
Dielectric Properties of Calcium Copper Titanates (CaCu₃Ti₄O₁₂) Synthesized by Solid State Reaction

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Abstract: The conventional solid-state reaction technique was used to obtain CaCu₃Ti₄O₁₂ (CCTO) Ceramics. The crystal structure, microstructure and dielectric properties of polycrystalline CCTO samples sintered at different temperatures were investigated. X-ray diffraction (XRD) patterns showed no change in crystal structure phase of samples sintered at different temperatures. The SEM showed normal grain growth in CCTO samples sintered at 1090 °C, while abnormal grain growth was observed in samples sintered at 1140°C. The chemical composition of the calcined powder determined by EDS corresponds to CaCu₃Ti₄O₁₂. Dielectric constant of CCTO ceramic sintered at 1090 °C showed weak frequency dependence in the range of 100 Hz to 1 MHz, and gave a value of 10⁴ measured at room temperature and 100 Hz. While the samples sintered at 1140°C showed significant frequency dependence and gave a value of 10⁵. The dielectric loss was about 0.3 for the sample sintered at 1090 °C while it was close to 1 for the sample sintered at 1140 °C.

Keywords: Electronic Material/ Dielectric Properties/ CCTO/ Perovskite- Like Structure.

1. INTRODUCTION

High dielectric constant materials have numerous important applications in electronic devices such as capacitors, static and dynamic random access memories. The commonly used high dielectric constant materials are ferroelectrics and relaxor ferroelectrics such as BaTiO₃. However, these perovskite materials exhibit high dependence on temperature and the existence of the transition temperature is generally a problem in applications. Recently, the perovskite-like body-centered cubic material CaCu₃Ti₄O₁₂ (CCTO) was reported to have a high dielectric constant of 10⁴- 10⁵ at a wide range of temperatures from 200 to 600 K⁽¹⁻⁵⁾. The high dielectric properties of CCTO are different from classic ferroelectric or relaxors, which show a high dielectric constant near its Curie temperature (associated with change in crystal structure). On the other hand the perovskite - like compound CaCu₃Ti₄O₁₂ having the structure shown in Fig. (1)⁽³⁾, does not show any change in crystal structure of CCTO in the temperature range of 35- 1273 K^(4,6).

The explanation for the giant dielectric constant of CCTO is still unknown. Many investigators have been trying to understand whether the giant dielectric constant of CCTO is intrinsic to a perfect crystal or extrinsic where it originates from defects, inhomogeneities, etc. Subramanian *et al.*⁽⁴⁾ analyzed the intrinsic origin of such giant dielectric constant in CCTO, and they interpreted why the giant dielectric constant was indicated without the ferroelectric transition in the present compound. That is, the polarizability and dielectric constant are enhanced by tension on the Ti-O bonds, but the transition to a ferroelectric state is frustrated by TiO₆ octahedra tilt structure that accommodates the square planar coordination of Cu²⁺. The twinning structure is another intrinsic origin for the giant dielectric constant in CCTO⁽⁴⁾. Adams *et al.*⁽⁷⁾ argued against an intrinsic interpretation, and they suggested several extrinsic models for the origin of giant dielectric constant in this material, which are generally based on the barrier layer effects.

It was found that, the dielectric properties of polycrystalline CCTO specimens depend closely on microstructure^(7,8), composition⁽⁴⁾, and processing parameters⁽⁹⁾. Adams *et al.*⁽⁷⁾ reported that, course- grained CCTO ceramics (average grain size:~> 100 μm) sintered at 1100 °C for 20 h showed a permittivity 2 orders of magnitude higher than fine-grained CCTO ceramics (average grain size:~ 5 μm) sintered at 1100 °C for 3 h.. They explained the large capacitance in course-

grained ceramics in terms of barrier layer formed at the grain boundaries. Thin insulating second phase and reoxidized resistive layers near the boundary were considered as two possible reasons. It was found that ⁽¹⁰⁾, the microstructure and dielectric properties of polycrystalline CCTO were sensitive to the Cu-contents. CCTO with Cu-deficiency exhibit the microstructure of uniform grain size distribution, whereas CCTO with Cu-stoichiometry and Cu-excess show microstructure of bimodal grain size distribution. Ceramics with Cu-stoichiometry show the highest low-frequency dielectric permittivity. Any off-stoichiometry will result in the decrease of low-frequency dielectric permittivity.

