

Synthesis of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ by modified Sol-gel method with Hydrothermal process

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Abstract. $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ powders were synthesized by modified Sol-gel method with Hydrothermal process using $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Ti}(\text{OC}_3\text{H}_7)_4$ and freshly extracted egg white (ovalbumin) in aqueous medium. The precursor was calcined at 800, 900 and 1000 °C in air for 8 h to obtain nanocrystalline powders of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. The calcined $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ powders were characterized by XRD, TEM and EDX. The XRD results indicated that all calcined samples have a typical perovskite $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ structure and a small amount of CaTiO_3 , CuO and TiO_2 . TEM micrographs showed particle size 100 - 500 nm and EDX results showed elements of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ powders have calcium, copper, titanium and oxygen.

1. Introduction

Dielectric ceramics play key roles in modern microelectronic and microwave communication systems. In an attempt to miniaturize device size, much attention has been devoted to discover materials with giant dielectric constant, good thermal stability and Ba/Pb-free. Recently, there has been a great interest in synthesis and characterization of a perovskite-like compound, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, (CCTO) [1-3]. This non-ferroelectric material exhibits giant dielectric constant ($\epsilon' \sim 10^4 - 10^5$) [1-3] in the kilohertz region over the temperature range from -173 to 327 °C [1, 2]. This material does not undergo any structural change over the same temperature range although its dielectric constant abruptly decreases to less than 100 below -173 °C. In addition to its interesting dielectric property, CCTO has remarkably strong linear current-voltage characteristics without the addition of dopants [4]. These excellent properties render this material particularly attractive for a wide range of applications.

CCTO powder was generally prepared by a standard solid-state reaction method [1-3]. This method requires tedious work and a high temperature in the powder preparation process. Moreover, it suffers from the disadvantages of inhomogeneity. In contrast, synthesis from a solution affords the reaction with a homogeneous mixing of the metal ions at the atomic scale, shorter reaction time, and at lower temperature in the powder preparation process [5]. However, it has been only a few reports on the solution methods to synthesize CCTO powders [6-10]. Therefore, alternative simple solution routes by utilization of cheap, nontoxic and environmentally benign precursors for preparation of CCTO powders are still a challenge. Egg white proteins are well known for their gelling, foaming and emulsifying characteristics, in addition to their high nutrition quality [11, 12]. Due to its solubility in water and its ability to associate with metal ions in solution, egg white has been used as a binder cum gel forming material in shape forming of bulk and porous ceramics [13-15]. Egg white has been used as a matrix for entrapment of aluminum ions generating gel precursor which resulted in α -alumina particles with crystalline sizes of 15-80 nm after heat treatment as low as 330°C [16]. To the best of our knowledge, this biosynthesis route has not been extended to the preparation of any complex oxide

materials. Our group has reported the use of egg white solution for the preparations of plate-like clusters of CeO_2 nanocrystalline particles 6-30 nm in diameter [17] and nanoparticles of NiFe_2O_4 with particle sizes of 60-600 nm [18].

In this study, we report the synthesis of CCTO powder prepared by the hydrothermal process using $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, Titanium(diisopropoxide) bis(2, 4-pentanedionate) and freshly extracted egg white (ovalbumin) in aqueous medium. The synthesized fine CCTO powders were characterized X-ray diffraction (XRD), transmission electron microscopy (TEM) and Energy Dispersive X-ray Spectrometer (EDX).

2. Experimental procedure

The solution of calcium, copper and titanium was prepared by a simple egg white solution route. In a typical procedure, 60 ml of egg white was first mixed with 40 ml de-ionized water (3:2 ratio) under vigorous stir at room temperature (27 °C) until homogeneous solution was obtained. Subsequently, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99.9% purity, Kento, Japan), $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99.5% purity, Carlo Erba Reagenti, Italy), and 75 wt% Titanium(diisopropoxide) bis(2, 4-pentanedionate) in 2-propanol (99%, Acros organics, USA) in a mole ratio corresponding to the nominal composition of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. These chemicals were added to the egg white solution under vigorous stir at room temperature for 2 h to obtain a well-dissolved solution. At this step, the extracted egg white was acted as a matrix for entrapment of Ca, Cu, and Ti ions generating gel precursor [16-18]. Throughout the whole process described above, no pH adjustment was made. Then, the mixed solution was treated hydrothermally in autoclaves at 150 and 200 °C for 8 h. The resulting precipitates were washed several times with deionized water and dried at 60-80 °C. The dried precursor was crushed into powder using mortar and pestle.

