$CaCu_3Ti_4O_{12}$: Low-Temperature Synthesis by Pyrolysis of an Organic Solution

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The giant-dielectric-constant material $CaCu_3Ti_4O_{12}$ (CCTO) has been synthesized by pyrolyzing an organic solution containing stoichiometric amounts of the metal cations, which is done at lower temperature and shorter reaction time than the conventional solid-state reaction. A stable solution was prepared by dissolving calcium nitrate, copper(II) nitrate, and titanium(IV) isopropoxide in 2-methoxyethanol. This solution was pyrolyzed and heat-treated to achieve single-phase CCTO. The phases, microstructures, and dielectric properties of intermediate and final samples were characterized by X-ray diffraction, scanning electron microscopy, and dielectric spectroscopy.

Introduction

$CaCu_3Ti_4O_{12}$ (CCTO) has recently generated considerable interest because of its dielectric constant, which is very large (up to 1×10^5 at room temperature) and independent of frequency and temperature in the ranges DC to 1×10^6 Hz and 100−600 K.[1,2] The high dielectric constant is unusual because the material has a centrosymmetric cubic structure down to 35 K, so it cannot be ferroelectric, unlike the materials most often used in high-dielectric applications, which are ferroelectric. Several explanations for the origin of this property have been proposed.[3−9] Figuring prominently in these is the observation that the electrical properties depend greatly on the ceramic microstructure (such as average grain size and pellet density) and processing conditions (such as oxygen partial pressure, sintering temperature, and cooling rate).[3,10,11] Accordingly, the large dielectric constant has been attributed to an extrinsic mechanism, e.g., barrier-layer capacitances, presumably at twin boundaries,[1] or at the interfaces between sample and contacts[4,5] or between grains and grain boundaries.[3,6,7]

Other compounds in the system $ACu_3Ti_4O_{12}$ also have large dielectric constants, though none so large as CCTO.[12] We have previously investigated compounds $ACu_3Ti_4O_{12}$ (A = Ca, $Bi_{2/3}$, $Y_{2/3}$, and $La_{2/3}$) for complex permittivity, impedance, and electric modulus.[6,7] We typically observe a Debye-like relaxation in the complex permittivity and two electrical responses with very different response frequencies in the complex impedance of these materials. On the basis of our findings, we have suggested that the grains in the ceramic samples have a core−shell structure in which semiconducting grains are enclosed by insulating boundaries. The grains produce an electric response at higher frequencies and the boundaries produce a response at lower frequencies. The Debye-like relaxation can be explained by the Maxwell−Wagner relaxation at the interfaces between the grains and their boundaries.

CCTO is usually made by standard solid-state reactions from the metal oxides at high temperatures (typically 1000 °C for 20 h) with several intermediate grindings.[1,3,5,7,8] This method requires tedious work, relatively long reaction times, and high-temperature conditions and may still result in unwanted phases because of limited atomic diffusion through micrometer-sized grains. In contrast, synthesis from a solution affords intimate and homogeneous mixing of the metal ions at the atomic scale, thus reducing the diffusion path length required. Shorter diffusion lengths require shorter reaction times and lower temperatures.

Syntheses by techniques other than solid-state reactions have been reported. Jha et al. prepared CCTO by a polymeric citrate precursor route,[13] but their method is still relatively complex and needs a long heat-treatment time. CCTO thin

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films have also been made from the chemical solution method.[14,15]

In this article, we describe the experimental method for preparing a stable solution of the metal cations, fabricating the powdered CCTO therefrom at relatively low temperatures and short reaction times, and preparing and characterizing sintered samples for their dielectric properties.

