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# Synthesis of the Giant Dielectric Constant Material $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ by Wet-Chemistry Methods<sup>†</sup>

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$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO) has a giant dielectric constant of up to  $10^5$  at room temperature and great potential for technological application. In this work, we report two wet-chemistry methods to synthesize CCTO at relatively low temperatures and short reaction times. The pure-phase sample was obtained at 800 °C for 0.5 h, and the grain size of a pellet sample sintered at 1030 °C has a homogeneous distribution in the range of 0.4–1.5  $\mu\text{m}$ .

## Introduction

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO) has been extensively investigated recently because of its giant dielectric constant, with values up to  $10^5$  at room temperature.<sup>1,2</sup> The large dielectric constant is very unusual because CCTO is not a ferroelectric. Because its dielectric properties depend primarily on the ceramic microstructure (such as the average grain size and pellet density) and processing conditions (such as the oxygen partial pressure, sintering temperature, and cooling rate), an intrinsic mechanism for the giant dielectric constant seems to be excluded. Most studies have attributed the giant value to the Maxwell–Wagner effect (internal barrier layer capacitor) at the interface of grains and grain boundaries,<sup>3–6</sup> while Lunkenheimer et al. believe they are due to electrode polarization effects.<sup>7,8</sup>

CCTO is usually made by standard solid-state reactions from stoichiometric ratios of  $\text{CaCO}_3$ ,  $\text{CuO}$ , and  $\text{TiO}_2$  at high temperatures.<sup>1,3,5,6</sup> This method requires repetitive grinding and firing at high temperatures and long reaction times (e.g., 1000 °C and 20 h), but the resulting sample may still contain secondary phases or unreacted components. In contrast, wet-chemistry methods start with a homogeneous liquid solution of cation ingredients, with metal cations mixed in stoichiometric ratios at the atomic scale. Therefore, pure samples at

the nanometer scale could theoretically be obtained at lower temperatures and shorter reaction times than that afforded by solid-state reactions. Only a few such methods to make CCTO have been reported in the literature. They include polymerized complex methods<sup>9,10</sup> and sol–gel methods.<sup>11,12</sup> These methods are still relatively complex, though, and need long heat-treatment times.

We have previously reported a relatively simple pyrolysis method to make CCTO.<sup>13</sup> By pyrolyzing a stable chemical solution we obtained pure CCTO at 700 °C and 2 h of reaction time. However, this method still has the disadvantage that it involves handling chemicals in a glovebox and refluxing solutions. In this report, we present two simple wet-chemistry methods to make a pure phase of CCTO at a relatively low temperature (800 °C) and a very short reaction time (0.5 h) without using a glovebox or refluxing the solutions.

## Experimental Section

We have synthesized pure CCTO by two different wet-chemistry methods, which we term the combustion method and the pyrolysis method. Calcium nitrate tetrahydrate [ $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , 99.99%], copper(II) nitrate hemipentahydrate [ $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ , 99.99%], titanium(IV) isopropoxide ( $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$ , 97%), anhydrous citric acid (99.5+%), acetylacetone (2,4-pentanedione, 99+%), and anhydrous ethylene glycol (99.8%) were used as raw materials in all reactions.

In the combustion procedure, 2.84 g (0.010 mol) of titanium(IV) isopropoxide was first mixed with 1.00 g (0.010 mol) of acetylacetone for 5 min with constant stirring using a magnetic stirrer. Then 1.92 g (0.010 mol) of citric acid previously dissolved in deionized water was added to the titanium solution and stirred for 30 min. A total of 0.59 g (0.0025 mol) of calcium nitrate tetrahydrate and

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1.74 g (0.0075 mol) of copper(II) nitrate hemipentahydrate were dissolved in 20 mL of deionized water and added to the titanium–citric acid solution with constant stirring, resulting in a clear green solution. Several drops of aqueous ammonia (34%) were added to the solution. The solution was heated to 80 °C with constant stirring to evaporate the water, resulting in a highly viscous blue gel. As soon as this gel was formed, it was placed in a preheated box oven at 450 °C for 15 min. The resultant voluminous, porous sample was ground into powder and divided into portions, and each portion was heat-treated at 500–800 °C for different periods of time, from 5 min to 2 h. At each temperature, the sample was placed in the preheated oven and taken out at the same temperature at the end of the allotted time period for subsequent analysis by X-ray diffraction.

