

Research Article

Nanosize $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ Green Synthesis and Characterization of a Precursor Oxalate Obtained from *Averrhoa carambola* Fruit Juice and Its Thermal Decomposition to the Perovskite

Ekane Peter Etape ¹, Josepha Foba-Tendo,¹ Beckley Victorine Namondo,¹ Divine Mbom Yufanyi,² Hypolite Mathias Kamta Tedjiekeng,³ Roussin Lontio Fomekonga,³ and Lambi John Ngolui³

¹Department of Chemistry, Faculty of Science, University of Buea, P.O. Box 63, Buea, Cameroon

²Department of Fundamental Science, HTTTC, University of Bamenda, P.O. Box 39 Bambili, Cameroon

³Department of Chemistry, E.N.S. Yaoundé, BP 47 Yaoundé, Cameroon

Correspondence should be addressed to Ekane Peter Etape; ekane20022001@yahoo.fr

Received 25 August 2020; Revised 17 September 2020; Accepted 22 September 2020; Published 8 October 2020

Academic Editor: Marcela Elisabeta Barbinta-Patrascu

Copyright © 2020 Ekane Peter Etape et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Improving on the very high temperatures used in solid-state synthesis routes to prepare CCTO ignited the idea of using oxalate routes which make use of organic solvents in the synthesis of CCTOX as oxalate intermediates to the decomposition product, CCTO. The use of commercial oxalic acids and oxalate has not only recorded a solubility problem which reflects on the size, shape, homogeneity, and morphology of the final product but also has an environmental impact originating from the solvents used. Both the composition and morphology of these inhomogeneities play a role in the behaviour of the final product, pointing out the need to assess the dependence of size, shape, homogeneity, and morphology and the material performance on the sample synthesis history. In this study, nanosized particles of calcium copper titanium oxide, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO), were successfully synthesized by pyrolysis of the corresponding heterometal oxalate precursors obtained via coprecipitation using the edible carambola fruit juice as a precipitating agent and investigated in detail. The precursors were characterized, and the results revealed the formation of a single molecular precursor represented by the formula $\text{CaCu}_3(\text{TiO})_4(\text{C}_2\text{O}_4)_8 \cdot 9\text{H}_2\text{O}$ (CCTOX). The decomposition products, obtained via calcination in air, were subsequently subjected to thermal treatments at different temperatures for 4 hours. The morphology and microstructure were characterized, and analysis showed the formation of a single phase, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) with CuO and CaTiO_3 as impurity. It was observed from microscopy that the samples obtained from sintering at 600°C for four hours had discrete particles with regular morphology, limited size distribution, high degree of homogeneity, and multiple dimensions ranging between 10 and 35 nm and showed some degree of ellipticity in shape. Increasing the sintering temperature from 600°C to 700°C and 800°C increased the grain growth in the ceramic as well as the densification. The method makes advantage of the fact that oxalate precursors decomposed at relatively lower temperatures and the fact that the oxalate in the juice is in the solution which downplays both the solubility and environmental pollution problems since no additional solvents are used.

1. Introduction

Miniaturization of electronic devices with giant dielectric constants is a challenge in microelectronics. Oxides of the type $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) have received research interest because of their very high dielectric constant at room tem-

perature, which is around 10^4 to 10^5 at 1 kHz and good temperature stability in a wide temperature range from 100 to 600 K [1]. The cause of this exceptionally high dielectric constant is still debatable, though it has been attributed to grain boundary capacitance and extrinsic defects rather than to the intrinsic properties that result from the crystalline

structure of the material [2]. This dielectric material has been shown in multifunctional fields, such as electroceramic, electronic, and microwave devices such as capacitors, gas sensors, and varistors [3, 4].

CCTO has a perovskite-like structure derived from the cubic perovskite (ABO_3) by an octahedral tilt distortion caused by size mismatch and the nature of the A-site. The size difference between the Ca^{2+} and Cu^{2+} ions causes the TiO_6 octahedral to produce a structure where three-quarters of the sites have square-planar coordination and are occupied by Jahn–Teller distorted Cu^{2+} ions [1]. The synthesis methods has control over the particle size, phase purity, and morphology which themselves have a great deal to contribute to material properties and applications, and various methods for the synthesis of CCTO have been reported. The conventional solid-state reaction between stoichiometric starting materials of CaCO_3 , TiO_2 , and CuO followed by calcination at high temperatures (1000–1050°C) for prolonged periods (24–48 hours) has widely been used for synthesizing CCTO [1, 5]. This method is very cumbersome with the final product not only containing impurities (secondary phases and unreacted components) but also poor powder characteristics, represented by a coarse particle size, wide particle size distribution, irregular particle morphology, and a high degree of inhomogeneity [6].