Experimental Section

Polycrystalline samples of CCTO were synthesized by means of chemical solution pyrolysis. Stoichiometric quantities of calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$) and copper(II) nitrate hemipentahydrate ($Cu(NO_3)_2 \cdot 2.5H_2O$) were dissolved in 2-methoxyethanol at 90 °C with constant stirring using a magnetic stirrer. The resulting solution was refluxed at 110 °C for 2 h in a three-neck flask assembly to remove the waters of hydration, and was then cooled to room temperature. A stoichiometric amount of titanium(IV) isopropoxide ($Ti[OCH(CH_3)_2]_4$), previously mixed in a glovebox with acetylacetone, was then injected into the solution with a syringe, and the solution was again refluxed at 110 °C for 2 h. Because titanium(IV) isopropoxide is very sensitive to moisture, mixing it in acetylacetone inhibits it from decomposition. Apart from the preparation of the titanium solution, all other steps were completed in air.

The final solution made as described is very stable. We found that even adding distilled water could not make it gelate. It is thus a good precursor for making CCTO films by the dipping and spin-coating methods. In this work, we made powdered CCTO by pyrolyzing the solution.

We placed a portion of the resulting solution in a box oven preheated to 500 °C for 15 min, then increased the oven temperature to 700 °C for 2 h. The final samples were ground into powder, cold-pressed into pellets of 13 mm diameter and 0.5 mm thickness, and sintered at 1050 °C for 4 h. The temperature was increased from room temperature to 1050 °C at 5 °C/min and furnace-cooled to room temperature after sintering.

We examined the crystallinity and phases at each step in the procedure with a Scintag PAD V powder X-ray diffractometer. Grain sizes were determined by a JEOLJSM840A scanning electron microscope set at 5 kV. Sample surfaces were gold-coated prior to examination by SEM.

We examined the complex impedance with a Novocontrol high-resolution dielectric spectrometer in the temperature range -150 to 200 °C and frequency range 1×10^{-1} to 1×10^{6} Hz. Gold films were sputtered on both faces of the pellet as electrodes. The applied AC voltage was 1 V.

We obtained the complex impedance Z^* in the usual way, i.e., $Z^* = V^*/I^*$, where V^* and I^* are the applied voltage and resulting current, respectively. The complex permittivity ϵ^* was calculated as follows

$$\epsilon^* = \epsilon' - i\epsilon'' = \frac{1}{i\omega C_0 Z^*} \qquad (1)$$

where ω is the angular frequency $\omega = 2\pi\nu$ and $i = \sqrt{-1}$. $C_0 = \epsilon_0 S/d$ is the empty cell capacitance, where S is the sample area and d is the sample thickness.

Results and Discussion

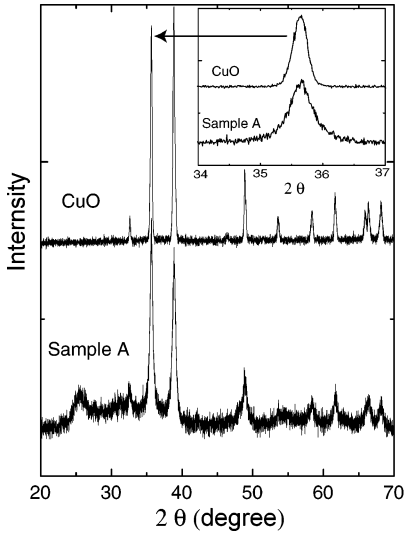

Figure 1. X-ray diffraction patterns of commercial copper(II) oxide and sample A obtained by treating the solution at 500 °C for 15 min.

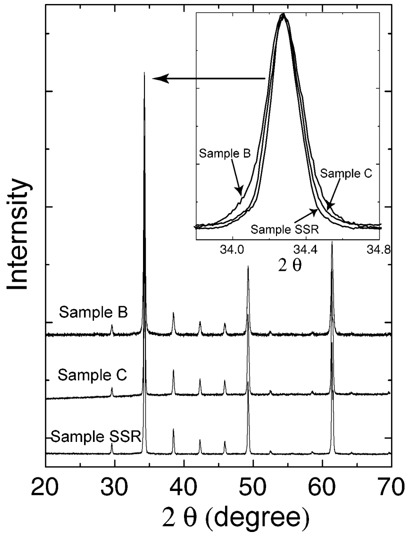

Figure 2. X-ray diffraction patterns of samples B, C, and SSR. Sample B was made by treating the solution at 500 °C for 15 min and 700 °C for 2 h, sample C is sintered sample B at 1050 °C for 4 h, and sample SSR was made from solid-state reactions of $CaCO_3$, CuO, and TiO_2 at 1000 °C for 20 h.

