# Effective synthesis to fabricate a giant dielectric-constant material $CaCu_3Ti_4O_{12}$ via solid state reactions

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In this study, we effectively synthesized a giant dielectric-constant material $CaCu_3Ti_4O_{12}$ (CCTO) by using a solid-state reaction method that was composed of two main chemical reactions. Comparing with typical calcining conditions, our procedures are much less energy- and time-consuming. When preparing our CCTO, we applied a momentarily high temperature heating at the end of the calcination, then followed it by a typical sintering process. We found this additional heating converts the otherwise mixed-phase products into a pure phase and the CCTO samples prepared this special way possess a large dielectric constant, up to 19,000.

Key words: Solid state reaction, Ceramics, Sintering, Dielectric constant.

## Introduction

$CaCu_3Ti_4O_{12}$ (CCTO) is a pervoskite-like ceramic with a gigantic dielectric constant ($\varepsilon'$) that reaches as high as $10^5$ over a wide frequency range, ~100 Hz to 1 MHz, and temperature range, 100 to 400 K [1-3]. Ordinarily giant dielectric constants are associated with ferroelectric materials, however, there is no structural anomaly found in CCTO. Therefore, the mechanism of its giant dielectric constant has become an interesting and forefront research topic in condensed matter physics. Several models have been put forward by different groups to explain its origin: for example, itsintrinsic atomic structure [1], microstructure [1,3-6], and extrinsic interfacial structure [7-13]. Our aim is to study fabrication procedures leading to high $\varepsilon'$ that enhance our understanding of its basic mechanism.

CCTO is usually prepared by using a solid-state reaction route, which begins with calcining stoichiometric ratios of $CaCO_3$, CuO, and $TiO_2$ at high temperatures and for long reaction times, such as 1000 °C overnight [4], 1000 °C for 20 h [14], 1000 °C for 24 h [15, 16, 17], and 1050 °C for 12 h [18]. In this investigation, we adopted a two-step approach: we first calcined at a low temperature of 900 °C for only 10 h; then raised the temperature up to 1100 °C in a short period of 10 minutes. After sintering, we obtained a pure phase CCTO with a dielectric constant as high as 19,000. In order to elucidate the mechanism behind the fabrication processes of CCTO, we propose a two-step chemical reaction, which will be discussed below.

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Our results show that the calcining process is instrumental in enhancing the dielectric constant.

## Experimental Procedure

CCTO ceramic powder was synthesized from stoichiometric amounts of $CaCO_3$ (99.0%), CuO (99%), and $TiO_2$ (98%). The three types of starting powders were mixed by hand grinding for 2 h in a porcelain motor. Then the mixture was separated into two portions for different calcining processes: the first portion was calcined at 900 °C for 10 h and named sample A. The other portion, named B, was first calcined at the same temperature and duration as A, then its temperature was brought up to 1100 °C in 10 minutes duration at a rate of 20 °C minute$^{-1}$. Both samples were allowed to cool to room temperature at the end of their calcining processes by turning off the heat of the furnace. We estimate that it required 7 minutes to cool down from 1100 °C to 900 °C. Hence B had been calcined above 900 °C for only 17 minutes longer than A.

Next, the calcined samples A and B were separately ground by hand again for 0.5 h. Then disks 10 mm in diameter and 1 mm in thickness were made by cold-pressing at a pressure of 400 bar (40 MPa) and sintered at different temperatures for 10 h. Disks made from A and B were sintered at 950 °C and named A-1 and B-1, respectively. Another disk also from B was sintered at 1000 °C and named B-2. The heating rate in our furnace was maintained at 20 °C minute$^{-1}$. After heating, the furnace was cooled back down to room temperature.
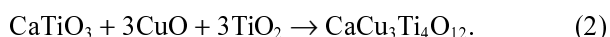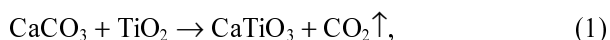
For the electrical characterization, silver paint was applied on both surfaces of the sintered disks, which had been lightly polished with SiC papers, and then fired at 300 °C for 2 h.
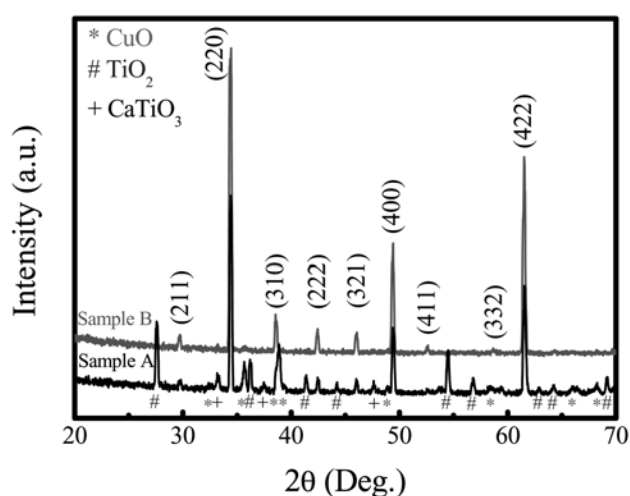
The crystalline structures were examined by X-ray diffraction (XRD) at room temperature. Surface morphologies were investigated by a scanning electron microscope (SEM, LEO 1450 VP). The dielectric constant was measured in the frequency range of 40 Hz-30 MHz at an AC voltage of 1 V at room temperature using impedance analyzers (Agilent 4285A, 75 kHz-30 MHz, and NF Electronic 2330, 40 Hz-100 kHz).