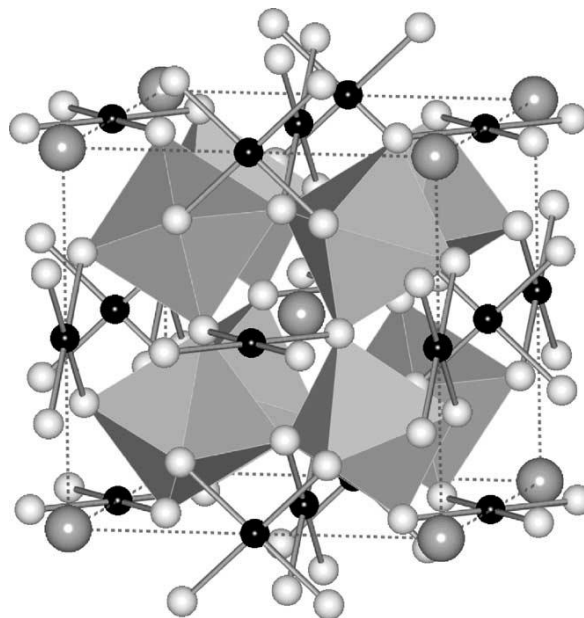


Fig1. The $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ structure drawn with TiO_6 octahedra, Cu as black spheres, O as white spheres, and Ca at the origin and cube center ⁽³⁾.

Yeoh *et al.* ⁽¹¹⁾ through an SEM investigation observed the excess CuO as a separate phase surrounding the $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ grains. The samples with excess CuO showed lower dielectric constant (< 10000), compared to samples with very low CuO content (~ 50000). Capsoni *et al.* ⁽¹²⁾, in studying the effects of CuO segregation for samples prepared through a solid state method, found that CuO segregation improved the effective dielectric constant of the ceramic, attributing this to the increase on disorder at the grain boundaries. Previous studies ⁽¹³⁾ also have showed that high values of dielectric permittivity are obtained for CCTO based multiphase pellets (CCTO + CuO + CaTiO_3). Following the discovery of carbon nanotube ⁽¹⁴⁾ for ultracapacitor applications, CCTO nanotubes have been recently prepared successfully by sol gel technique⁽¹⁵⁾. In this work, the Copper sulfate has been used as a source of CuO. This might lead to the formation of a more homogeneous mixture necessary for the perfect formation of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ after high temperature calcination.

2. EXPERIMENTAL PROCEDURE

Polycrystalline ceramic powder of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ was prepared by conventional solid-state reaction method using stoichiometric amount of CaCO_3 , TiO_2 and copper sulfate as starting materials. The amount of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ powder was dissolved in deionized water and mixed with the CaCO_3 and TiO_2 mixed powders. The water was evaporated to precipitate the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ on the surface of the particles of the mixed powders. The powders were dried at 120°C for 24 hours and then calcined at 1000°C for 5 & 24 hours. The calcined powders were milled in ethyl alcohol using a ball mill with zirconia balls for 24 hrs. The milled powders were dried at 120°C for 24 hrs and sieved using a $120\ \mu\text{m}$ sieve. The formation of the monophase compound of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ was confirmed by X-ray powder diffraction (XRD – Shimadzu, Japan) using Cu K_α radiation. The polycrystalline powder was then cold pressed uniaxially into a disk at a pressure of 50 MPa using a hand press to get pellets of 10 mm diameter and 2 mm thickness. The pellets were sintered in air at 1050 , 1090 , and 1140°C for 5 h. Microstructure and grain size distribution of the as sintered surfaces of the different samples were studied using scanning electron microscopy (SEM - JSM – 5400, Jeol, Japan). Element analysis was carried out using EDX associated with the SEM. For the

capacitance measurements the sintered pellets were painted with silver paste and heat treated at 550°C for 1 hr. The capacitance measurements were conducted using impedance analyzer (4192 A, LF Hewlett & Packard – 5 Hz to 13 M Hz) in air at temperatures from room temperature to 300°C .