Other methods used to synthesize CCTO in literature include microwave heating [7], sol-gel method [3, 8], wet-chemical method [9], pyrolysis [9], coprecipitation [10], and polymeric precursor route [11]. Pyrolysis has the disadvantage of involving the handling of chemicals in a glove box and refluxing solutions. The sol-gel process uses metal alkoxides as the starting materials, which are costly and extremely sensitive to the atmospheric conditions such as moisture, light, and heat. In contrast, wet chemistry methods afford intimate and homogeneous mixing of the metal ions in stoichiometric ratios at the atomic scale. Pure samples at the nanometer scale could be obtained at lower temperatures and shorter reaction times than that resulting from solid-state reactions. CCTO has also been obtained by the pyrolysis of coprecipitated oxalate at high temperatures (>950°C) for 10 hours. The CCTO obtained had $\text{CaTiO}_3 + \text{CuO}$ as the impurity phase [12]. The phase purity was only achieved after sintering the powder at 1050°C. It has been observed that the physical properties such as particle size and shape as well as the dielectric properties highly depend on the synthesis technique. The best dielectric properties were shown by the ceramics prepared via the solid-state route despite the high temperature used, while using wet chemistry method is a better approach to obtain a homogeneous and controlled microstructure. A new trend in this area should be in the direction of finding new synthesis methods able to give a homogenous micro- or nanostructure. Such techniques could help reduce the synthesis temperature and achieve high permittivity.

We are reporting an environmentally friendly, facile, cost-effective, and green synthesis method for the synthesis of calcium copper titanate oxalate precursor and its subsequent thermal decomposition at relatively low temperatures and sintering time to CCTO. We use a naturally available

resource (*Averrhoa carambola* L. fruit juice) rather than the commercial sources for the synthesis of metal oxalates. The use of this natural renewable resource is of environmental significance and, in the case of free oxalic acid rich fruits (e.g., *Averrhoa carambola* L.), could result in a significant reduction in the level of the free acid, thus adding value to the elimination of toxic components through reaction with metal ions. This could also open up the possibility of high value exploitation of spoiled fruits.

Averrhoa carambola, known as carambola or star fruit, is an attractive, exotic, tropical, and shrub-like ornamental tree of the *Oxalidaceae* family [13]. It is an excellent source of oxalic acid, with oxalic acid contents that can be as high as 1 wt. % of wet mass (representing about 74% of the total acid content depending on the level of maturity of the fruits) [14].

In this paper, we present a facile and green approach for the synthesis of the mixed metal copper titanate oxalate precursor. Our approach is based on coprecipitation of the mixed metal ion solution and the fruit juice extract without the use of hazardous organic compounds or surfactants.

2. Experimental

2.1. Chemicals. Titanium trichloride (20% in 3% hydrochloric acid) (Alfa Aesar, Germany), calcium chloride (Merck), copper chloride (Fluka), and lanthanum trichloride (Merck) were of analytical grade and were used without further purification. HPLC grade fruit juice was also used.

2.2. Processing of the Fruit Juice. Ripe carambola fruits were harvested, washed under running tap water, and crushed in a blender. The juice was extracted by squeezing through cheese cloth. The collected juice was centrifuged for 20 mins at 3000 rpm, the supernatant was filtered, and the filtrate was collected which was previously characterized [15] and was kept in a freezer for further use.

2.3. Synthesis of the Oxalate Precursor. A solution (0.06 M) of calcium copper titanium composite metal chloride ion was prepared by dissolving the various metal ion chlorides in distilled water. The chlorides were divided into two different solutions. The first one contained stoichiometric amount of calcium chloride and copper (ii) chloride (hydrate) in 200 mL of distilled water, and the second contained stoichiometric amounts of TiCl_3 . This procedure allows obtaining two limpid solutions without the apparition of either a precipitate or gel. 100 mL of the juice extract was poured into a 250 mL round bottom flask immersed into a water bath maintained at 80°C. 50 mL, from each of the chloride solutions, was simultaneously added onto the juice while stirring. The mixture was further stirred for 1 hour. The slurry was allowed to cool at room temperature then aged for 8 hours. The precipitate obtained was filtered, washed several times with distilled water, then ethanol, and oven dried at 100°C for 1 hour.

