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Phase and Thermal Properties of Calcium Copper Titanate (CaCu₃Ti₄O₁₂)/Barium Titanate (BaTiO₃) Composites

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ABSTRACT: Barium Titanate (BT) and Calcium Copper Titanate (CCTO) are renowned for their high dielectric properties, and they have been extensively researched for the miniaturization of microelectronic devices. Integrating CCTO's high dielectric constant property with BT's low loss as a composite could leverage the benefits of both compounds. This research explores the phase and thermal behavior of BT and CCTO in their composite form, synthesized via the solid-state reaction method. The composite mixture was formulated according to BaTiO₃.xCaCu₃Ti₄O₁₂, where x = 0.2, 0.5, 1, 1.2, and 1.5 mol%. A semi-quantitative analysis confirmed the composition, with minor variations potentially arising from milling factors. Notably, the milling process led to the formation of oxygen vacancies, as observed from the TGA/DSC analysis.

Keywords: Calcium Copper Titanate, Barium Titanate, Composite Composition, Phase, Thermal Properties

1. Introduction

Since technology has continued to advance, numerous types of advanced ceramics have been created for various industrial applications. Advanced ceramics have had their chemical composition altered and internal structure to achieve the desired ceramic properties, such as superior mechanical properties, resistance to oxidation or corrosion, thermal, electrical, optical, or magnetic properties to meet industry demands. Research on using advanced ceramics in electronic devices, such as capacitors, insulators, substrates, integrated circuit packages, piezoelectric, magnets, and superconductors, is among the most widely pursued fields of study [1].

Glazer [1] has outlined materials with high dielectric constants can store substantial energy. In contrast, those with low dielectric constants are less capable of energy storage in an electric field. Dielectric materials are characterized by their ability to store energy under these conditions. One such material is CaCu₃Ti₄O₁₂, calcium copper titanate (CCTO). The CCTO, which has a body-centered cubic perovskite structure, is highly regarded in scientific circles due to its impressive dielectric constant. At room temperature, the dielectric constant for bulk CCTO is approximately 100,000 at 1kHz [2]–[4], and it maintains good temperature stability in the range from 100 K to 600 K [5].

Rahman et al. [2] has reported that due to its large dielectric constant and ability to store large amounts of energy, CCTO is a potential candidate for use in microelectronic devices. As a result, small-sized devices with significant energy storage capacities can be produced. Although CCTO has a very high dielectric constant [6]–[11], this property also has a high dielectric loss (>0.05), which is a drawback and undesirable for microelectronic applications [12]–[15]. To overcome this problem, it is suggested that CCTO be produced as a composite with another high-dielectric material, barium titanate (BT), which has a high dielectric constant (10,000) but is not as high as CCTO. This is a good combination because BT has a very low dielectric loss, which can be very useful in lowering the dielectric loss of the produced composite.

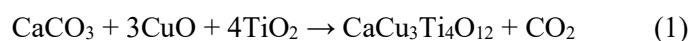
In this study, composites of BT and CCTO were synthesized, and their phase and thermal properties were observed to investigate if any secondary phase existed between both compounds or if any reaction occurred during the sintering process of the composite.

2. Experimental

2.1 Raw Material for CaCu₃Ti₄O₁₂ Powder Preparation

2.1.1 Weighing of CCTO Starting Materials

CaCO₃ (R&M Chemicals), CuO (R&M Chemicals), and TiO₂ (R&M Chemicals) with high purity were prepared as a starting material by weighing according to stoichiometric ratio using a high precision balance up to four decimal places to get an accurate reading. Based on the chemical reaction in Equation 1, the mass of raw materials required for calcium carbonate, copper oxide, and titanium oxide were determined.



2.1.2 Mixing and Milling of CCTO Starting Materials

The raw materials were mixed and ground simultaneously with assisted ethanol for 24 hours in a ball milling process using zirconia balls as the grinding media. The ratio of powder-to-ball is 1:10. The mixture is then poured into a beaker and dried in an oven for 24 hours to remove the ethanol. Using a mortar and pestle, the mixed dried powder is ground to prevent agglomeration for the calcination process.

2.1.3 Calcination for CCTO Phase Formation

The powders were placed in an alumina crucible and calcined in a furnace at 900°C for 12 hours. The heating and cooling rates were controlled at 5°C/minute.

2.2 Raw Materials for BaTiO₃ Powder Preparation

2.2.1 Weighing of BT Starting Materials

BaCO₃ (R&M Chemicals) and TiO₂ (R&M Chemicals) with high purity are prepared as a starting material by being weighed according to the stoichiometric ratio (Equation 2) using a high precision balance up to four decimal places to get accurate readings.



2.2.2 Mixing and Milling of BT Starting Materials

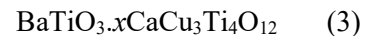
The raw materials were mixed and ground simultaneously with assisted ethanol at 120 rpm for 24 hours in a ball milling process using zirconia balls as the grinding media. The ratio of powder-to-ball is 1:10. The mixture was poured into a beaker and dried in an oven for 24 hours to remove the ethanol. Using a mortar and pestle, the mixed dried powder is ground to prevent agglomeration as a preparation for the calcination.

