

EFFECTS OF Y_2O_3 ON PROPERTIES OF $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ CERAMICS PREPARED BY MOLTEN SALT METHOD

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Abstract

In this research, the effects of Y_2O_3 on the properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics, abbreviated as CCTO, prepared using the molten salt method, were studied. Additionally, the ceramics were referred to as CCTYO with varying amounts of Y_2O_3 , denoted as $\text{CaCu}_3\text{Ti}_{4-x}\text{Y}_x\text{O}_{12-x/2}$, where x ranged from 0.01 to 0.05 by mol. The sintering temperatures were adjusted to be in the range of 1050 - 1080°C. The influence of Y_2O_3 dopant on the phase structure, microstructure, density, electrical properties and Vickers micro-hardness was investigated. It was found that all XRD patterns of CCTYO ceramics with various Y_2O_3 doping exhibited phase structures could be matched with a JCPDS file number 75-2188. The grain morphology of CCTYO ceramics appeared as rectangular-like shapes, and increased with increasing sintering temperature. The CCTYO ceramics of all Y_2O_3 variations have the highest density at a sintering temperature of 1050°C. The dielectric properties of all CCTYO ceramics sintered at 1050°C was measured at a frequency of 1 kHz. It was observed that when 0.01 mol of Y_2O_3 was added as a dopant, the CCTYO ceramics exhibited the highest dielectric constant of 14100 at room temperature and the lowest dielectric loss of 0.04. Furthermore, the CCTYO ceramics for all Y_2O_3 variations, sintered at 1050°C, exhibited the highest Vickers micro-hardness of approximately 10 GPa.

Keywords: CCTYO ceramics, Density, Dielectric properties, Vickers micro-hardness

Introduction

Currently, electronic materials have been rapidly developed, with improvements in efficiency and performance. Electrical properties are crucial in enhancing the overall performance of electronic devices, such as improved electrical conductivity and higher electrical capacity. The study of dielectric properties and materials with high dielectric constants has gained significant attention, particularly for applications in important electronic devices like capacitors and memory devices

(Almeida *et al.*, 2004). Materials with high dielectric constants, such as BaTiO_3 (BT) and $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT), have been widely utilized in various technological applications. However, these materials often exhibit significant dielectric constant changes with temperature, posing limitations in their development. Additionally, PZT contains toxic elements, adding environmental concerns to its use. Recently, the material $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) has emerged as a promising

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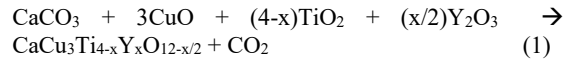
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dielectric material. It has garnered attention due to its non-toxic composition and high dielectric constant of approximately 10^4 at temperatures ranging from 100 to 500 K. CCTO has found applications in various electronic devices, such as capacitors, global positioning systems (GPS), and filters (Chen and Zhang, 2010). Despite its high dielectric constant, CCTO suffers from high dielectric loss, requiring additional doping with Y_2O_3 to enhance its dielectric properties. The aim is to maintain a high dielectric constant while reducing dielectric loss. Previous research has indicated that the addition of Y_2O_3 contributes to the enhancement of the dielectric properties of CCTO such as Saji and Choe found that the dielectric loss of the $CaCu_3Ti_{4-x}Y_xO_{12-x/2}$ thin film when $x = 0.02$ decreased to 0.07 at a frequency of 1 kHz (Saji and Choe, 2009). Luo *et al* reported that the ceramic of $CaCu_3Ti_{4-x}Y_xO_{12-x/2}$, when $x = 0.05$, exhibits a dielectric loss below 0.1 in the frequency range from 1 to 300 kHz, while still maintaining a high dielectric constant (Luo *et al.*, 2010). Xu and *et al* found that the $CaCu_3Ti_{4-x}Y_xO_{12-x/2}$ ceramic, when $x = 0.03$, has a dielectric loss of 0.047, while the $CaCu_3Ti_4O_{12}$ ceramic has a dielectric loss of 0.071 at a frequency of 10 kHz (Xu *et al.*, 2017). The Y_2O_3 is a functional additive material widely used in various fields such as energy, aerospace, fluorescence, electronics, high-tech ceramics, and more. This is due to its outstanding physical properties, such as high dielectric constant, good heat resistance, strong corrosion resistance, and ability to be used as a reaction vessel. It is utilized extensively as a conductive material, high-temperature resistant material, and fire-resistant material. As a raw material or additive substance, the Y_2O_3 is widely used in various applications, especially in high-temperature conductive materials, crystal laser materials, ceramic structures, catalytic materials, electro-ceramics, high-performance metal alloys, and other related fields (Rao *et al.*, 2023). This study explores the use of Y_2O_3 as a dopant in CCTO ceramics, aiming to improve its dielectric characteristics.

