



## **Phase Formation and Morphological Features of Calcium Copper Titanate by Modified Solid State Process**

**ASHNARAYAN SAH,<sup>1</sup> SOUMYA MUKHERJEE,<sup>2\*</sup>  
MOHAMMED SHAHNAWAZ<sup>3</sup> and SATH BANERJEE<sup>1</sup>**

<sup>1</sup>Department of Metallurgical and Materials Engineering, Jadavpur University,  
Kolkata - 700032, West Bengal, India.

<sup>2</sup>Department of Metallurgical and Materials Engineering, Kazi Nazrul University,  
Asansol - 713340, West Bengal, India.

<sup>3</sup>Department of Electronics and Telecommunication Engineering, Heritage Institute of Technology,  
Kolkata - 700107, West Bengal, India.

### **Abstract**

Perovskite calcium copper titanate possesses giant dielectric constant making it suitable candidate for possible applications in microelectronic components, advanced transistors, energy storage capacitors. Generally, this grade of material is synthesized by chemical route to improve homogeneity, controlled size growth for enhanced properties. In the present research, simple synthesis process was adopted using precursors of high purity oxides like Calcium carbonate, titania, Copper oxide without any use of complicated synthesis routes and costly chemical precursors. Molar ratio of oxides used was about 1:3:4 with mechano-chemical activation in agate mortar for 20, 25 and 30 hours respectively in dry condition. After milling, powders obtained were made to undergo annealing at fixed temperature of 900 °C for 26 hours soaking period. Phase analysis was carried to determine the phase along with crystallite size calculation. Bonding information of the synthesized sample was analyzed to obtain the M-O coordination and vibration - stretching analysis of the bonds. Morphological features were also noted using FESEM (Field Emission Scanning Electron Microscopy) for understanding grains and granular boundaries. Both FTIR (Fourier Transform Infra Red Spectroscopy) and XRD (X - Ray Diffractogram) analyses confirm the compound formation in terms of molecular structure responsible to obtain the proper phase.



### **Article History**

Received: 07 March 2019

Accepted: 12 April 2019

### **Keywords:**

Calcium Copper  
FTIR;  
Morphology;  
Titanate;  
XRD.

**CONTACT** Soumya Mukherjee ✉ [smmukherjee3@gmail.com](mailto:smmukherjee3@gmail.com) 📍 Department of Metallurgical and Materials Engineering, Kazi Nazrul University, Asansol - 713340, West Bengal, India.



© 2019 The Author(s). Published by Oriental Scientific Publishing Company

This is an Open Access article licensed under a Creative Commons Attribution-NonCommercial-ShareAlike 4.0 International License  
Doi: <http://dx.doi.org/10.13005/msri/160105>

## Introduction

Perovskite having  $ABO_3$  formula is a versatile ceramic structure with applications as semiconductor, catalyst, sensors, memory devices and others. Calcium Copper titanate is a modified perovskite structure material (also referred as aurivillius structure) having applications in the above mentioned domain in addition to application as magnetic materials after doping. The parent structure of perovskite is modified due to superimposition of body centered ordering of Ca, Cu along with prominent tilting of Titanium centred octahedral.<sup>1</sup> The ceramic is also known as colossal relative permeability due to high dielectric constant of about  $10^4$ . High dielectric constant also influences the volume of the electrical devices in applications. The origin for large dielectric constant is still under investigations. It has been reported in research studies that  $TiO_2$  and perovskite oxide lose oxygen during high temperature sintering while reoxidation occurs during cooling. During cooling re-oxidation occurs at the surface layers and at the grain boundaries as a cause of rapidly falling temperature and availability of short time. As a consequence, insulating layers are formed at surface and grain boundaries while the bulk grain remains semiconducting in nature.<sup>2</sup> The giant dielectric constant of the material is found to be almost independent of temperature in the range 100 - 400K. Chung *et al.* observed non-linear dielectric coefficient in the ceramic perovskite to be about 900 quite higher than ZnO which is used as classical varistor. Calcium copper titanate also exhibits high dielectric loss limiting its application in the domain of devices. This hindrance of the material is made to overcome by undergoing substitution at proper site. The scientific reason behind such suppression of dielectric loss may be due to retardation of barrier layer formation at grain boundaries. Material is noted to follow non-ohmic characteristics at such conditions.<sup>3</sup> The mentioned perovskite is observed to be synthesized by sol-gel process<sup>1,4,5,6</sup> mechanochemical process<sup>7,8</sup> solid state processing<sup>9,10</sup> hydrothermal<sup>11</sup> and others. Some other popular methods of synthesis are combustion synthesis method or self propagating high temperature synthesis, sonochemical assisted and co-precipitation technique. Calcium copper titanate is noted to be applied for capacitors, antennas, microwave devices and sensors. Porous polycrystalline nanostructure is found to be quite