2.4. Thermal Decomposition of the Complexes. A sample of the dry precursor (0.5 g) was ground and placed in a ceramic crucible, and the crucible placed in the furnace systematically heated to 550°C where a constancy of mass was observed. On

the other hand, the crucible was placed in the furnace that had been preheated to the desired sintering temperature of 600°C, 700°C, and 800°C and sintered in air continued for 4 h. The sample in each situation was allowed to cool down at room temperature in the furnace. The residues for systematic and isothermal decomposition, respectively, obtained were weighed and kept for further analysis. They represent, respectively, 48.1% and 45.56% of the precursors.

2.5. Characterization Techniques. FT-IR spectra were recorded from 4000 to 400 cm^{-1} on a PerkinElmer Spectrum on two universal attenuated total reflectance Fourier-transform infrared (UATR-FT-IR) spectrometers. Thermogravimetric analysis (TGA) was obtained using a Pyris 6 PerkinElmer TGA 4000 thermal analyser. The TGA analysis was conducted between 30°C and 900°C under nitrogen atmosphere at a flow rate of 20 mL/min and a temperature ramp of 10°C/min. The XRD diffractograms of the precursors and the decomposition products were recorded on a Bruker D8 Advance X-ray diffractometer using a Cu $K\alpha$ radiation source ($\lambda = 0.15406$ nm, 40 kV, and 40 mA). Scans were taken over the 2θ range from 10° to 100° in steps of 0.01° at room temperature in open quartz sample holders. The phase was identified with the help of the Bruker DIFFRAC plus evaluation software in combination with the ICDD powder diffraction database (International Centre for Diffraction Data). The surface morphology of samples was examined by a scanning electron microscope (SEM) (JEOL JSM-5600 or TESCAN VEGA III XMU Q150 TE). Prior to examination, samples were prepared by mounting about 0.5 mg of the powder onto a 5 mm \times 5 mm double-sided carbon tape, on an aluminum stub. The powder was then sputter-coated for 40 seconds with carbon gold. Using an EDAX analyzer (Thermo Electron Noran System (NSS-300) EDS) attached to the SEM analyzer could also detect the oxygen concentration. The morphologies of the samples were confirmed by transmission electron microscopy (TEM, Leo922 Model from Zeiss) at an accelerating voltage of 120 kV. TEM samples were prepared by dropping a sonicated water dispersion of the powder samples on a carbon-coated copper grid.

3. Results and Discussion

3.1. Wet Chemical Analysis. The wet chemical analyses of the dried precipitate CCT-OX) gave Ca: 1.4 g; Cu: 7.01; TiO: 9.53; C_2O_4 : 26.54; and H_2O : 5.935% (by wt.) calculated for $\text{CaCu}_3(\text{TiO})_4(\text{C}_2\text{O}_4)_8 \cdot 9\text{H}_2\text{O}$, Ca: 2.96; Cu: 13.99, TiO: 18.95, C_2O_4 : 52.10; and H_2O : 11.99%.

3.2. Infrared Spectrum of the Complex Oxalate Precursor. The formation of a monophasic oxalate is confirmed by the FT-IR analysis shown in Figure 1. The infrared bands observed below 1700 cm^{-1} are assigned to the oxalate vibrational modes. The sharp intense peaks at 1620 cm^{-1} are attributed to the asymmetric stretching vibrations of the OCO group, while those around 1450–1300 cm^{-1} are attributed to the asymmetric (C=O) and symmetric (C-O) stretching vibrations in the OCO group. The sharp medium intense peaks at 826 cm^{-1} and 737 cm^{-1} indicate the bonding of metal oxygen (M-O)