In the pyrolysis procedure, 2.84 g (0.010 mol) of titanium(IV) isopropoxide was first mixed with 1.00 g (0.010 mol) of acetylacetonone for 5 min with constant stirring using a magnetic stirrer, and then 6.21 g (0.10 mol) of ethylene glycol and 1.92 g (0.010 mol) of citric acid were successively added to the solution and stirred until all of the citric acid was dissolved. Finally, 0.59 g (0.0025 mol) of calcium nitrate tetrahydrate and 1.74 g (0.0075 mol) of copper(II) nitrate hemipentahydrate were added to the solution with constant stirring to get a stable solution. Several drops of aqueous ammonia (34%) were added, and the solution was placed in a preheated box oven at 450 °C for 15 min. The resultant voluminous, porous sample was ground into powder and heat-treated, as in the combustion method described above.

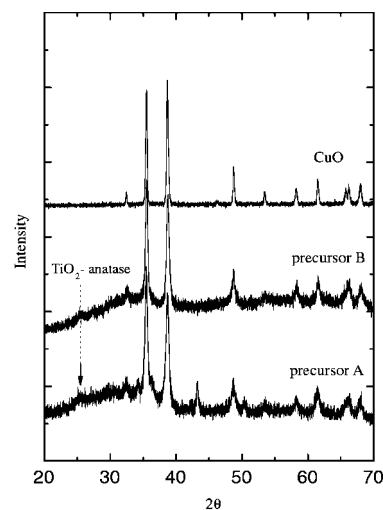
The sample after each heat treatment was characterized by a Scintag PAD V powder X-ray diffractometer. The resultant pure CCTO was cold-pressed into a pellet and then sintered at different temperatures for 4 h. The grain sizes of the pellet after sintering were examined by a JEOL JSM840A scanning electron microscope set at 5 kV.

The complex permittivity was examined with a Novocontrol high-resolution dielectric spectrometer in the temperature range of –150 °C to room temperature and the frequency range of  $1 \times 10^{-1}$  to  $1 \times 10^6$  Hz. Gold films were sputtered on both faces of the pellets as electrodes. The applied ac voltage was 1 V. The dielectric spectrometer first measured the complex impedance  $Z^* = V^*/I^*$  (where  $V^*$  and  $I^*$  are the applied voltage and resulting current, respectively) and then converted  $Z^*$  into complex permittivity  $\epsilon^* = \epsilon' - i\epsilon'' = 1 / i\omega C_0 Z^*$  where  $\omega$  is angular frequency  $\omega = 2\pi\nu$ ,  $i = (-1)^{1/2}$ , and  $C_0 = \epsilon_0 S/d$  is the empty cell capacitance, where  $S$  is the sample area and  $d$  is the sample thickness.