## Results and Discussion

In Fig. 1, we compare the XRD patterns obtained for the calcined samples A and B. Apparently, the patterns are similar and most of the peaks are identified to correspond to those of a body-centered cubic perovskiterelated CCTO phase of space group *Im3* with a lattice parameter of about 7.39 Å. However, small amounts of $CaTiO_3$, $CuO$ and $TiO_2$ phases are found in A, as are highlighted at the bottom of the figure. $CaTiO_3$ is a new phase, not one of the three starting powders, that only exists in A. While in B, no secondary phase is found, which implies that all the starting powders were consumed to form a pure phase CCTO, after only 17 minutes of additional heating. Based on this observation, it is reasonable to assert that CCTO was not formed in a one-step chemical reaction: $CaCO_3 + 3CuO + 4TiO_2 \rightarrow CaCu_3Ti_4O_{12} + CO_2\uparrow$. Instead it is divided in two steps:

$$CaCO_3 + TiO_2 \rightarrow CaTiO_3 + CO_2\uparrow, \qquad (1)$$

$$CaTiO_3 + 3CuO + 3TiO_2 \rightarrow CaCu_3Ti_4O_{12}. \qquad (2)$$

Unlike most of previous research [2, 14, 15, 17, 18], the whole calcining process of B took very little more time than 10 h, and was mostly held at a relatively lower temperature, 900 °C. For example, Li and Schwartz [19] performed similar calcinations at 1000 °C for 12 h, and compounds other than CCTO were still identified in
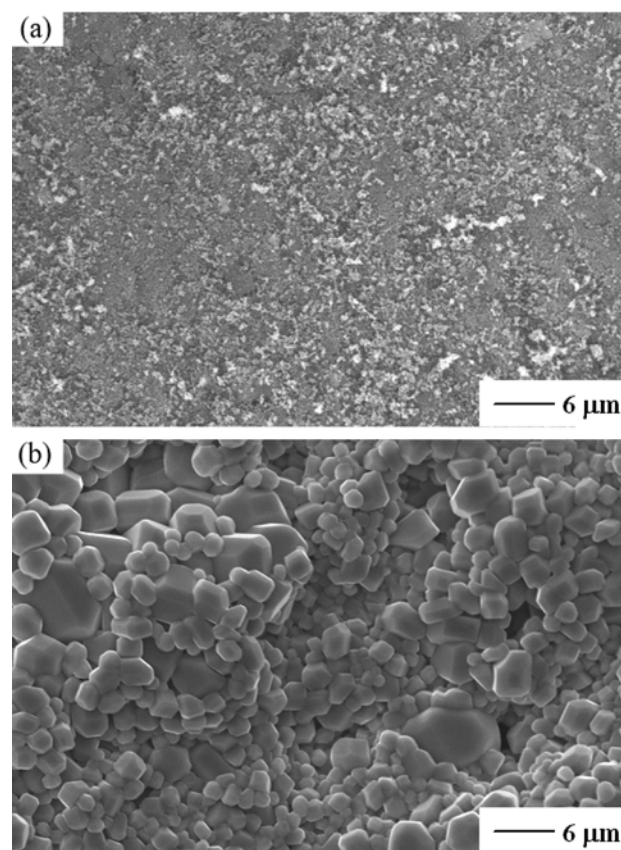
their XRD patterns; whereas in our sample B, we achieved pure phase CCTO in less time and at a lower temperature. Comparing the different calcining processes, we suggest that momentarily heating the reactants to 1100 °C is an essential step in completing the solid state reactions.