(indicating the presence of Ca^{2+} , Cu^{2+} , and Ti^{3+} bonded to the oxalate ion) and are assigned to ($\nu_{\text{O}-\text{C}} = \text{o} + \delta \text{Cu}-\text{O}$) and ($\delta \text{Ti}-\text{O} + \nu_{\text{O}-\text{C}} = \text{o}$). Moreover, the absence of the free IR $\nu_{\text{C}=\text{O}}$ vibration expected at 1735–1705 cm^{-1} , suggests that the entire carboxylate group of the oxalate is engaged in the formation of the coordination compound. The broad absorption band in the 1750–1620 cm^{-1} region can be resolved into multiple peaks which are better discernible in the region 1450–1200 cm^{-1} (this arise from the mixed vibration). The absorption band occurring between 1650 cm^{-1} and 1850 cm^{-1} assigned to C=O stretching vibration. They have been attributed to the splitting observed due to different interactions in the crystal field. The strong IR bands occurring around 1500–1400 cm^{-1} and 1400–1300 cm^{-1} are assigned to asymmetric stretching (ν_{asCOO^-}) and symmetric (ν_{sCOO^-}) modes, respectively. These are associated with the stretching vibrations of the carboxylate (COO^-) group. The fact that there are four clearly decipherable components indicates the presence of oxalate with C_{2v}/C_2 point group symmetry, which is a direct evidence for the prevalence of bidentate oxalate ions. The bridging oxalate groups with the planar (D_{2h}) or twisted (D_{2d}) conformations show only two absorptions arising from the C-O stretching vibrations ($\nu_{\text{C}=\text{O}}$). On the other hand, the bidentate oxalate groups show four ν -type absorptions as can be expected from their C_{2v} symmetry. The oxalate like the malonate is a flexible and versatile ligand. The occurrence of two carboxylate groups in 1 or 2 positions allows this ligand to adopt simultaneously chelating bidentate and different carboxylate bridging modes through one or both carboxylate groups. The bisbidentate behaviour forbidden by steric reasons to malonate is signaling in the oxalate, and this dramatically affects the structure and properties of the oxalate complexes. The oxalate ligand occupies one or two coordination positions and neutralizes two positive charges of the metallic copper ion ($\text{Cu}(\text{II})$), allowing the possibility of the bisbidentation and/or the inclusion of other ligands in the coordination sphere of the metal.

3.3. Thermal Analysis. A verification of the thermal behaviour of CCT-OX was carried out by thermal analysis (TGA).

The TGA/DTG graph of the complex is shown in Figure 2, where four weight loss portions were observed. The complex decomposed to a residue of approximately 48.1% of the original weight (juice complex) at 600°C to a relatively stable intermediate which finally decomposed to the final product after sintering at the decomposition temperature for four hours. This final stage revealed a further weight loss of 2.54% which compares with 45.41% residue ($\text{CaCu}_3\text{Ti}_4\text{O}_{12}$) expected from the decomposition of $\text{CaCu}_3(\text{TiO})_4(\text{C}_2\text{O}_4)_8 \cdot 9\text{H}_2\text{O}$. This pattern agrees with some minute differences with that proposed in literature [15]. The first weight loss (18.1%) corresponds to the elimination of nine molecules of water and two molecules of carbon dioxide (18.4%) giving birth to $\text{CaCu}_3(\text{TiO})_4(\text{C}_2\text{O}_4)_5(\text{CO}_3)_3 \cdot \text{CO}_2$ which is believed to be an intermediate. Using commercial oxalic acid, this intermediate is obtained after two decomposition steps. The second weight loss (29.9%) is attributed to the elimination of seven molecules of carbon dioxide and five molecules of carbon monoxide which leads to the production