The dried precursor then was calcined in box-furnace at 800, 900 and 1000 °C for 8 h in air. The calcined powder precursors were reground and passed through 106 μm sieve (Test sieve, Endecotts Limited, England) to break up large agglomerates. The prepared CCTO powders were characterized by X-ray diffraction (SHIMADZU, XRD 6100, Japan), transmission electron microscopy (FEI, TECNAI G2 20, USA) and Energy Dispersive X-ray Spectrometer (FEI, TECNAI G2 20, USA).

3. Results and Discussion

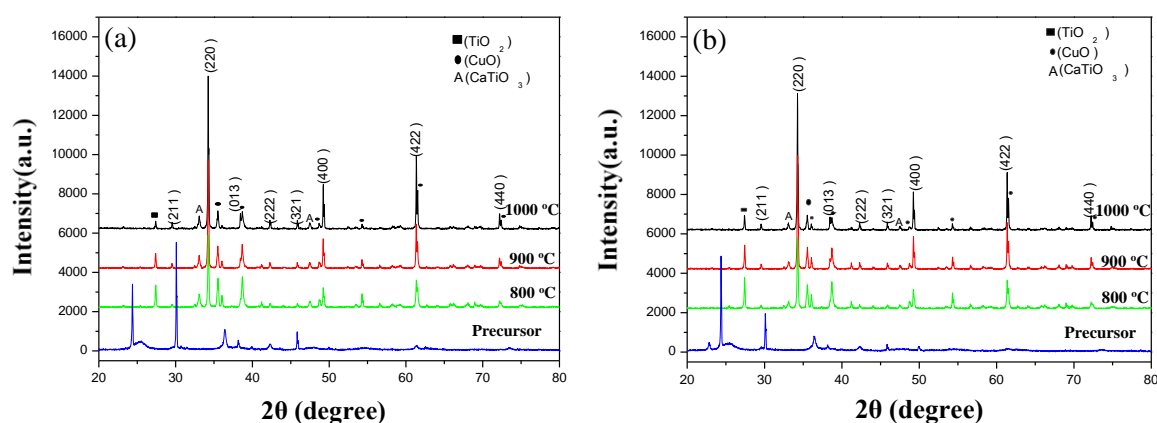


Figure 1 XRD patterns of CCTO base-powders prepared by hydrothermal process at (a) 150°C/8h and (b) 200°C/8h, respectively. All powders calcined in air for 8 h at 800, 900 and 1000 °C.

Figure 1 shows XRD patterns of dried precursor, which prepared by hydrothermal process for 8 h at 150°C and 200°C, and powders after calcination in air at 800, 900 and 1000 °C for 8 h. For the powders calcined at 800-1000 °C, the main peaks of the sample are comparable to those of the

standard powder XRD pattern of CCTO in the JCPDS card No. 75-2188. In addition, the following phases of CaTiO_3 (JCPDS card no. 82-0228), CuO (JCPDS card no. 80-0076) and Anateses- TiO_2 (JCPDS card no. 87-0920) are also observed. It is suggested by Guilleemet-Fritsch et al.[19] that the pure CCTO phase is obtained only when the ratio of calcium, copper and titanium are close to the stoichiometric ones. The CaTiO_3 phase appears if an excess of titanium is present, and at the same time when the copper content slightly decreases. It is also suggested that the excess of titanium leads to the precipitation of CaTiO_3 , even if there is no excess of calcium [19]. Since both calcium and titanium form a second phase, copper is then in excess, with respect with the stoichiometry of CCTO. Hence, the precipitation of the copper oxide (CuO) is observed, beside the CCTO and CaTiO_3 phase.