A. X-ray Diffraction Measurements. Each prepared sample was examined by X-ray diffraction after each step in the synthesis. In the first step, we treated the solution at 500 °C for 15 min by placing it directly into a preheated oven. We refer to the resulting sample as sample A. Figure 1 shows its X-ray diffraction pattern. There are two relatively strong peaks at 35.63 and 38.87° and several broad peaks in the range 20−70°. The former peaks correspond to copper(II) oxide, the diffraction pattern for which is also shown for comparison in Figure 1. The latter peaks are probably from calcium oxide and titanium(IV) oxide in amorphous phases. All peaks are relatively broad, indicating small particle dimensions.[16]

After this first step, we reheated the sample to 700 °C for 2 h to obtain what we designate as sample B, whose diffraction pattern is shown in Figure 2. It is single-phase CCTO, with all peaks attributable to its cubic crystal structure.[17] We have thus produced CCTO at a much lower

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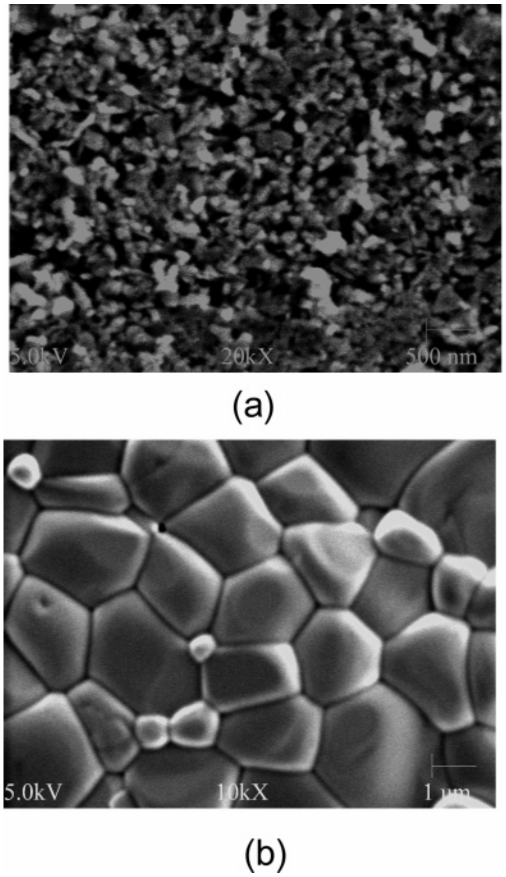

Figure 3. SEM images of (a) sample B and (b) sample C. Sample B was made by treating the solution at 500 °C for 15 min and 700 °C for 2 h. Sample C is sintered sample B at 1050 °C for 4 h.

reaction temperature and shorter time than required for the solid-state reaction, i.e., 1000 °C for 20 h.

In the third step, we cold-pressed the sample into a pellet and sintered it at 1050 °C for 4 h. We refer to this as sample C, whose diffraction pattern is also shown in Figure 2. The diffraction peaks for sample C are narrower than those of sample B, indicating the particle sizes have increased because of the high-temperature sintering.

Figure 2 also shows the X-ray diffraction pattern of a CCTO sample we prepared by solid-state reaction, designated sample SSR. This sample displays the narrowest diffraction peaks, implying it has the largest grain sizes.