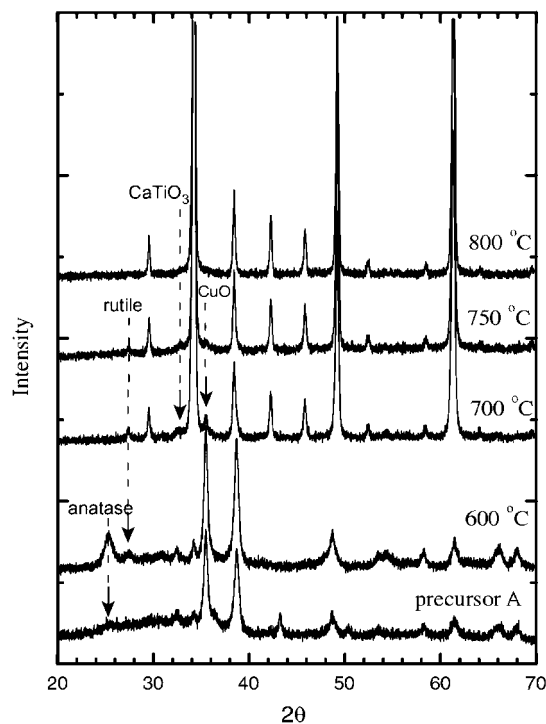
## Results and Discussion

**A. Combustion Method.** In the combustion method, the calcium/copper/titanium/citrate aqueous solution became a viscous, transparent, blue gel when the water was evaporated. After the heat treatment at 450 °C for 15 min, all of the organic materials were burned out and a voluminous porous black sample was left, which we term precursor A. The X-ray diffraction pattern of this is shown in Figure 1. Most of the peaks are due to copper(II) oxide, whose diffraction pattern is also displayed. The peak at about 43.3° was not identified, but it is not due to  $\text{TiO}_2$  (rutile or anatase), CaO,  $\text{CaCO}_3$ , or  $\text{CuCO}_3$ . The broad peak at 25.6° is probably due to the anatase structure of  $\text{TiO}_2$ , but a definitive assignment is difficult because it is not well crystallized.

Portions of precursor A were heat-treated at different temperatures and time periods. Figures 2 and 3 present the X-ray diffraction patterns of the resultant products after heat treatments at various temperatures for 0.5 and 2 h, respec-

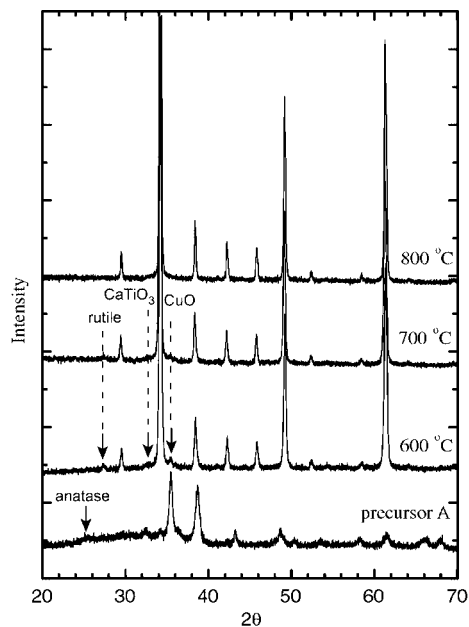


**Figure 1.** X-ray diffraction patterns of precursors A and B and commercial copper(II) oxide. Precursor A is obtained by treating the Ca/Cu/Ti/citrate gel at 450 °C for 15 min in the combustion method. Precursor B is obtained by treating a Ca/Cu/Ti/citrate/ethylene glycol solution at 450 °C for 15 min in the pyrolysis method.



**Figure 2.** X-ray diffraction patterns of the resultant products after precursor A was heat-treated for 0.5 h at different temperatures.

tively. First, consider Figure 2, which shows half-hour heat-treatment samples. After treatment at 600 °C, the principal diffraction peaks are still attributable to  $\text{CuO}$ , but the diffraction peak of anatase ( $\text{TiO}_2$ ) is more intense and a small peak at 27.3° from the rutile structure of  $\text{TiO}_2$  is apparent. At 700 °C, the principal phase of the sample is CCTO, anatase ( $\text{TiO}_2$ ) is no longer apparent, and  $\text{CuO}$  and rutile ( $\text{TiO}_2$ ) are the major impurities. A small peak also appears at 32.7°, which we attribute to  $\text{CaTiO}_3$ . At 750 °C, the sample still contains a few  $\text{CuO}$ , rutile ( $\text{TiO}_2$ ), and  $\text{CaTiO}_3$  diffraction peaks. At 800 °C, the sample has become pure CCTO, with no detectable impurities.



**Figure 3.** X-ray diffraction patterns of the resultant products after precursor A was heat-treated for 2 h at different temperatures.