2.2.3 Calcination for BT Phase Formation

Well-combined dried powder was ground with a mortar and pestle. Then, an alumina crucible was used to store the mixture during the calcination process at 1200°C for 4 hours in a furnace. The heating and cooling rates were set at 5°C/minute.

2.3 Mixing of BaTiO₃ and CaCu₃Ti₄O₁₂ Powder

BT and CCTO powder were weighted based on the stoichiometry ratio in Equation 3, where the x = 0, 0.2, 0.5, 1.0, 1.2, and 1.5 mol%.



The weight of each composition is shown in Table 1. Each of the compositions was mixed for at 120 rpm for 16 hours in a ball mill. The stoichiometric amounts of the precursors were added to a polyethylene container with zirconia balls as the grinding media with a ratio of powder-to-ball is 1:10. The mixtures were tested for phase and thermal properties using Bruker D2 Phaser X-Ray Diffractometer and TGA DSC 2 HT Mettler Toledo.

Table 1: Composition of BaTiO₃.xCaCu₃Ti₄O₁₂

Composition (x mol%)	0	0.2	0.5	1.0	1.2	1.5
Calculated weight of BT (g)	20	13.1	8.6	5.5	4.8	4.0
Calculated weight of CCTO (g)	0	6.9	11.4	14.5	15.2	16.0

3. Results and Discussion

Utilizing the solid-state reaction method, CCTO powder was successfully synthesized from a mixture of initial raw materials through a calcination process. This process resulted in a color change of the mixture from greyish to brown [6]. An XRD analysis was conducted to verify the completeness of the reaction during calcination. The data interpretation was facilitated by Bruker Diffract.EVA software. The observed peak of CCTO corresponded with COD 1532158, as depicted in **Fig. 1** (CCTO), with no secondary peaks or remaining starting materials.

Fig. 1 (BT) presents the XRD pattern of the BT powder, formed after heat-treating at 1200°C for 4 hours. The XRD results from this study affirmatively confirmed that the single BT phase retains a cubic crystal system. Following the calcination process, the powder turned white. The measured peak of the single phase of BT corresponded with COD 1507757, as depicted in **Fig. 1** (BT).

The mixture powders with different compositions of CCTO were analyzed using XRD in **Fig. 1**. The increased CCTO mol% caused the increase of CCTO peaks in the XRD and, in another way, decreased the BT

peak. Semi-quantitative (S-Q) XRD analyses were carried out to measure this composition amount and identify the homogeneity after milling.

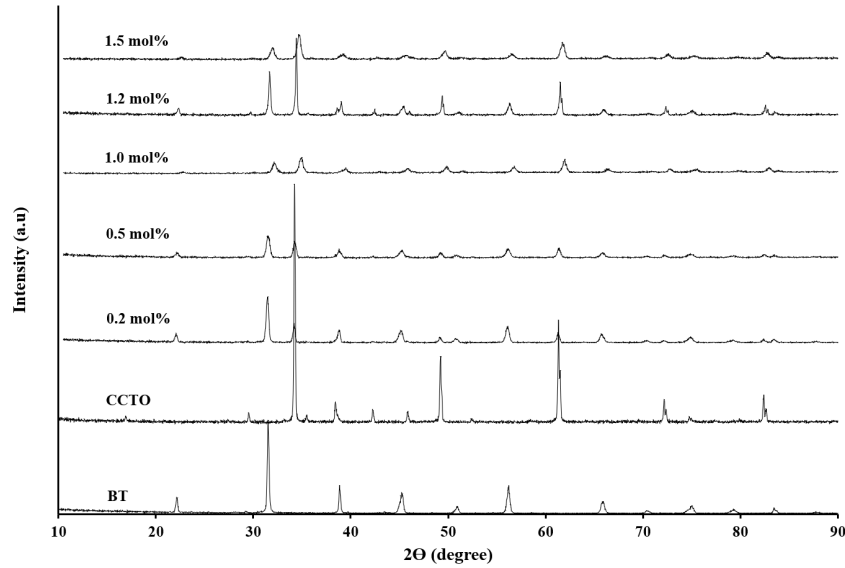


Figure 1: Composition of BT/CCTO mixture

Fig. 2 shows the comparison result of wt% from weighted samples before the ball mill and the S-Q analysis after the milling. This can be seen as only a minor difference between both conditions. It is suggested the sample should be increased (higher than 20g) or have a longer milling time (more than 16 hours) to reduce the gap and ensure the samples are at the expected compositions. Among the samples, the BT always recorded less wt% from the S-Q result compared to the wt% before the milling. It is impossible for CCTO to have wt% after milling that is higher than wt% before milling, and this can be expected from the diffusion of BT compound during the milling less active (less chemical energy) compared to CCTO that caused the formation of variation or inhomogeneous sampling for S-Q results.