B. SEM Examinations. Actual grain dimensions were examined by SEM. An image of cold-pressed sample B is shown in Figure 3a, showing grain dimensions in the 200−400 nm range. Grain dimensions in sample C, which underwent high-temperature sintering, increased to 2−3 μm, as shown in Figure 3b. In both cases, before and after sintering, grain sizes are in a narrow distribution. For comparison, we also show SEM images in Figure 4a and b of sample SSR after being sintered at 1100 °C for 5 and 15 h, respectively. Ordinarily, powdered CCTO has grain dimensions in the range 2−5 μm. After 5 h of sintering, though, sample SSR has some grains in the range 10−30 μm, whereas many others are still their original sizes, resulting in an inhomogeneous distribution of particle sizes.

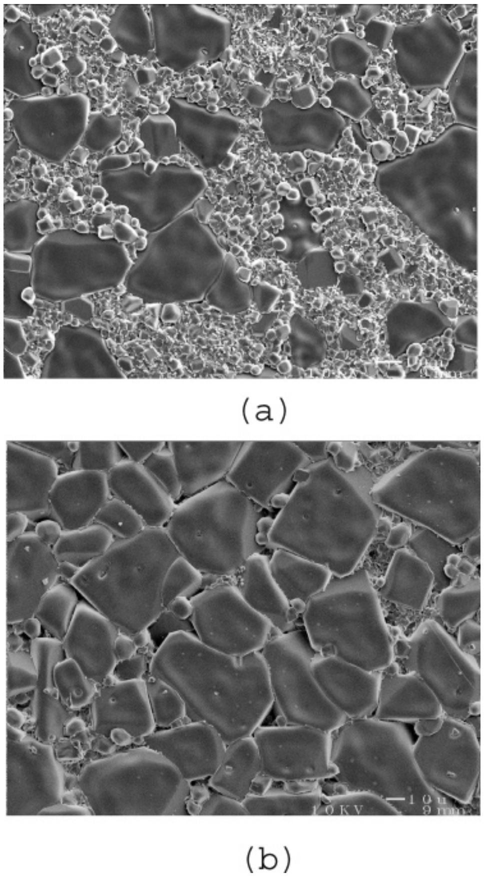

Figure 4. SEM images of sample SSR sintered at 1100 °C for (a) 5 and (b) 15 h. Sample SSR was made from solid-state reactions of $CaCO_3$, CuO, and TiO_2 at 1000 °C for 20 h.

This discontinuous grain growth was also observed by Fang et al.[11] After 15 h of sintering, all grains have the larger dimensions.

C. Dielectric Measurements. We now examine the frequency and temperature dependence of the permittivity ($\epsilon^* = \epsilon' - i\epsilon''$) for sample C, i.e., CCTO after cold-pressing and high-temperature sintering. (We could not measure the permittivity of samples without sintering because the samples were otherwise too porous.) We obtained ϵ^* from the measured complex impedance Z^* using eq 1. The results are shown in Figure 5, in which one may see that the dielectric behaviors of samples C and SSR[7] are identical. Specifically, each has a Debye-like relaxation with a steep decrease in ϵ' at the frequency where ϵ'' displays a relaxation peak. In addition, ϵ' is independent of frequency and temperature over a wide range. The relaxation frequency also shifts to higher frequencies with increasing temperature.

The Debye-like relaxations at different temperatures can be fitted to the empirical Cole−Cole equation[18]

$$\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega) = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + (i\omega\tau)^\alpha} \qquad (2)$$

where ϵ_s and ϵ_∞ are the static and high-frequency limits of the dielectric constant, respectively, τ is the most probable relaxation time, and α is a constant with values between 0 and 1. For an ideal Debye relaxation, $\alpha = 1$. If $\alpha < 1$, the

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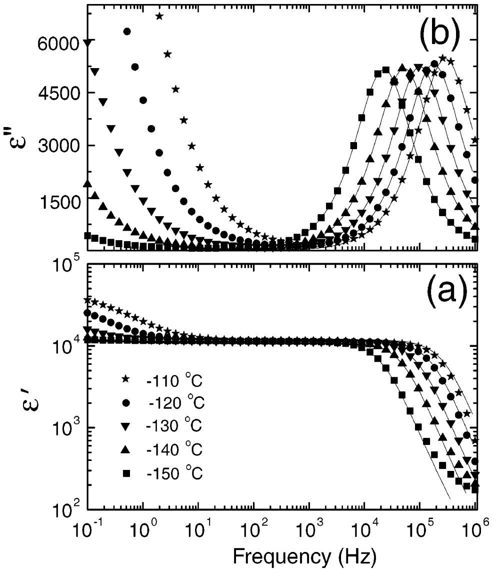

