_4O_{12}$ where A may be a rare earth or Bi.[1,8] More extreme examples are $Cu_3Ti_2Ta_2O_{12}$, $Cu_3Ti_2Sb_2O_{12}$, and $Cu_2Ta_4O_{12}$ where there are no A site cations.[8] Thus, the A site vacancies in SCTO are not surprising. The manner in which these vacancies are compensated in SCTO is surprising. Titanium substitution on the Cu site implies square planar coordination, which is apparently unknown for Ti(IV) in oxides. The Ti(IV) coordination in oxides is usually octahedral, but can be tetrahedral or square pyramidal. A factor favoring substitution of Ti on the Cu site is that the Ti−O and Cu−O distances in this structure are essentially the same (Table 1).

Conductivities for SCTO derived from the complex impedance data are plotted in Figure 3. This plot is similar to a plot reported for CCTO.[6] There is a conducting phase ($\sim 10^{-2}$ S/cm) with a small temperature dependence of conductivity and a phase having much lower conductivity, which is significantly activated (∼0.7 eV).

Our thermoelectric power measurements show that SCTO is an n-type conductor with Seebeck coefficient values of -300 μV/K at 400 K and -210 μV/K at 500 K. Our samples of SCTO are too insulating to measure the Seebeck coefficients below 400 K. The higher conductivity of CCTO allows a reliable Seebeck coefficient to be determined at a temperature as low as 350 K, where we find a value of -110 μV/K.

The conductivity ($\sim 10^{-2}$ S/cm) and activation energy (∼0.09 eV) for the conducting phases in CCTO and SCTO are typical[10] of reduced $SrTiO_3$ with a room-temperature carrier concentration of $10^{17}/cm^3$, suggesting a similar concentration of electrons in the Ti 3*d* conduction band of CCTO and SCTO even though the materials have not been intentionally reduced. The impact of a Cu−O conduction band can be discounted because there are no extended Cu−O−Cu connections. The question then becomes how do $ACu_3Ti_4O_{12}$ phases

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become reduced, given that they are synthesized under conditions that normally give fully oxidized, insulating titanates? The clue may be the Ti we find on Cu sites in SCTO. Upon heating, Cu(II) becomes unstable and reduces to Cu(I). The reduction of CuO to Cu_2O occurs at 1025 °C in air, but Cu(II) reduction to Cu(I) can occur as low as 440 °C on heating oxides in air.[11] We suggest that during synthesis of CCTO a slight reduction of Cu(II) to Cu(I) occurs and this is compensated by a slight substitution of Ti(IV) on the Cu site to maintain the average oxidation state on this site at two and achieve overall charge balance for the compound. On cooling, the Cu(I) would convert to Cu(II) with the liberated electrons going into the Ti 3*d* conduction band as indicated below, where Ti^{3+} represents charge carriers in the Ti 3*d* conduction band.

$$\underset{\text{High temperature}}{Ca^{2+}(Cu_{1-3x}{}^{2+}Cu_{2x}{}^{1+}Ti_x{}^{4+})_3Ti_4{}^{4+}O_{12}} \quad \text{vs} \quad \underset{\text{Low temperature}}{Ca^{2+}(Cu_{1-x}{}^{2+}Ti_x{}^{4+})_3(Ti_{4-6x}{}^{4+}Ti_6{}^{3+})O_{12}} \qquad (1)$$

An *x* value of less than 0.0001 could account for the conductivity of the conducting regions. This deviation from ideal stoichiometry is far too small to detect by refining site occupancies from diffraction data. In the case of SCTO, there is much more Ti on the Cu site, but most of this is compensated by Sr vacancies; only a very small amount is compensated by Cu(I). Higher synthesis temperatures for CCTO give higher values of *x* and materials that are more conducting with higher κ and higher loss. The highest κ is observed in CCTO crystals prepared from the melt because this is the highest possible synthesis temperature.

The activation energy that we find for the conducting phase in SCTO (Figure 3) in the low-temperature range (373−644 K) is very similar to that found for CCTO from data measured over the temperature range 104−400 K. In the high-temperature range of our measurements on SCTO, we find that the conductivity of the conducting phase decreases with increasing temperature. Such behavior is unexpected given the level of the conductivity and the activation energy found at lower temperatures. However, this is the behavior anticipated based on eq 1.

In summary, this study has identified a defect not previously established for the CCTO type structure: Ti on the Cu site. The Ti on Cu sites may indirectly provide the charge carriers for the Ti 3*d* band, which are necessary to form conducting regions. The difference between CCTO and other compounds with the CCTO structure is that the insulating barriers are within grains in CCTO whereas these barriers are only between grains for other compounds. Thus, the enhancement of κ is modest, except in the case of CCTO. It is also possible that Ti on Cu sites has a role at the twin boundaries in CCTO, giving a modified coordination for Ti and an insulating barrier.

Supporting Information Available: Experimental details including complex impedance plots (pdf) and a CIF file for structure details. This information is available free of charge via the Internet at http//pubs.acs.org.

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