In this research aims to study the ceramic material $CaCu_3Ti_{4-x}Y_xO_{12-x/2}$, where Y_2O_3 is added as a dopant in quantities ranging from 0.01 to 0.05. The ceramics will be sintered at temperatures between 1050-1080°C. Subsequently, the study will investigate the phase structure, microstructure, density, dielectric properties and Vickers hardness of the ceramic material.

Materials and Methods

In this research, the reagent grade $CaCO_3$, CuO , TiO_2 and Y_2O_3 powders were used as starting materials. In accordance with the calculated proportions obtained from equation (1).



The materials which were ground and mixed for 24 h in ethanol using zirconia grinding media. The finely ground mixture was then dried and further reduced in size using an agate mortar. The resulting powder was sieved to separate particles by size, yielding a uniform particle size distribution. This material is referred to as CCTYO mixture powder.

The mixture salt was prepared by placing NaCl and KCl in an oven at 100°C for 1 h to remove moisture. The salts were then weighed to achieve a 1:1 by molar ratio. Subsequently, they were mixed together in an agate mortar, forming the mixture salt. This mixture salt was then combined with the CCTYO mixture powder obtained earlier in a 1:1 by weight ratio. The resulting mixture was subjected to calcination at a temperature of 700°C for 8 h with heating rate 5°C/min to form CCTYO powder. The salt was removed from the resulting powder by washing it with hot de-ionized water many times and then testing for the absence of free chloride ions using a silver nitrate solution in the wastewater from washing the salt and drying it once again.

The calcined CCTYO powder was ball milled with 3% PVA in ethanol for 12 h using the same method as mentioned earlier. The slurry was dried, sieved and pressed into a disc shape and sintered at 1050, 1060, 1070, and 1080 °C for 8 h with heating of 5°C/min.

The sintered CCTYO pellets were checked for phase formation by X-ray diffraction (XRD). The microstructures of the ceramics were characterized using a scanning electron microscopy (SEM). The average grain size was determined using the linear-interception method, and the density was calculated using the Archimedes method with distilled water as the fluid medium. Dielectric properties were examined by LCR meter. The Vickers micro-hardness of these ceramics was investigated by Vickers micro-hardness tester.

Results and Discussion

Figure 1 shows XRD patterns of $\text{CaCu}_3\text{Ti}_{4-x}\text{Y}_x\text{O}_{12-x/2}$ ceramics for all Y_2O_3 substitutions ($x = 0.01, 0.03$, and 0.05) sintered at temperatures $1050, 1060, 1070$, and 1080°C . The cubic perovskite structure was found for all samples. The analysis was carried out based on the basis CCTO of Joint Committee on Powder Diffraction Standard (JCPDS) data file number 75-2188 (Powder Diffraction File, 2000). and no secondary phases can be detected within the detection limit of XRD pattern for CCTO. The amount of Y_2O_3 in these samples may have been too small to be detected by XRD (Puchmark *et al.*, 2007; Binhayeeniyi *et al.*, 2010; Puchmark and Rujijanagul, 2012; Zheng *et al.*, 2013). The results of XRD patterns of $\text{CaCu}_3\text{Ti}_{4-x}\text{Y}_x\text{O}_{12-x/2}$ ceramics sintered at 1050°C were used to determine the lattice parameter values by Rietveld refinement. The lattice

parameter values of $\text{CaCu}_3\text{Ti}_{4-x}\text{Y}_x\text{O}_{12-x/2}$ ceramics when $x = 0.01, 0.03$ and 0.05 are $7.393 \text{ \AA}$, $7.394 \text{ \AA}$, and $7.396 \text{ \AA}$, respectively. These values compared with CCTO of JCPDS data file number 75-2188 was $7.391 \text{ \AA}$ (Powder Diffraction File, 2000) and Xu *et al* reported CCTO lattice parameter was $7.386 \text{ \AA}$ (2017). The Y atoms have partially replaced Ti atoms, and since the atomic radius of Y is larger than that of Ti, the lattice parameter of CCTYO is larger than that of CCTO, as reported in the standard JCPDS database number 75-2188 (Cheng *et al.*, 2019; Powder Diffraction File, 2000). The lattice parameter of the $\text{CaCu}_3\text{Ti}_{4-x}\text{Y}_x\text{O}_{12-x/2}$ increases with the increasing amount of added Y_2O_3 doping.