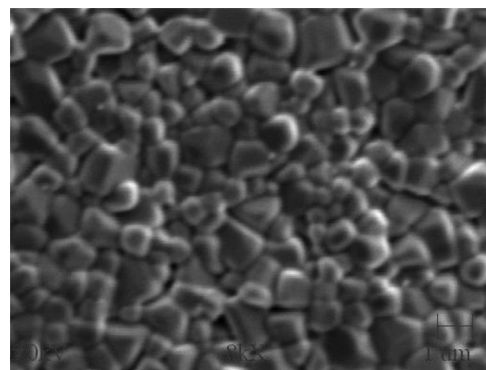
Two-hour heat-treatment samples are presented in Figure 3. In contrast to the half-hour treatment time at 600 °C, 2-h treatment at 600 °C of precursor A results in pure CCTO with small amounts of CuO, rutile ( $\text{TiO}_2$ ), and  $\text{CaTiO}_3$ . The impurities drastically decrease at 700 °C and become undetectable at 800 °C.

We pressed the pure CCTO obtained at 800 °C for 2 h into a pellet using a hydraulic press and then sintered at 1030 and 1040 °C for 4 h. We examined the grain dimensions of the pellet by scanning electron microscopy (SEM) after sintering and show the images in Figure 4. They show that, after 4 h at 1030 °C, the grain sizes have a narrow distribution in the range of 0.4–1.0  $\mu\text{m}$ . At 1040 °C, some grains have grown to as large as 20  $\mu\text{m}$ .

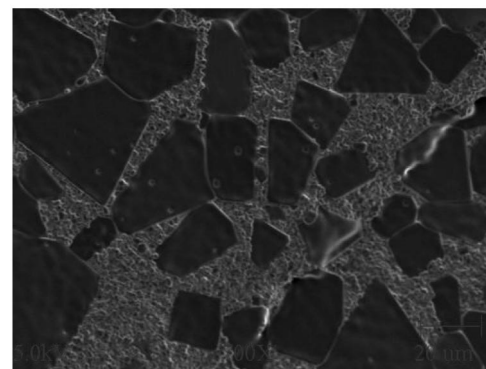
**B. Pyrolysis Method.** In the pyrolysis method, the  $\text{Ca/Cu/Ti}$ /citrate/ethylene glycol solution was placed directly into a preheated oven at 400 °C to get a voluminous black product termed precursor B. Its X-ray diffraction pattern is shown in Figure 1 and is similar to that of precursor A but without the unidentified peak at 43.3°. As with precursor A, it shows all of the diffraction peaks of CuO and a broad peak of  $\text{TiO}_2$  (anatase).

Figure 5 shows the X-ray diffraction patterns of the resultant products after heat treatment of precursor B at different temperatures and times. After 1 h at 600 °C, its pattern has not changed except for several small peaks attributable to  $\text{TiO}_2$  (rutile and anatase) and other unidentified phases. After 1 h at 700 °C, it has formed CCTO with trace amounts of  $\text{TiO}_2$  (rutile), CuO, and  $\text{CaTiO}_3$  as impurities. After 0.5 h at 800 °C, a similar sample is formed but with fewer impurities. When the heat-treatment time is increased to 1 h at this temperature, the impurities become undetectable.

Figure 6 presents SEM images of CCTO pellets prepared at 800 °C for 1 h and then sintered at 1030 and 1040 °C for 4 h. At 1030 °C, CCTO made by this method has particle dimensions in the range of 0.5–1.5  $\mu\text{m}$ , which is a little larger than those made by the combustion method. The grains only