Figure 5. Frequency dependence of permittivity ϵ^* in sample C at several temperatures: (a) real part ϵ' and (b) imaginary part ϵ''. Sample C is sintered sample B that was obtained by treating the solution at 500 °C for 15 min and 700 °C for 2 h.

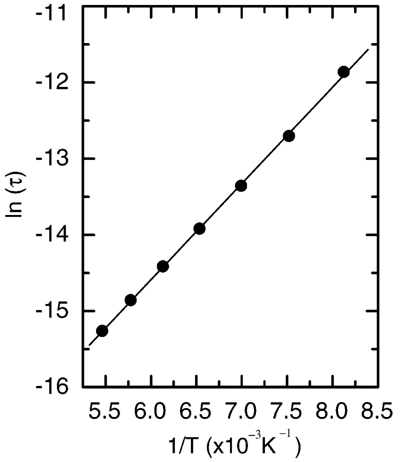

Figure 6. Arrhenius plot of dielectric relaxation time.

relaxation has a distribution of relaxation times, leading to a broader peak shape. The solid lines in Figure 5 are the fitted results with α values in the range 0.945−0.950 at different temperatures.

Moreover, the fitted τ values at different temperatures follow the Arrhenius law

$$\tau = \tau_0 \exp(E/(k_B T)) \tag{3}$$

where τ_0 is the prefactor, E is the activation energy for the relaxation, k_B is the Boltzmann constant, and T is the absolute temperature. Figure 6 shows the plot of ln τ versus $1/T$, in which the solid line is the fitted result using eq 3. From the fitting, we obtain the activation energy of the dielectric relaxation: 0.109 eV.

From Figure 5a, we obtain a dielectric constant ϵ' of sample C of 11 590 at −150 °C and 1 Hz, about 15% higher than the 9340 of sample SSR under the same experimental conditions.[7] CCTO has been reported to have very different values of the dielectric constant because of different microstructures in the ceramic samples.[10,11] Fang et al. observed that the dielectric constant of CCTO becomes higher than 1×10^4 only when there are large grains (10−20 μm) in the sintered ceramic samples.[11] They summarized that large grains may play a role in enhancing the dielectric constant. On the contrary, we find that CCTO exhibits a large dielectric constant with small grain sizes (2−3 μm). The grain sizes of the powdered CCTO fabricated by the solid-state reaction is often in the range 2−5 μm, which are 10 times larger than that in our sample B. Usually, it is easier to reduce the volume of voids inside a pellet by pressing a sample composed of small grains. We therefore believe that the density of the sample is the key factor that gives rise to the large dielectric constant in our sample C.

As mentioned previously, two electrical responses are usually observed in the complex impedance in the CCTO system that can be attributed to semiconducting grains and insulating grain boundaries. Two similar responses were detected in sample C in this present experiment as well.

D. Activation Energies of Electrical Responses. We next examine the activation energies of the aforementioned electrical responses from grains and grain-boundaries in sample C. The activation energy is associated with the height of the potential-energy barrier restricting the motion of charge carriers. To calculate the activation energy of an electrical response, one first calculates, at different temperatures, the response time $\tau = 1/(2\pi\nu)$ from the response frequency ν at which the imaginary part of the complex impedance has a maximum value; one then fits these values to eq 3. For sample C, the electrical response frequency of grain boundaries is in the measured frequency range with temperatures above 0 °C. Using this method, we obtained an activation energy of 0.58 eV, which is very close to 0.60 eV, the value reported for CCTO made by solid-state reaction.[3] The electrical response from grains has a very high response frequency because of their small resistance and capacitance; it can only be observed at −150 °C in the measured frequency range. We consequently cannot use the same method to get its activation energy. We can, however, deduce from the equivalent circuit of Maxwell−Wagner relaxation that the activation energy of the grains is approximately equal to that of the Debye-like relaxation obtained above.[6]