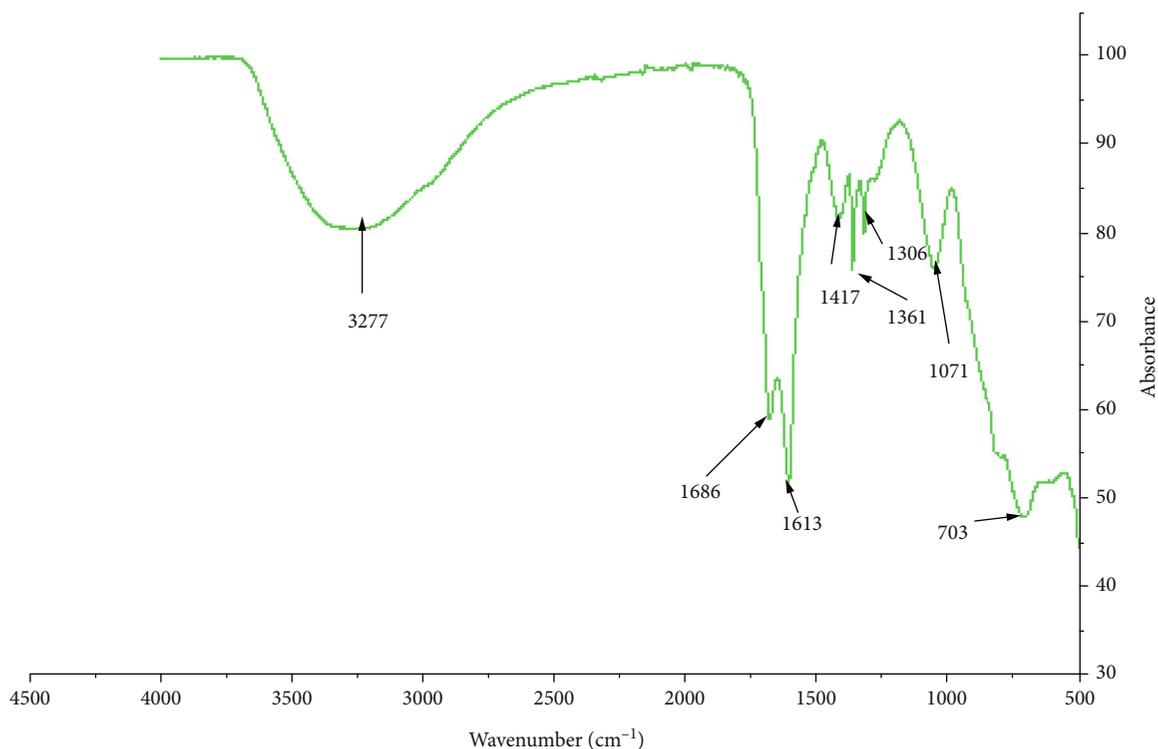


FIGURE 1: FT-IR spectrum for the as-prepared sample using the fruit juice of *Averrhoa carambola*.

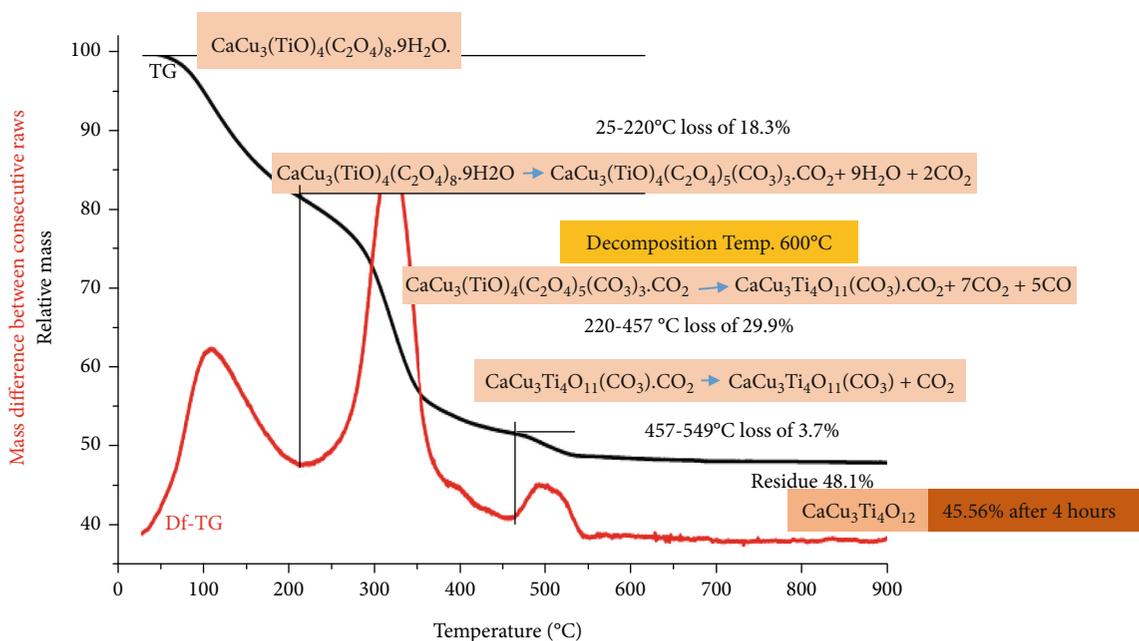


FIGURE 2: TGA and DTG graphics showing the decomposition for the as prepared precursor using *A. carambola* fruit juice.

of CaCu₃Ti₄O₁₁(CO₃)·CO₂ as the second intermediate. The next weight loss (3.7%) observed between 457°C and 549°C was attributed to the loss of one molecule of carbon dioxide (3.25%) resulting in the production of CaCu₃Ti₄O₁₁(CO₃) (48.1%). The final decomposition is observed only after sintering at the decomposition temperature (600°C) for four hours and with the elimination of one molecule of carbon

dioxide from CaCu₃Ti₄O₁₁(CO₃) leading to the final product CaCu₃Ti₄O₁₂ (45.56%). The third intermediate seems quite stable at 600°C. Increasing the sintering temperature from 600 to 700°C did not lead to any further weight loss.