Figure 2(a)-(d) shows SEM micrographs surface of Y_2O_3 -doped CCTYO ceramics with concentrations ranging from 0.01 to 0.05 , sintered at temperatures between 1050 - 1080°C . It can be observed that the surface of CCTYO ceramics, for

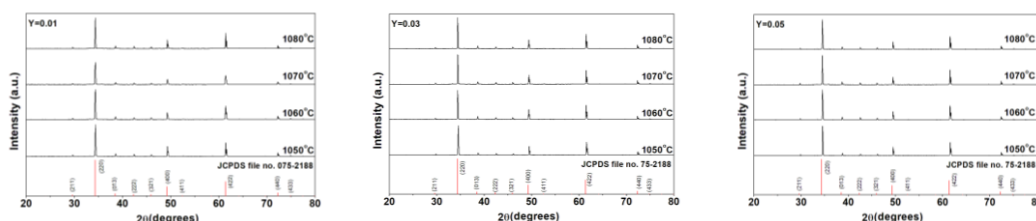


Figure 1. The XRD patterns of CCTYO ceramics sintered at 1050 - 1080°C for 8 h, with varying Y_2O_3 substitutions at $0.01, 0.03$, and 0.05 by molar

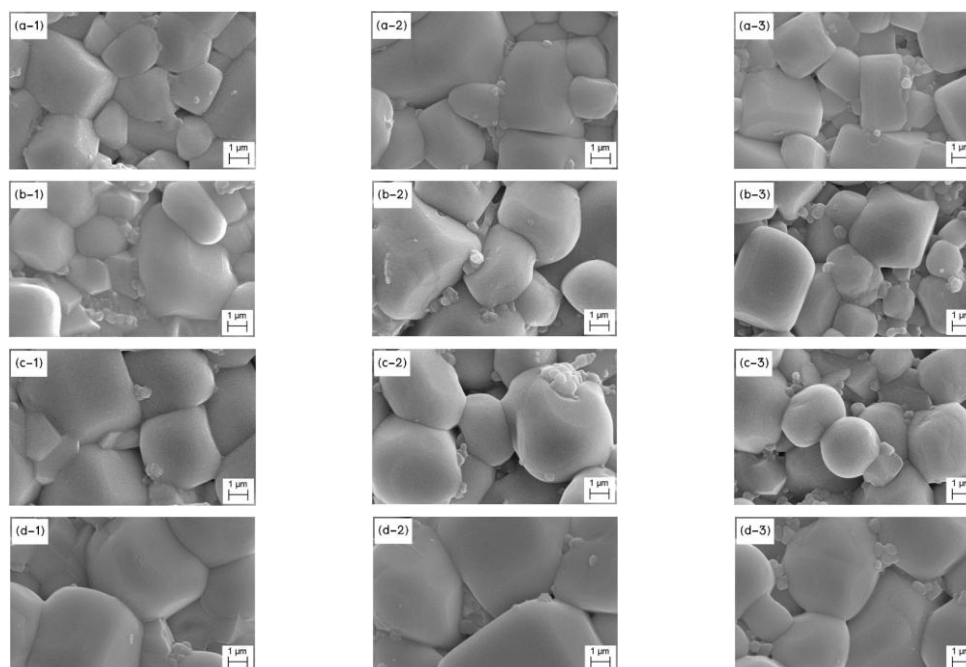


Figure 2. SEM photographs of CCTYO sintered at 1050 - 1080°C for 8h various the Y_2O_3 content by molar: (a-1) 1050°C , 0.01 , (a-2) 1050°C , 0.03 , (a-3) 1050°C , 0.05 , (b-1) 1060°C , 0.01 , (b-2) 1060°C , 0.03 , (b-3) 1060°C , 0.05 , (c-1) 1070°C , 0.01 , (c-2) 1070°C , 0.03 , (c-3) 1070°C , 0.05 , (d-1) 1080°C , 0.01 , (d-2) 1080°C , 0.03 and (d-3) 1080°C , 0.05