In Fig. 2, we present SEM images of two different disks. The first one, shown in Fig. 2(a), is of a disk composed of a mixture of the three starting powders after hand grinding. We notice that it is composed of uniformly distributed fine grains with a size of the order of 200 nm. After calcination, we find that the microstructures of both samples A and B are very similar, so we only present the image of B in Fig. 2(b). We observe that its grains with a size of a few µm, are much larger than those before the calcination, and, more importantly, there are also a lot of µm sized voids. We attribute the latter to the release of $CO_2$ in the first reaction step (Eq. (1)) of the calcining process. Since both A and B pass through essentially the same preparation steps, it is no surprise that they have a similar morphology. Apparently, grain growth is negligible during the short period when B was subjected to the additional heating.
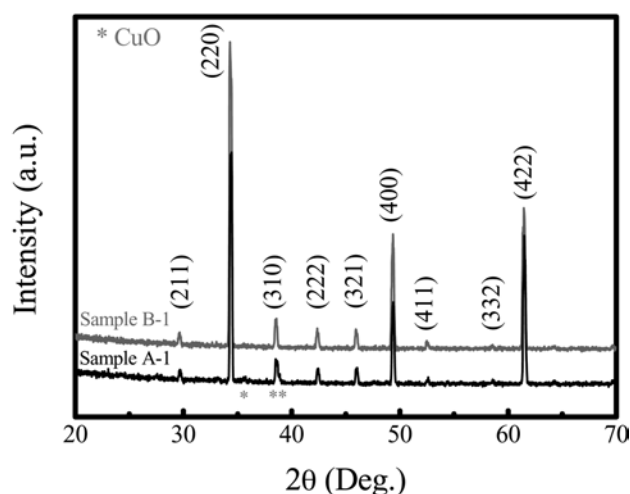
We further investigated the interplay between sintering and calcining. By sintering samples A and B, we obtained samples A-1, B-1 and B-2. As expected, samples B-1 and B-2 are very similar in their XRD patterns, since



**Fig. 1.** X-ray diffraction patterns of the samples A and B. Symbols *, #, + refer to diffraction peaks of $CuO$, $TiO_2$, and $CaTiO_3$, respectively.
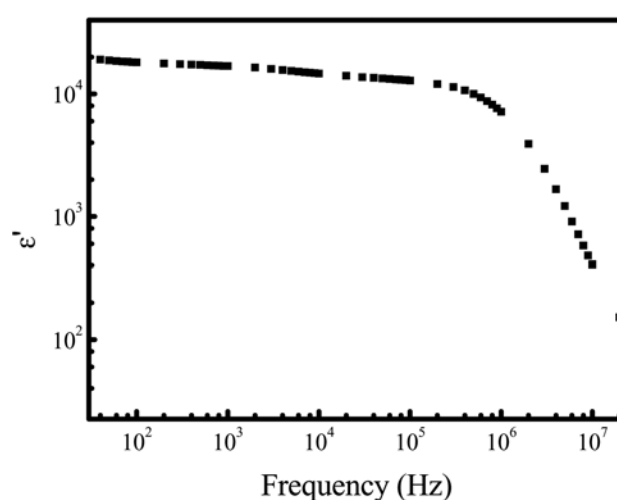


**Fig. 2.** SEM images showing the microstructures of (a) a disk composed of the three starting powders and (b) a disk of sample B.

their sintering temperatures only differ by 50 °C. The XRD of samples A-1 and B-1 are shown in Fig. 3. We noticed that B-1 is undoubtedly pure CCTO, but there are still CuO peaks present in A-1, which are the three diffraction peaks at 35.56°, 38.73° and 38.96°, corresponding to the (002), (111), and (200) reflections, respectively. We note that the last two peaks overlap with the CCTO (310) peak. More importantly, $CaTiO_3$ and $TiO_2$ phases have disappeared after sintering. This result demonstrates that the chemical reaction, Eq. (2), continued in A-1 during sintering, which shows that even after 10 h at 950 °C, we still can not completely get rid of all the other phases. It also confirms that the momentary high temperature heating at the end of calcination is crucial in obtaining the pure phase CCTO efficiently. Henceforth, high dielectric constant samples can be fabricated.

Finally, we measured ε' of our samples at room temperature. We found that sample A-1 has a significantly smaller ε' than that of B-1 (~400 vs 1700 at 1 kHz). In Fig. 4, we present the measured results of B-2, in which we notice a typical behavior of a CCTO that maintains ε' of about 19,000 over a wide frequency range and has a Debye-like relaxation with a steep descent at 1 MHz. At the same time, we find ε' of B-1 is about 10% of that of B-2. We attribute this difference to the effects of grain size and void density. Indeed we found that B-2 has larger grains and a significantly smaller density of voids. It is generally recognized that more compacted CCTO tend to have higher ε' [20, 21], and our results are consistent with this observation. In addition, similar sintering conditions were adopted by Shao *et al.*, but their ε' is only about 1,200 because of their different calcining conditions [21]. There are other groups adopting different calcining and sintering temperatures, both at 1000 °C or higher, and for longer periods, from 12 to 24 h. Yet their ε's, which range from 8,000 to 12,000 [1, 2, 14, 22], are smaller than ours. Thus, based on our finding, we believe that the additional calcining step is crucial to fabricating high ε' CCTO.