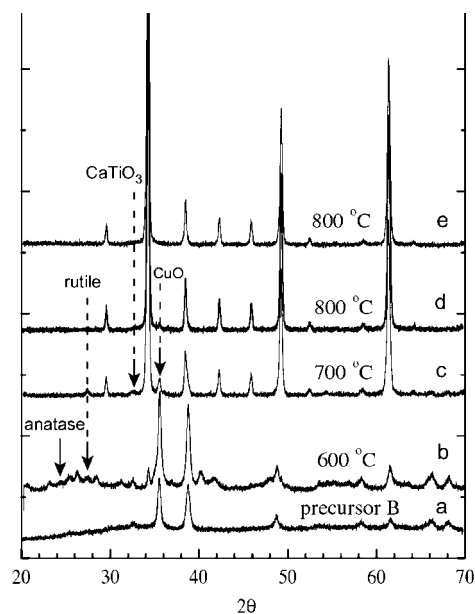


(a)



(b)

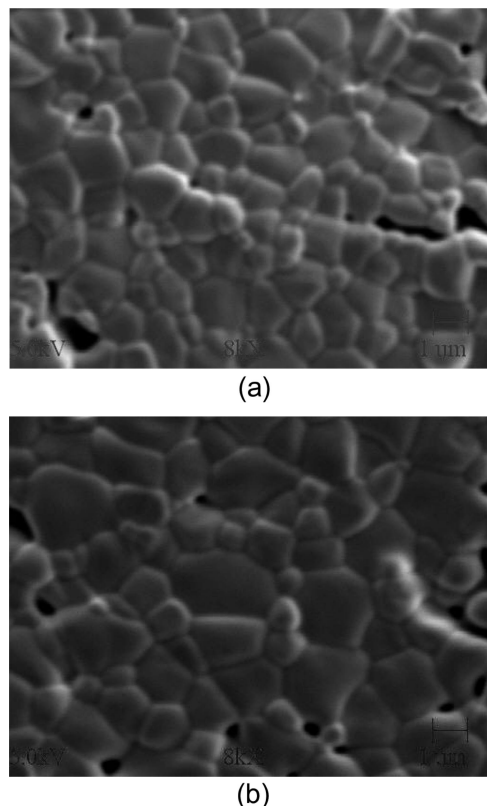
**Figure 4.** SEM images of CCTO made at 800 °C for 2 h by the combustion method, sintering for 4 h at 1030 °C (a) and 1040 °C (b).



**Figure 5.** X-ray diffraction patterns of the resultant products after precursor B was heat-treated for 1 h (b, c, and e) and 0.5 h (d) at different temperatures.

grow to 3  $\mu\text{m}$  at 1040 °C unlike 20  $\mu\text{m}$  in Figure 4b. These pellets are still very porous because larger grain sizes need higher temperatures to be densified.

Titanium isopropoxide is usually used as the titanium source in making titanates by wet-chemistry methods. However, it is very sensitive to the moisture in air so it must be handled in a glovebox. Acetylacetonone is often used as a stabilizing agent because it reacts exothermally with titanium

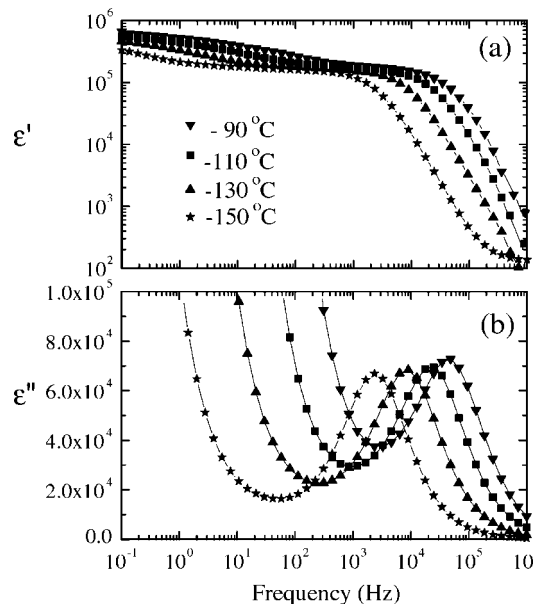


**Figure 6.** SEM images of CCTO made at 800 °C for 1 h by the pyrolysis method, sintering for 4 h at 1030 °C (a) and 1040 °C (b).