all Y_2O_3 substitutions and sintering temperatures, exhibits a quasi-rectangular morphology. For the CCTYO ceramics, at every variation of Y_2O_3 content, sintering at 1050°C (figures 2(a-1)-(a-3)) results in a relatively tight surface with fewer pores compared to increasing the sintering temperature. When the Y_2O_3 content is increased, it is observed that the densification and grain size of the CCTYO ceramic decreases, and the porosity increases. The addition of Y-doped ceramic CCTO results in a reduction in grain size compared to reports by Puchmark and Rujijanagul (2011) and Xu *et al.* (2017), where the grain sizes of CCTO without Y doping were as large as 26.9 and 3.5-15 μm , respectively. The decrease in grain size of this ceramic may be attributed to the ability of Y^{3+} ions to inhibit grain growth of CCTO (Deng *et al.*, 2016; Xu *et al.*, 2017) and the out diffusion of rear-earth oxide could stop the grain boundaries from moving, which lead to fine grains (Liu *et al.*, 2011). Moreover, with an increase in the sintering temperature, the grain size of the ceramic is found to be larger.

When plotting the density values of CCTYO ceramic and amount of Y_2O_3 concentrations various sintering temperatures (1050, 1060, 1070, and 1080°C), the resulting graph is shown in Figure 3. The corresponding data is provided in Table 1.

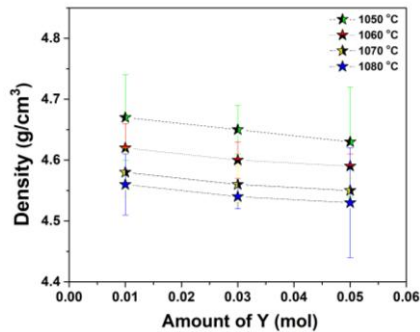


Figure 3. The density of CCTYO ceramics varied depending on the amount of Y_2O_3 substitution (0.01, 0.03, and 0.05 molar) sintered at $1050 - 1080^\circ\text{C}$.

From the graph in Figure 3 and the data in Table 1, the investigation into the density of

CCTYO ceramic with varying Y_2O_3 concentrations of 0.01, 0.03, and 0.05 molar, sintered at $1050 - 1080^\circ\text{C}$ for 8 h, using the Archimedes' method, reveals that for each Y_2O_3 variation, the CCTYO ceramic attains its maximum density at a sintering temperature of 1050°C . Additionally, it is observed that at the same sintering temperature, as the Y_2O_3 concentration increases, the density of CCTYO ceramic slightly decreases. This observation aligns with the surface morphology of CCTYO ceramic by scanning electron microscopy in Figure 2, which illustrates an increase in pore quantity as the sintering temperature rises. Furthermore, when the Y_2O_3 concentration is increased, the ceramic exhibits decreased density. This implies that the optimal Y_2O_3 concentration, facilitating the highest density of CCTYO ceramic, is achieved at a minimal quantity of 0.01 molar, specifically at the sintering temperature of 1050°C .

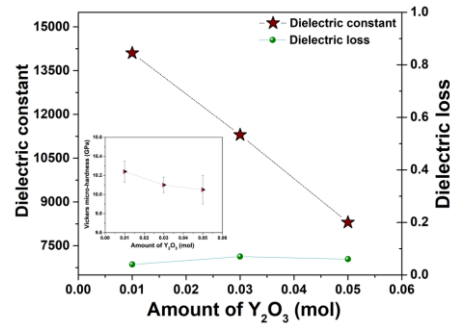


Figure 4. The dielectric constant and dielectric loss of CCTYO ceramics sintered at 1050°C and various Y_2O_3 . Insert graph is Vickers micro-hardness of these ceramics

From the graph in Figure 4, it is evident that Y_2O_3 -doped CCTYO ceramics with only 0.01 by molar substitution, sintered at 1050°C and measured at a frequency of 1 kHz at room temperature, exhibit the highest dielectric constant of 14100 and the lowest dielectric loss of 0.04. These values are consistent with the maximum density, it is found that ceramics with higher density exhibit higher dielectric constant values. However, the relationship between dielectric constant and ceramic density cannot be precisely determined by a single theory because the dielectric constant of a material depends