beneficial for sensor applications. One of the significant properties of Calcium Copper titanate based sensor is the ability to detect, monitor gases and toxic species without decomposition or changes in their molecular arrangement.<sup>12</sup> In the present article, modified solid state process is adopted to synthesize utilizing proper molar ratio. The synthesized material is analyzed for phase determination by XRD, stretching bonding and M - O co-ordinations by FTIR analysis while morphology is studied by FESEM.

## Experimental Procedure

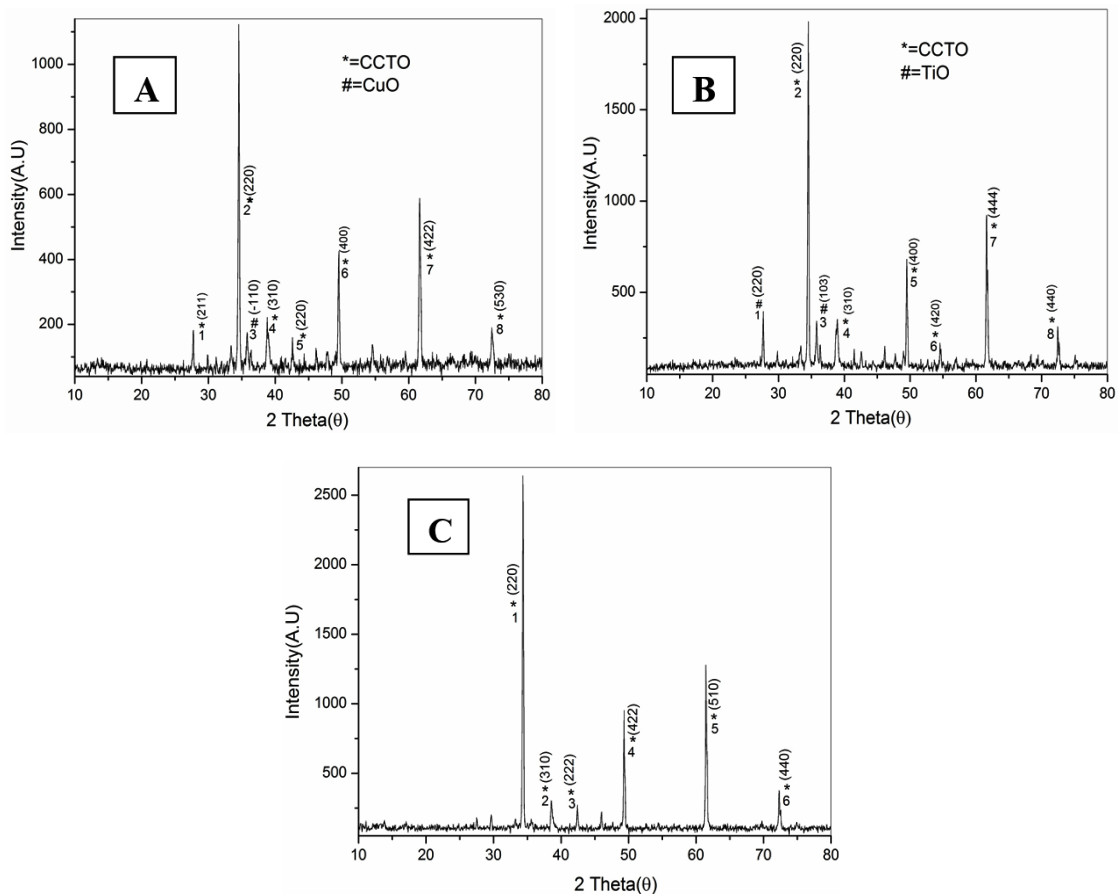
In the synthesis of perovskite (Aurivillius) Calcium Copper Titanate, Calcium Carbonate, Cupric Oxide and titania (AR Grade, Merck India) were selected as precursors. All the powders were taken in a proper stoichiometric ratio of  $CaCO_3:CuO:TiO_2$  as 1:3:4 and made to undergo milling activation in arid condition. Milling activation was carried for 20 hours, 25 hours and 30 hours respectively followed by annealing at 900 °C for 26 hours. Phase analysis was carried by XRD (Rigaku, Ultima III,  $Cu K\alpha 1.54\text{\AA}$ , 50KV, 40mA) for synthesized powder samples. Scan range for the sample was 10 to 90° with scan rate of 5°/min along with determination of crystallite size and planes of orientation. Morphology of the sample was studied using FESEM, Hitachi S-4800 in powder state. The sample was placed on carbon tape with conducting coating over it to prevent static charge accumulation for better resolution and imaging. Bonding and metal co-ordination analysis was carried for powder samples by FTIR analysis (IR Prestige - 21, Shimadzu) after mixing it with KBr for pellet preparation. Pellets were prepared for FTIR analysis by undergoing pressing under pressure of 6t /  $cm^2$  in hydraulic press.