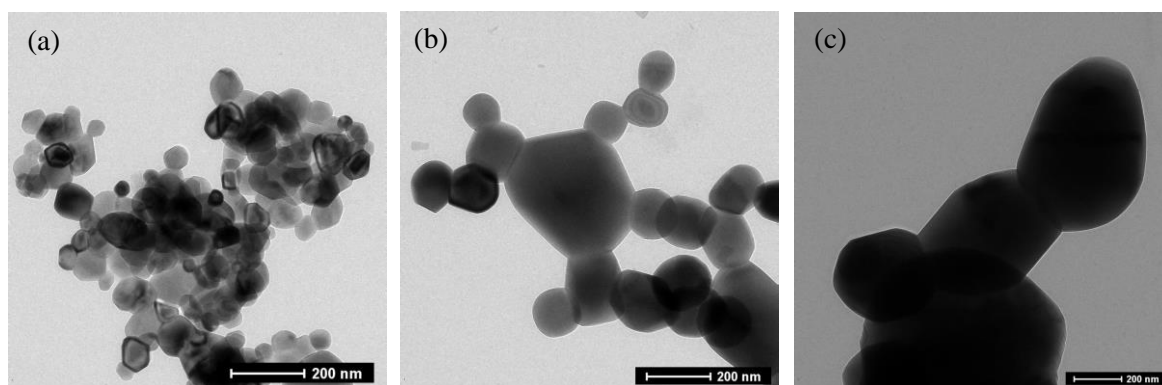


Figure 2 TEM images of CCTO powders, which prepared by hydrothermal process at 150 °C/8h calcined in air for 8 h at (a) 800, (b) 900 and (c) 1000 °C, respectively.

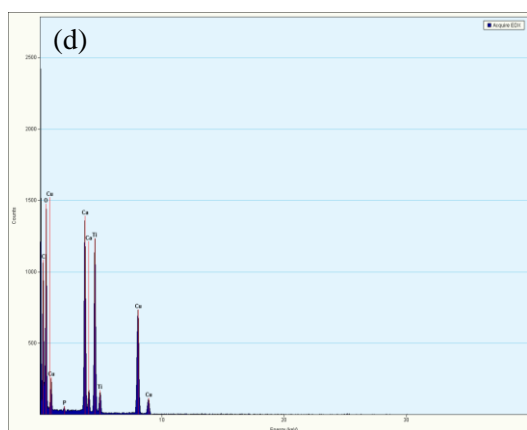
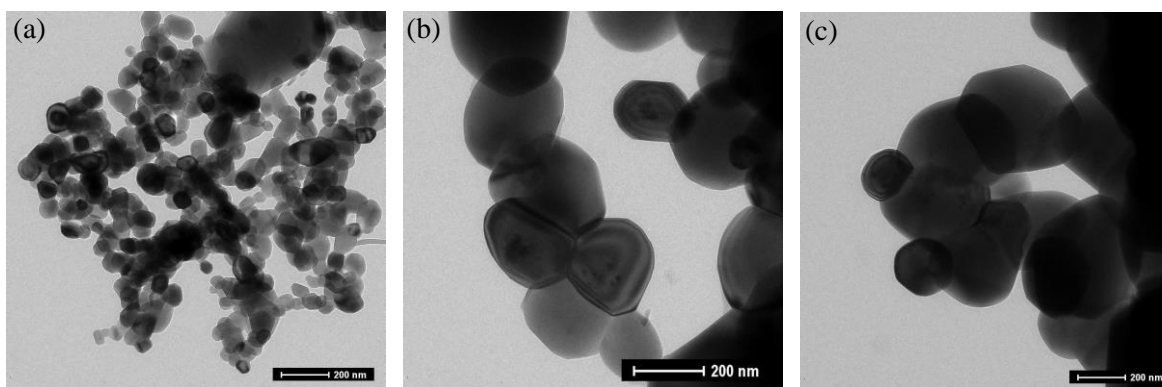


Figure 3 TEM images of CCTO powders, which prepared by hydrothermal process at 200 °C/8h calcined in air for 8 h at (a) 800, (b) 900 and (c) 1000 °C, respectively. (d) EDX spectrum of CCTO powders, which prepared by hydrothermal process at 200 °C/8h calcined in air for 8 h at 1000 °C.