3.4. Powder X-Ray Diffraction Analysis. The powder X-ray diffraction data for the precursor (CCT-OX) shown in

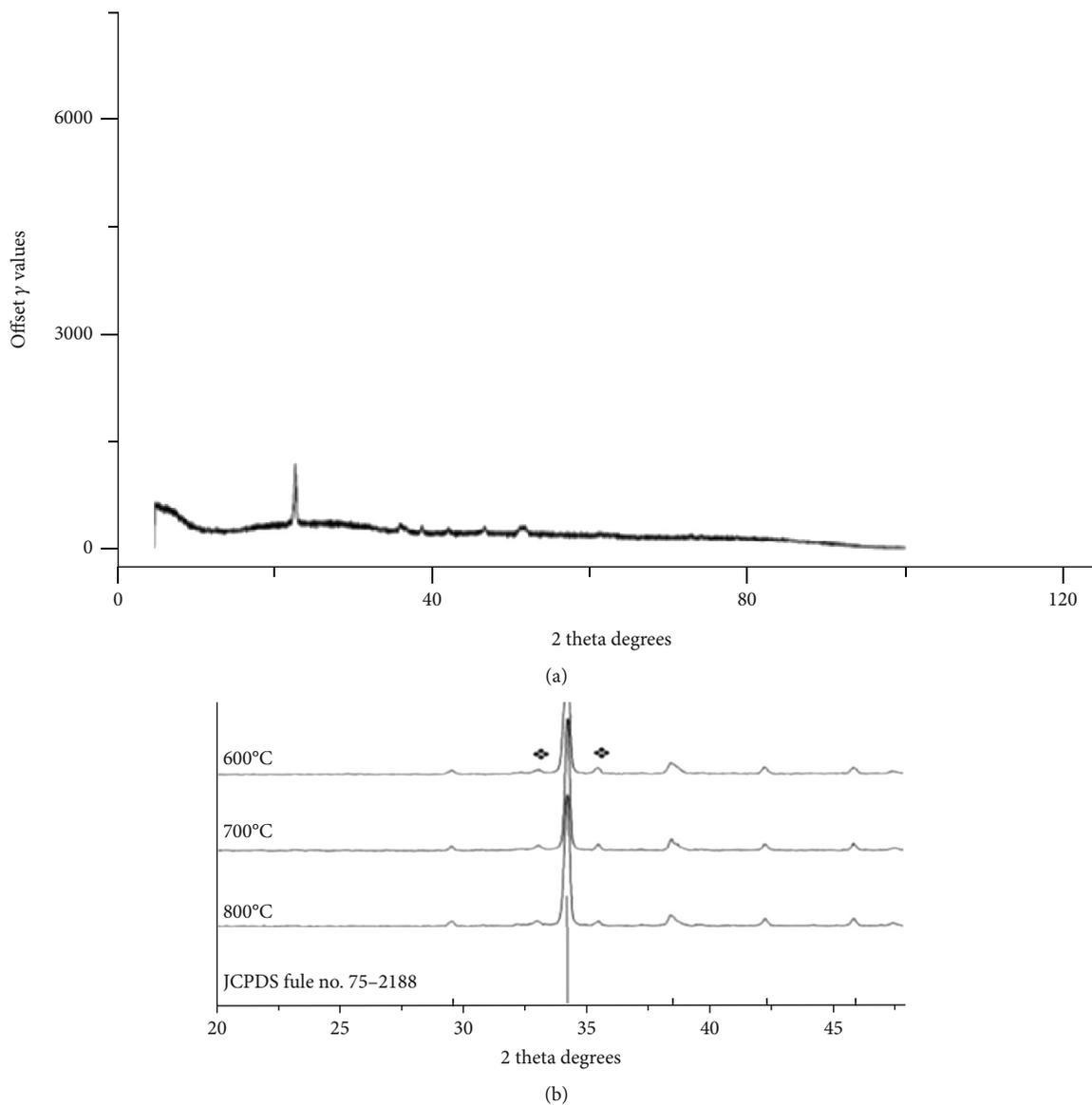


FIGURE 3: (a) PXRD for the as-prepared precursor (CCTOX) using *A. carambola* fruit juice. (b) PXRD for the decomposition product at 600°C, 700°C, and 800°C for 4 hours.

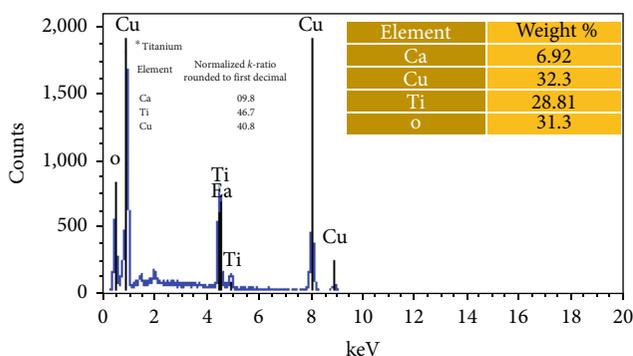


FIGURE 4: EDAX elemental composition for the decomposed product (CCTO).