Table 1. The density of CCTYO ceramic varied with different Y_2O_3 concentrations of 0.01, 0.03, and 0.05 molar, when sintered at $1050 - 1080^\circ\text{C}$ for 8 h

Sintering temperature ($^\circ\text{C}$)	Density of $\text{CaCuTi}_{4-x}\text{Y}_x\text{O}_{12-x/2}$ (g/cm^3), x is		
	0.01	0.03	0.05
1050	4.67 ± 0.07	4.65 ± 0.04	4.63 ± 0.09
1060	4.62 ± 0.04	4.60 ± 0.03	4.59 ± 0.02
1070	4.58 ± 0.04	4.56 ± 0.03	4.55 ± 0.02
1080	4.56 ± 0.05	4.54 ± 0.02	4.53 ± 0.09

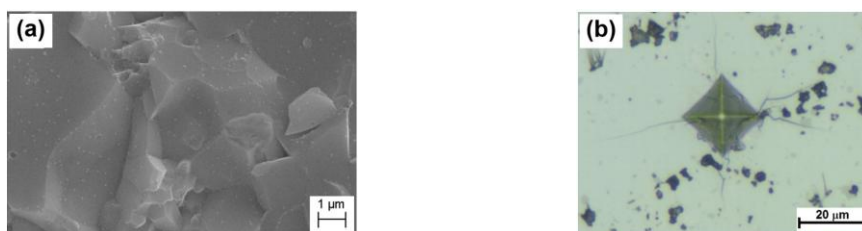


Figure 5. The SEM photograph of fracture and OM photograph of Vickers micro-hardness print of CCTYO ceramic sintered at 1050°C and 0.01 molar of Y_2O_3 doped

on its state and structure, which affect the arrangement of particles and areas within the material. The ceramic also exhibited a higher grain density than the CCTYO ceramic under other research conditions. It can be observed that the results of the dielectric properties at room temperature are in good agreement with the reported density results (Hsiang *et al.*, 2008; Chaudhari and Bichile, 2013; Pattipaka *et al.*, 2016; Warangkanagool, 2018; Zhang *et al.*, 2020; Warangkanagool and Bongkarn, 2022).

The density of ceramics is related to the internal structure of the material. Therefore, even a slight presence of pores within ceramics can affect their strength. Ceramics with higher density often exhibit good resistance to corrosion due to fewer pores, resulting in increased strength. From Figures 2(a-1) to 2(a-3), it can be observed that the microstructure of CCTYO ceramics with added Y_2O_3 shows a slight increase in pore formation, leading to a slight decrease in ceramic strength. The graph inserted in Figure 4 is a representation of the Vickers micro-hardness values of CCTYO ceramic doped with Y_2O_3 in amounts of 0.01, 0.03, and 0.05 by molar, sintered at a temperature of 1050°C. It can be observed that the Vickers micro-hardness values for all samples are approximately close, around 10 GPa, with the highest value achieved when the ceramic is doped with Y_2O_3 in 0.01 by molar. Figure 5(a) shows SEM photograph of the fracture intra-granular mode and Figure 5(b) shows OM photograph of Vickers micro-hardness print of the highest Vickers micro-hardness value of CCTYO ceramic sintered at 1050°C and 0.01 molar of Y_2O_3 doped. A strengthening of the grain boundaries is associated with an intra-granular mode of fracture, which promotes crack propagation through the grain rather than along the grain boundary (Wang *et al.*, 2008, Warangkanagool, 2013). This aligns with the ceramic density values at the same sintering temperature. This result is similar to those observed in literature (Puchmark *et al.*, 2006, Sanjoom and Puchmark, 2011, Yuan *et al.*, 2017), which reported an increase in hardness with increasing density.

Conclusions

The CCTYO ceramic prepared using the molten salt method, with a slight doping of 0.01 Y_2O_3 by molar, and sintered at a temperature of 1050°C, exhibits a phase structure in the cubic perovskite form. It has a maximum density, Vickers micro-hardness and the dielectric constant at its maximum value and the minimum dielectric loss were observed at room temperature with 1 kHz of frequency.

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