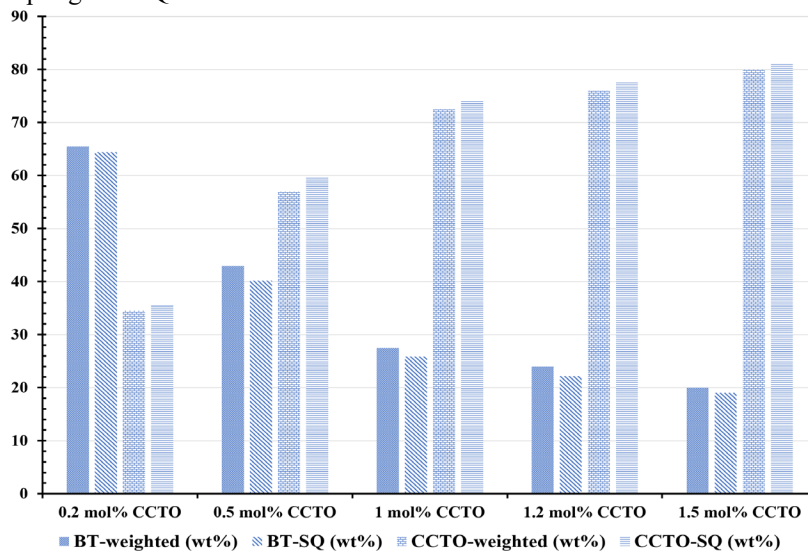


Figure 2: Comparison of wt% from weighted samples and S-Q analysis

Thermogravimetric (TGA) and differential calorimetric analysis (DSC) measurements were conducted, with the results are shown in Fig. 3. Up to 100°C, all samples show a decrease in weight due to the moisture loss in the air. However, over the temperature range of room temperature to 900°C, the sample weight increase might be due to the oxidation process of both of the compounds. Since oxidation already occurred during the calcination process, reoxidation during the TGA measurement can originate from the formation of a large amount of oxygen vacancy during the milling process [7].

DSC results from the temperature change also proved this, and the heat flow indicated the early endothermic reaction at around 100°C came from the evaporation of water inside the sample, followed by the exothermic reaction of oxidation that came from the mixtures of compounds [16].

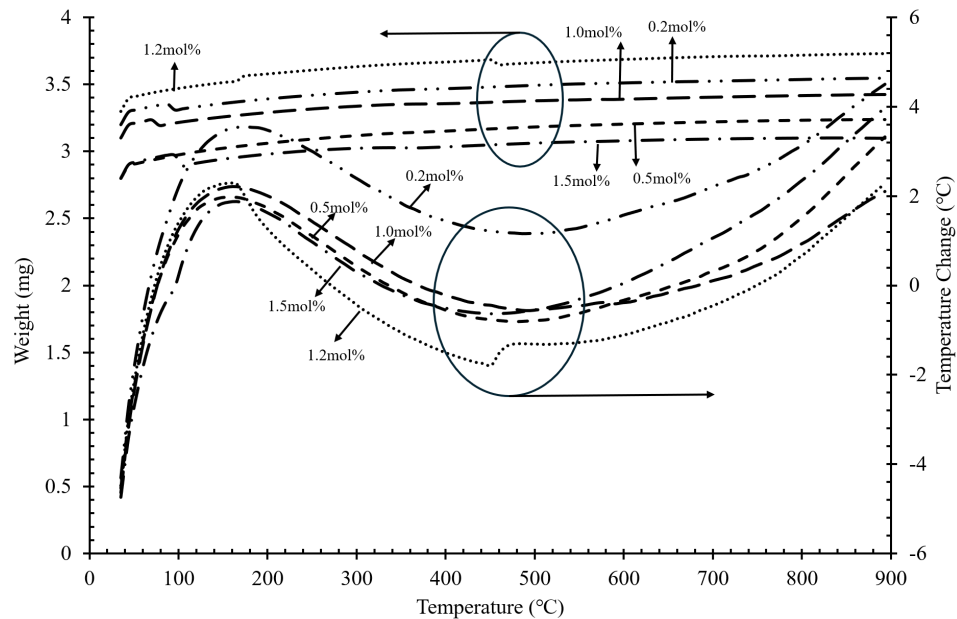


Figure 3: Thermogravimetric and differential thermal analysis

4. Conclusions

The study demonstrated that the BT/CCTO composite can be synthesized using the solid-state reaction method. However, the milling process requires optimization, as the weight percentage of the BT compound in all samples decreased after ball milling, as confirmed by the S-Q analysis. This decrease could be attributed to the presence of compounds with lower molecular weights and chemical energy compared to CCTO. Notably, thermal analysis detected a robust reoxidation process, suggesting the formation of oxygen vacancies during the milling process for both compounds. Given that these oxygen vacancies can influence electrical properties. This factor should be considered during the sintering process for the fabrication of microelectronic devices.

Conflict of Interest

The authors declare that they have no conflict of interest.

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