## Results and Discussions

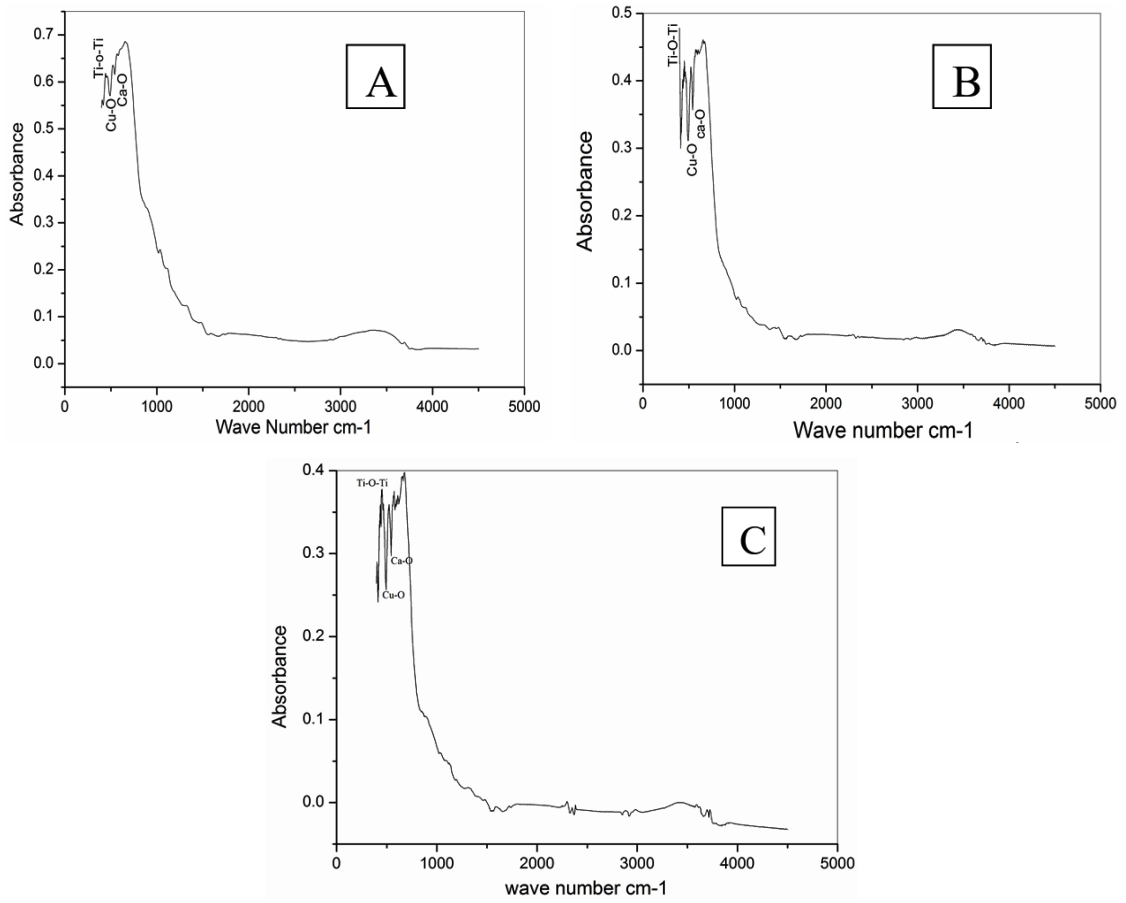
Above figures execute XRD of the synthesized samples. In all cases sharp intense peaks are noted without any convolution or peak splitting. Intense sharp peaks are indications of crystalline nature of the synthesized materials. There is no trace of diffuse peaks or humps in the material matrix. The XRD patterns confirm the single phase structure. All three samples are made to undergo three different milling time variations but same soaking period at constant temperature of about 900 °C is maintained. At this fixed composition sharp peaks are noted