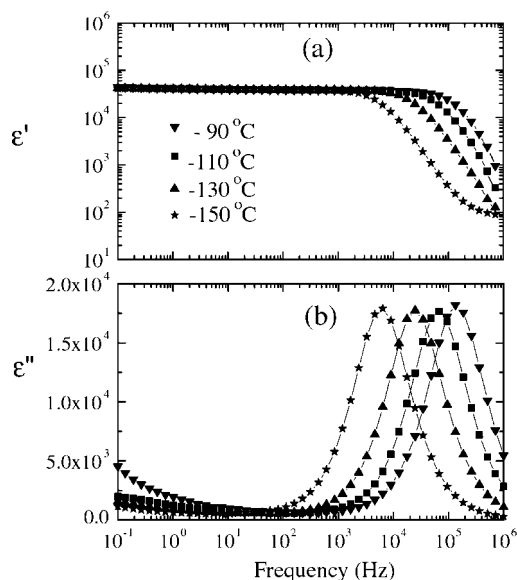
isopropoxide to form a titanium alkoxide in which the coordination number of titanium increases from four to five.<sup>14,15</sup> The titanium alkoxide is significantly more stable against moisture so that, in the present synthesis procedures, it can be handled in air and form homogeneous solutions when mixed with an aqueous citric acid solution in the combustion method or when mixed with hydrated substances such as calcium nitrate tetrahydrate or copper nitrate hemipentahydrate in the pyrolysis method.

The X-ray diffraction patterns of precursors A and B (shown in Figure 1) show that they contain crystalline copper(II) oxide and poorly crystallized  $\text{TiO}_2$  (anatase). This indicates that the metal nitrates and titanium isopropoxide formed oxides in the first step of the heat treatment. CCTO was thereafter produced by solid-state reaction between copper(II) oxide and other amorphous or crystalline metal phases. The mixtures of precursor materials must therefore be intimately mixed at the nanoscale level so that pure CCTO can be produced at such relatively low temperatures and short reaction times compared to those in the solid-state reaction conducted directly from the metal oxides.

**C. Dielectric Measurements.** The frequency and temperature dependencies of the permittivity ( $\epsilon^* = \epsilon' - i\epsilon''$ ) for the samples made from the combustion (Sample Comb) and pyrolysis methods (Sample Pyro) are shown in Figures



**Figure 7.** Frequency dependence of permittivity  $\epsilon^*$  in the sample made from the combustion method at several temperatures: (a) real part  $\epsilon'$ ; (b) imaginary part  $\epsilon''$ .



**Figure 8.** Frequency dependence of permittivity  $\epsilon^*$  in the sample made from the pyrolysis method at several temperatures: (a) real part  $\epsilon'$ ; (b) imaginary part  $\epsilon''$ .

7 and 8, respectively. The dielectric behaviors of both samples are similar to the reported results.<sup>1,13</sup> Specifically, they all have a Debye-like relaxation with a steep decrease in  $\epsilon'$  at the frequency where  $\epsilon''$  displays a relaxation peak, and  $\epsilon'$  is independent of the frequency and temperature over a wide range. At  $-150$  °C and 113.38 Hz, the measured dielectric constant of Sample Comb is 159330 and that of Sample Pyro is 39008. We note that variation of the dielectric constant between the two samples does not necessarily mean that one synthesis technique is superior to the other, because the dielectric constant of CCTO strongly depends on the microstructures of the samples.<sup>16</sup> We also note that Sample Comb displays another relaxation below 100 Hz apart from

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the Debye-like relaxation above 1000 Hz. This second relaxation was caused by the space charge between the electrodes and the samples, a result of the electrode deposition.

### Conclusions

We have synthesized at relatively low temperatures and short heat-treatment times the giant dielectric constant material CCTO by using two wet-chemistry methods. In both methods, the metal oxides are formed in the first heat-

treatment step and CCTO is produced by a subsequent solid-state reaction. The CCTO has homogeneous grain sizes with dimensions in the range of 0.4–1.5  $\mu\text{m}$  at 1030 °C for 4 h.

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