**Fig. 4.** Dielectric constant ε' of sample B-2 as a function of frequency at room temperature.

## Conclusions

In this study, we have synthesized a giant dielectric-constant material CCTO by using a modified solid-state reaction. We adopted a more efficient process than most other workers, yet the dielectric constants we obtained are as high as 19,000. We notice that the dielectric constant of the CCTO samples is also sensitive to the sintering temperature. We interpret the whole fabrication process based on a two-step chemical reaction, and deduce the essential step that leads to a giant dielectric constant. Further investigations on different fabrication temperatures and durations are underway and will be presented later.

## Acknowledgements

## References

1. M.A. Subramanian, D. Li, N. Duan, B.A. Reisner, A.W. Sleight, J. Solid State Chem. 151 (2000) 323-325.
2. A.P. Ramirez, M.A. Subramanian, M. Gardel. G. Blumberg, D. Li, T. Vogt, S.M. Shapiro, Solid State Commun. 115 (2000) 217-220.
3. C.C. Homes, T. Vogt, S.M. Shapiro, S. Wakimoto, A.P. Ramirez, Science 293 (2001) 673-676.
4. D.C. Sinclair, R.B. Adams, F.D. Morrison, A.R. West, Appl. Phys. Lett. 80 (2002) 2153-2155.
5. C.C. Homes, T. Vogt, S.M. Shapiro, S. Wakimoto, M.A. Subramanian, A.P. Ramirez, Phy. Rev. B 67 (2003) 092106.
6. C.F. Yang, Jpn. J. Appl. Phys. 35 (1996) 1806-1813.
7. P. Lunkenheimer, V. Bobnar, A.V. Pronin, A.I. Ritus, A.A. Volkov, A. Loidl, Phys. Rev. B 66 (2002) 052105.
8. P. Lunkenheimer, R. Fichtl, S.G. Ebbinghaus, A. Loidl, Phys. Rev. B 70 (2004) 172102.
9. J. Yang, M. Shen, L. Fang, Mater. Lett. 59 (2005) 3990-3993.



**Fig. 3.** X-ray diffraction patterns of samples A-1 and B-1, sintered at 950 °C for 10 h.

10. G. Chiodelli, V. Massarotti, D. Capsoni, M. Bini, C.B. Azzoni, M.C. Mozzati, P. Lupotto, Solid State Commun. 132 (2004) 241-246.

11. G. Zang, J. Zhang, P. Zheng, J. Wang, C. Wang, J. Phys. D: Appl. Phys. 38 (2005) 1824-1827.

12. J. Li, A.W. Sleight, M.A. Subramanian, Solid State Commun. 135 (2005) 260-262.

13. C.P. Sun, J.J. Liu, J.Y. Lin, C.G. Duan, W.N. Mei, H.D. Yang, J. Phys.: Condens. Matter 20 (2008) 285214.

14. J.J. Liu, C.G. Duan, W.N. Mei, R.W. Smith, J.R. Hardy, J. Appl. Phys. 98 (2005) 093703.

15. T.B. Adams, D.C. Sinclair, A.R. West, J. Am. Ceram. Soc. 89 (2006) 2833-2838.

16. S. Aygün, X.L. Tan, J.P. Maria, D. Cann, J. Electroceram. 15 (2005) 203-208.

17. W.P. Chen, W. Xiang, M.S. Guo, W.C. You, X.Z. Zhao, H.L.W. Chan, J. Alloy. Compd. 422 (2006) L9-L12.

18. W. Kobayashi, I. Terasaki, Appl. Phys. Appl. 87 (2005) 032902.

19. W. Li, R.W. Schwartz, Phys. Rev. B 75 (2007) 012104.

20. W.Q. Ni, X.H. Zheng, J.C. Yu, J. Mater. Sci. 42 (2007) 1037-1042.

21. S.F. Shao, J.L. Zhang, P. Zheng, W.L. Zhong, C.L. Wang, J. Appl. Phys. 99 (2006) 084106.

22. L.X. Feng, X.M. Tang, Y.Y. Yan, X.Z. Chen, Z.K. Jiao, G.H. Cao, Phys. Stat. Sol. (a) 203 (2006) R22-R24.