Figure 2-3 shows TEM images of the calcined CCTO base-powders. It is clearly seen from the TEM bright-field images that both powder samples consist of nanocrystalline CCTO particles, whose size increases with increasing calcination temperature. The CCTO powders (Figure 2), which prepared by hydrothermal process for 8 h at 150°C, calcined at 800, 900 and 1000 °C contains nanoparticles of 116.96 ± 10 , 258.93 ± 7 and 565.65 ± 31 nm, respectively. The CCTO powders (Figure 3), which prepared by hydrothermal process for 8 h at 200°C, calcined at 800, 900 and 1000 °C contains nanoparticles of 105.42 ± 6 , 206.39 ± 6 and 386.45 ± 15 nm, respectively. The observed particle sizes are in good agreement. Moreover, EDX spectra of the CCTO powders (Figure 3(d)), which prepared by hydrothermal process for 8 h at 200°C, calcined at 1000 °C show the presence of Ca, Cu and Ti. The EDX result is in good agreement with the results obtained from the XRD.

4. Conclusions

CCTO nano-powders have been synthesized by modified Sol-gel method with hydrothermal process. The synthesized powders were characterized by XRD, TEM and EDX. This work demonstrates that the hydrothermal route using a simple egg white solution can be used for preparation of giant dielectric CCTO powders. We believe that the current simple, cost effective and environmental friendly synthesis method using egg white solution can be extended to prepare fine particles of other interesting oxide or complex oxide materials.

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References

- [1] Ramirez A P, Subramanian M A, Gardel M, Blumberg G, Li D, Vogt T and Shapiro S M 2000 *Solid State Commun.* **115** 217
- [2] Subramanian M A, Dong L, Duan N, Reisner B A and Sleight A W 2000 *J. Solid State Chem.* **151** 323
- [3] Homes C C, Vogt T, Shapiro S M, Wakimoto S and Ramirez A P 2001 *Science* **293** 673
- [4] Chung S, Kim I and Kang S 2006 *Nat. Mater.* **3** 774
- [5] Cushing B L, Kolesnichenko V L and O'Connor C J 2004 *Chem. Rev.* **104** 3893
- [6] Jha P and Arora Pand Ganguli A K 2003 *Mater. Lett.* **57** 2443
- [7] Jin S, Xia H, Zhang Y, Guo J and Xu J 2007 *Mater. Lett.* **61** 1404
- [8] Liu J, Sui Y, Duan C, Mei W N, Smith R W and Hardy J R 2006 *Chem. Mater.* **18** 3878.
- [9] Masingboon C, Maensiri S, Yamwong T, Anderson P L and Seraphin S 2008 *Appl. Phys. A* **91** 87
- [10] Masingboon C, Prasit T, Maensiri S, Yamwong T and Seraphin S 2008 *Mater. Chem. Phys.* **109** 262
- [11] Vadehra D V and Nath K R 1973 *CRC Crit. Rev. Food. Technol.* **4** 193
- [12] Mine Y 1995 *Trends in Food Sci. Technol.* **6** 225
- [13] Lyckfeldt O, Brandt J and Lesca S 2000 *J. Eur. Ceram. Soc.* **20** 2551
- [14] Dhara S and Bhargava P 2001 *J. Am. Ceram. Soc.* **84** 3045
- [15] Dhara S and Bhargava P 2003 *J. Am. Ceram. Soc.* **86** 1645
- [16] Dhara S 2005 *J. Am. Ceram. Soc.* **88** 2003
- [17] Maensiri S, Masingboon C, Laokul P, Jareonboon W, Promarak V, Anderson P L and Seraphin S 2007 *Cryst. Growth Des.* **7** 950
- [18] Maensiri S, Masingboon C, Boonchom B and Seraphin S 2006 *Scripta Mater.* **56** 797
- [19] Guillemet-Fritsch S, Lebey T, Boulos M and Durand B 2006 *J. Eur. Ceram. Soc.* **26** 1245