For compounds in the CCTO system, the Maxwell−Wagner relaxation can be described by an equivalent circuit consisting of a series array of two subcircuits, one representing grain effects and one grain boundaries.[6,7] In each subcircuit, the resistor and capacitor are in parallel. From this equivalent circuit, the dielectric relaxation time can be calculated as

$$\tau = \frac{R_g R_{gb}(C_g + C_{gb})}{R_g + R_{gb}} \tag{4}$$

where R_g, R_{gb} and C_g, C_{gb} are the resistance and capacitance of grains and grain boundaries, respectively. Because R_{gb} and C_{gb} are much larger than R_g and C_g,[3,6] we can approximate τ from eq 4 using

$$\tau \approx R_g C_{gb} = \tau_g \frac{C_{gb}}{C_g} \tag{5}$$

where $\tau_g = R_g C_g$ is the response time of the grains. It has been shown that C_g and C_{gb} are independent of temperature,[3,6] so τ and τ_g have the same temperature dependence and the electrical response of grains has the same activation energy as that of the observed dielectric relaxation.

On the basis of this analysis, we conclude that the activation energy for the response of the grains in sample C is 0.109 eV, whereas that of sample SSR is 0.093 eV[7] and that of other samples reportedly made by solid-state reaction is 0.08 eV.[3]

Summarizing all of the activation energy values, we notice that the grain boundaries of sample C have a much larger activation energy (0.58 eV) than that of the grains (0.109 eV), indicating that they have a higher energy barrier for the charge carriers to overcome. Therefore, the grain boundaries exhibit insulating properties. In contrast, the smaller activation energy of the grains causes them to display semiconducting properties similar to semiconducting titanate perovskites, such as La-doped $BaTiO_3$.[19]

To date, the origin of semiconducting grains and of insulating grain boundaries has not been clearly established, though Sinclair et al.[3] have proposed a plausible explanation that the semiconductivity of the grains arises from a small but significant loss of oxygen during ceramic processing in air at high temperatures, whereas furnace-cooling allows reoxidation to occur along the grain boundaries, which converts these regions into insulators. One may deduce from this model that grains made by different methods could have very different electrical properties. The fact that the activation energy (0.109 eV) of the grains in sample C is 17% larger than that (0.093 eV) of the grains in sample SSR may imply that there are fewer oxygen vacancies in the grains of sample C; this is reasonable because sample C was sintered from sample B, which was fabricated at low temperature (700 °C). One may expect it to be difficult for a CCTO sample to generate oxygen vacancies at low fabricating temperatures. Sintering at 1050 °C for 4 h may still cause oxygen loss, but the oxygen vacancies may be less than those in the grains of sample SSR that was fabricated at 1000 °C for 20 h and sintered at 1100 °C for 10 h. In any case, it is noteworthy to observe that the dielectric constant of sample C is larger than that of sample SSR. However, in this limited study, it is premature to associate the increase in grain activation energy of sample C with its large dielectric constant. To resolve this important issue, we believe more samples fabricated using the present approach under different experimental conditions have to be explored.

Conclusions

By pyrolyzing a stable chemical solution, we have synthesized at relatively low temperature and short treatment time the giant-dielectric-constant material CCTO with particle dimensions 200−400 nm. The grain dimensions increase to 2−3 μm after being cold-pressed into pellets and sintered at 1050 °C for 4 h. The dielectric behavior of the sintered sample is similar to that of CCTO made by solid-state reaction, i.e., there is a Debye-like relaxation in the sample and its dielectric constant of 11 500 is independent of frequency and temperature below the relaxation frequency.

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