within the  $2\theta$  scan range at  $34.55^\circ$ ,  $38.8^\circ$ ,  $49.50^\circ$  and  $61.65^\circ$  respectively. Small peaks can also be observed about  $2\theta$  values of  $27.75^\circ$ ,  $35.80^\circ$ ,  $42.60^\circ$  and  $75.30^\circ$  respectively. The peaks are indexed as per the (hkl) planes reported in JCPDS file (75 - 1149). Appearance of peaks corresponding to CCTO phase indicates formation of single phase compound. The above XRD peaks are in correspondence with findings by N. Tripathy *et al.*,<sup>13</sup> R. E. - González *et al.*<sup>7</sup> where synthesis is carried by solid state routes followed by sputtering and mechanochemical process. Some minor impurities like copper oxide is noted at about  $35.88^\circ$  after 20 hours milling, 26 hours annealing at  $900^\circ\text{C}$ . Similarly for 25 hours milling minor peaks of impure oxides of Ti is noted respectively. For 30 hours milling, sample is noted to be the most pure without any formation of other metal oxides instead of desired perovskite

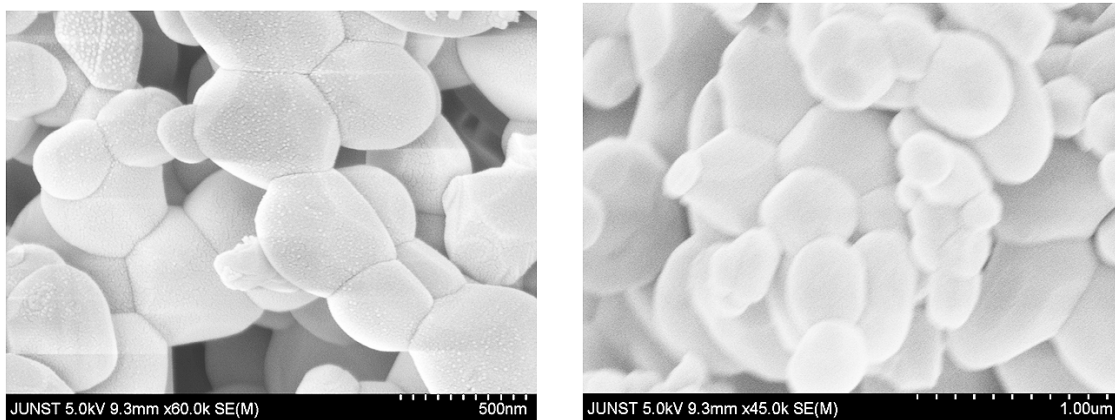
compound. Crystallite size obtained by Scherrers formula is noted to be about 84.47 nm, 82.66 nm for 20 hrs, 30 hours sample and around 122 nm for 25 hours mill sample. The sudden change may be due to formation of TiO as noted from XRD analysis. TiO is metastable in nature formed as intermediate during milling which later converts to perovskite after milling reaction followed by annealing. Due to development of minor secondary phase, nucleation, growth of phases undergo metastabilization and hence such possible drastic increase in crystallite size happens. Moreover, 30 hours milling followed by 26 hours heat treatment leads to pure calcium copper titanate without any presence of other oxides as noted from XRD analysis with reference to JCPDS of Titanium oxide (81 - 1286), Copper Oxide (80 - 1917) used as precursors.