Figure 3(a), were compared with those of the oxalates of the individual metal ions available from the International Centre for Diffraction Data (ICDD), and they showed a difference in the Bragg reflections and relative intensities. The strong lines for copper oxalate hydrate (1CDD: 00-21-0297), calcium oxalate hydrate (1CDD: 00-003-0110), and titanium oxalate hydrate (1CDD: 00-032-1386) are all absent. This confirms the appearance of a new precursor phase (CCTOX) resulting from the wet chemical preparation. Those of the decomposition product sintered at 600°C, 700°C, and 800°C for four hours, each presented on Figure 3(b), are identical for the three temperatures and present the dominance of the phase singular calcium copper titanium oxide in the presence of two-minute impurity phases which are attributed to the presence of CuO and CaTiO₃. This result matches with ICDD-01-175-1149 and JCPDS file card no 75-2178.

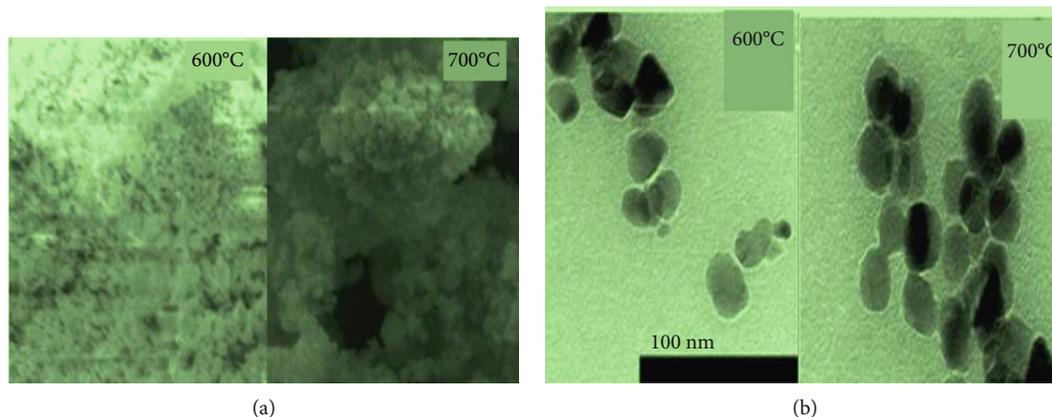


FIGURE 5: SEM (a) and TEM (b) image for the decomposition products at 600°C and 700°C for four hours.

3.5. EDS of the Decomposition Product of CCTOX. The representative EDS spectrum for the composition are shown in Figure 4 and integrated with the metal content and elemental compositions. The results indicate the presence of peaks at 0.8 KeV for Ca, 4.5 KeV to 5 KeV for Ti, and 8 KeV to 9 KeV for Cu and reveal a large extent that only copper, calcium, titanium, and oxygen were present in the matrix which confirmed the elemental purity of the constituent atoms in the microstructure of the prepared powders sintered at 600°C for four hours. Empirical formula calculations based on elemental composition, indicated nonstoichiometry in titanium and copper, which can be attributed to the presence of CaTiO_3 and CuO in the microstructure of the CCTO.

3.6. Morphology of the Decomposed Powders (SEM and TEM). The morphology and particle size distributions of the decomposed sample are presented on Figure 5. SEM results showed particles which are weakly agglomerated but whose level of agglomeration increased with the increase in sintering temperature, while TEM images of the obtained ceramic showed a dense microstructure with an average grain size 17 nm. The powders obtained from sintering at 600°C for four hours had discrete particles with regular morphology, limited size distribution, and high degree of homogeneity. The particles show some degree of ellipticity in shape and multiple dimensions ranging between 10 and 35 nm. Increasing the sintering temperature from 600°C to 700°C resulted in densification and increase in the grain growth within the ceramic.

4. Conclusion

Averrhoa carambola fruit juice has been used as a precipitating agent in the synthesis by coprecipitation of a single molecular precursor CCTOX ($\text{CaCu}_3(\text{TiO})_4(\text{C}_2\text{O}_4)_8 \cdot 9\text{H}_2\text{O}$) which decomposed at relatively low temperature to CCTO ($\text{CaCu}_3\text{Ti}_4\text{O}_{11}(\text{CO}_3)$). The technique is simple and environmentally friendly and does not require costly equipment, stringent reactions, or complex procedures yet produced excellent results (phase singular nanosized $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ particles which have a regular morphology, limited size distribution, high degree of homogeneity, some degree of ellipticity

in shape, and multiple dimensions ranging between 10 and 35 nm) at low decomposition temperature of 600°C and sintering period of four hours.

Data Availability

The datasets used and/or analyzed during the current study are available from the corresponding author upon reasonable request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

References

- [1] M. A. Subramanian, D. Li, N. Duan, B. A. Reisner, and A. W. Sleight, "High dielectric constant in $\text{ACu}_3\text{Ti}_4\text{O}_{12}$ and $\text{ACu}_3\text{-Ti}_3\text{FeO}_{12}$ phases," *Journal of Solid State Chemistry*, vol. 151, no. 2, pp. 323–325, 2000.
- [2] R. Parra, E. Joanni, J. W. M. Espinosa et al., "Photoluminescent $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ -based thin films synthesized by a sol-gel method," *Journal of the American Ceramic Society*, vol. 91, no. 12, pp. 4162–4164, 2008.
- [3] I.-D. Kim, A. Rothschild, T. Hyodo, and H. L. Tuller, "Microsphere templating as means of enhancing surface activity and gas sensitivity of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ thin films," *NanoLetters*, vol. 6, no. 2, pp. 193–198, 2006.
- [4] M. A. Ramirez, P. R. Bueno, J. A. Varela, and E. Longo, "Non-ohmic and dielectric properties of a $\text{Ca}_2\text{Cu}_2\text{Ti}_4\text{O}_{12}$ polycrystalline system," *Applied Physics Letters*, vol. 89, article 212102, 2006.
- [5] V. P. B. Marques, A. Ries, A. Z. Simoes, M. A. Ramirez, J. A. Varela, and E. Longo, "Evolution of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ varistor properties during heat treatment in vacuum," *Ceramics International*, vol. 33, pp. 1187–1190, 2007.
- [6] C. M. Wang, K. S. Kao, S. Y. Lin, Y. C. Chen, and S. C. Weng, "Processing and properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics," *Journal of Physics and Chemistry of Solids*, vol. 69, no. 2-3, pp. 608–610, 2008.
- [7] P. Thomas, L. N. Sathapathy, K. Dwarakanath, and K. B. R. Varma, "Microwave synthesis and sintering characteristics of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$," *Bulletin of Materials Science*, vol. 30, no. 6, pp. 567–570, 2007.

- [8] D. Maurya, P. Kumar, D. P. Singh, and D. C. Agrawal, "Effect of calcium variation on dielectric response of the sol-gel derived $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ thin films," *Indian Journal of Engineering & Materials Sciences*, vol. 15, pp. 107–110, 2008.
- [9] J. Liu, R. W. Smith, and W.-N. Mei, "Synthesis of the giant dielectric constant material $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ by wet-chemistry Methods," *Chemistry of Materials*, vol. 19, no. 24, pp. 6020–6024, 2007.
- [10] L. Marchin, S. Guillemet-Fritsch, B. Durand, A. A. Levchenko, A. Navrotsky, and T. Lebey, "Grain growth-controlled giant permittivity in soft chemistry $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics," *Journal of the American Ceramic Society*, vol. 91, no. 2, pp. 485–489, 2007.
- [11] P. Jha, P. Arora, and A. K. Ganguli, "Polymeric citrate precursor route to the synthesis of the high dielectric constant oxide, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$," *Materials Letters*, vol. 57, no. 16–17, pp. 2443–2446, 2003.
- [12] S. Guillemet-Fritsch, T. Lebey, M. Boulos, and B. Durand, "Dielectric properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ based multiphased ceramics," *Journal of the European Ceramic Society*, vol. 26, no. 7, pp. 1245–1257, 2006.
- [13] P. Dasgupta, P. Chakraborty, and N. N. Bala, "Averrhoa carambola: an updated review," *International Journal of Pharma Research & Review*, vol. 2, no. 7, pp. 54–63, 2013.
- [14] S. Napahde, A. Durve, D. Bharati, and N. Chandra, "Wine production from carambola (*Averrhoa carambola*) juice using *Saccharomyces cerevisiae*," *Asian Journal of Experimental Biological Sciences*, vol. 1, pp. 20–23, 2010.
- [15] N. Nguetack Marius Borel, J. Foba-Tendo, D. M. Yufanyi, E. Peter Etape, J. N. Eko, and L. John Ngolui, "Averrhoa carambola: a renewable source of oxalic acid for the facile and green synthesis of divalent metal (Fe, Co, Ni, Zn, and Cu) oxalates and oxide nanoparticles," *Journal of Applied Chemistry*, vol. 2014, Article ID 767695, 9 pages, 2014.