**Fig. 1: XRD of Calcium Copper Titanate synthesized after 20hrs milling (A), 25hrs milling (B) and 30 hours milling (C) activation after soaking at  $900^\circ\text{C}$  for 26 hours**



**Fig. 2: FTIR of Calcium Copper Titanate synthesized after 20hrs milling (A), 25hrs milling (B) and 30 hours milling (C) activation after soaking at 900°C for 26 hours**



**Fig. 3: FESEM morphology of Calcium Copper Titanate formed after 30 hours milling activation after soaking at 900°C for 26 hours**

Figure 2 represents FTIR spectra of the synthesized samples. Major peaks of vibration for M-O coordinations are noted within  $1000\text{ cm}^{-1}$  indicating the successful synthesis of inorganic structure. Absorption peaks are noted at about  $530\text{ cm}^{-1}$ ,  $450\text{ cm}^{-1}$ ,  $500\text{ cm}^{-1}$  mainly. The above absorptions are corresponding to Ca-O, vibration mode of the O-Ti and bending of Cu-O bonds present in the synthesized samples. The experimental characteristics bands are noted within the scan range of  $380\text{ cm}^{-1}$  to  $700\text{ cm}^{-1}$  encompassing the mixture of  $\text{CuO}_4$  and  $\text{TiO}_6$  groups. The above experimental bands and peaks indicate presence of CCTO as sample validating the XRD phase determination. The above experimental findings are in correspondence with the results of P. Thirumanathan *et al* who have studied optical, electrical properties of sol-gel synthesized calcium copper titanate powders.<sup>5</sup> Almeida observed three main absorptions at  $561$ ,  $516$ ,  $437\text{ cm}^{-1}$  and Ti-O vibrations at about  $653\text{-}550\text{ cm}^{-1}$  while for Ti-O-Ti it is about  $495\text{-}436\text{ cm}^{-1}$ .<sup>14</sup> Thus above findings are noted to be in correspondence with research article by Almeida *et.al* which focussed on mechanochemical alloying of Calcium copper titanate.

FESEM morphology of the best synthesized conditioned sample is noted after confirming the s from phase analysis and FTIR analysis on bonding, M-O information. From XRD analysis it is concluded that 30 hours milling followed by 26 hours soaking period at  $900\text{ }^\circ\text{C}$  yields the most pure perovskite. Morphology of the synthesized sample at the above mentioned conditions exhibit proper granular formation with strong agglomeration tendency. Few minute pores are noted within the agglomerated

form. Strong interconnections among grains are noted. Grains are having polygonal shape with conchoidal fracture face at top while some are having spherical morphology. Individual grains are around  $500\text{nm}$  to about  $200\text{nm}$ ,  $100\text{nm}$  in some cases. Grains are found to get interlocked in a particular fashion leading to floral one with conchoidal fracture granules around the central hub of the agglomerates. There is absence of any unwanted distortion observed in the matrix of the synthesized sample.

### Conclusions

Modified Solid State Process was utilized to prepare modified perovskite structure material Calcium Copper titanate. Crystallite size was noted to be about  $84.47\text{nm}$ ,  $82.66\text{nm}$  for 20 hrs, 30 hours sample and around  $122\text{ nm}$  for 25 hours mill sample. Bonding and stretching vibration analysis of M-O coordination were noted from FTIR analysis. FESEM analysis reveals the morphology to be granular in nature with strong agglomeration, minute porosity while grains were polygonal shape with conchoidal fracture.

### Acknowledgement

Corresponding would like to thank HOD, Department of Metallurgical & Materials Engineering for providing XRD facilities to study phase formation. Author also acknowledges Prof (Dr.) Kalyan Kumar Chappopadhyay, Director, SMSNT, Jadavpur Univerasity for providing FTIR and FESEM facilities.

### Funding Sources

There is no funding sources for carrying the experiment in the laboratory.

### References

1. Jesurani S., Kanagesan S., Velmurugan R., Kalaivani T. Phase formation and high dielectric constant of calcium copper titanate using sol-gel route. *J. Mater. Sc. Electron.* 2012;23:668-674.
2. Rai A. K., Singh N. K., Lee S. K., Mandal K. D., Kumar D., Om Parkash. Dielectric properties of iron doped calcium copper titanate,  $\text{CaCu}_2\text{9Fe0.1Ti}_4\text{O}_{12}$ . *J. Alloy. Compd.* 2011; 509:8901-8906.
3. Chung S. Y., Kim Il. D., Kang S. J. L. Strong nonlinear current-voltage behaviour in perovskite derivative calcium copper titanate. *Nat. Mater.* 2004;3:774-778.
4. Xu D., He K., Chen B., Xu Ch., Mua Sh., Lei. Jiao, Xi. Sun, Yang Y. Microstructure and electric characteristics of  $\text{AETiO}_3$  (AE=Mg, Ca, Sr) doped  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  thin films prepared by the sol-gel method. *PRO. NAT. SCI-MATER.* 2015;25L:399-404.
5. Thiruramanathan P., Marikani A., Madhavan D. Optical and Electrical Properties of Sol-

- Gel Synthesized Calcium Copper Titanate Nanopowders. *Int. J. Chem. Tech. Res.* 2015;8 No. 3:981-987.
6. Jesurani S., Kanagesan S., Velmurugan R., Thirupathi C., Sivakumar M., Kalaivani T. Nanoparticles of the giant dielectric material, Calcium Copper titanate from a Sol-gel technique. *Mater. Lett.* 2011;65:3305-3308.
  7. González R. E., Vega E., Tamayo R., Criado J. M., Díaz M. J. Mechanical Processing of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  with Giant Dielectric Properties. *Mater. Manuf. Processes.* 2014;29:1179-1183.
  8. Alizadeha M., Ardakani H. A., Amini R., Ghazanfari M. R., Ghaffari M. Structural and phase evolution in mechanically alloyed calcium copper titanate dielectrics. *Ceram. Int.* 2013;39:3307-3312.
  9. A.P. Ramirez, M.A. Subramanian, M. Gardel, G. Blumberg, D. Li, T. Vogt, S.M. Shapiro, Giant dielectric constant response in a copper-titanate. *Solid. State. Commun.* 2000;115: 217–220.
  10. Yu, Tim & Liu, Hanxing & Hao, Hua & Guo, Liling & Jin, Chengjun & Yu, Zhiyong & Cao, Minghe. (2007). Grain Size Dependence of Relaxor Behavior in  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  Ceramics. *Applied Physics Letters.* 91. 222911-222911. 10.1063/1.2820446.11.
  11. Oliveira L. H., de Moura A. P., Mazzo T. M., Ramírez M. A., Cavalcante L. S., Antonio S. G., Avansi W., Mastelaro V. R., Longo E., Varela J. A. Structural refinement and photoluminescence properties of irregular cube-like  $(\text{Ca}_{1-x}\text{Cu}_x)\text{TiO}_3$  microcrystals synthesized by the microwave hydrothermal method. *Mater. Chem. Phys.* 2012;136:130-139.
  12. Ahmadipour M., Ain M. F., Ahmad Z. A. A Short Review on Copper Calcium Titanate (CCTO) Electroceramic: Synthesis, Dielectric Properties, Film Deposition and Sensing Application. *Nano-Micro Lett.* 2016;8:291-311.
  13. Tripathy N., Das K. C., Ghosh S. P., Bose G., Kar J. P. Fabrication of high-k dielectric Calcium Copper Titanate (CCTO) target by solid state route. *IOP Conf. Series: Materials Science and Engineering.* 115 (2016) 012022 doi:10.1088/1757-899X/115/1/012022
  14. Almeida A. F. L., De Oliveira R. S., Go'és J. C., Sasaki J. M., Souza Filho A. G., Mendes Filho J., Sombra A.S.B. Structural properties of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  obtained by mechanical alloying. *Mater. Sci. and Engg. B.* 2002;96: 275-283.