3. RESULTS AND DISCUSSION

Figure (1) shows the x-ray diffraction patterns of the as milled powder mixture, the calcined powder at 1000°C for 5 & 24 hrs as well as a pellet sintered at $1050^\circ\text{C}/5\text{h}$. The sample sintered at 1050°C for 5 h and the powder calcined at 1000°C for 24 h show a single phase CCTO. All of diffraction peaks could be indexed by a body-centered cubic perovskite-related structure of space group Im_3 , which indicates that the CCTO prepared in the present study have a good polycrystalline structure. Another minor phase was detected only in the XRD of the powder calcined at $1000^\circ\text{C}/5\text{h}$. This phase has disappeared upon increasing the calcination time to 24 hrs, which indicates that the reaction was not complete after calcination at $1000^\circ\text{C}/5\text{hrs}$. In agreement with the present result, many authors^(10, 16, 17) reported that, no secondary phase could be directly detected from the XRD pattern, while Subramanian, *et al*⁽⁴⁾ reported the existence of CuO impurity in their samples of CCTO.

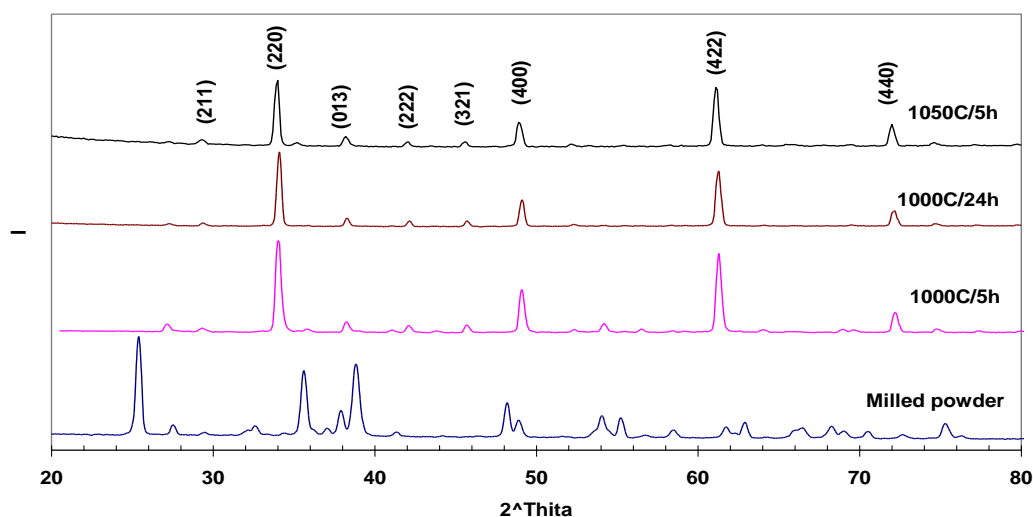


Fig2. XRD patterns of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ Powders: milled, calcined for different times and sintered at $1050^\circ\text{C}/5\text{h}$.

SEM micrographs of the CCTO pellets sintered at $1090^\circ\text{C}/5\text{h}$ and $1140^\circ\text{C}/5\text{h}$ are shown in Fig. (3a-b). The microstructures of both show a bimodal grain size, with small grains of size lying between 5 & $10\ \mu\text{m}$ and large grains of about $20\ \mu\text{m}$ for the pellet sintered at $1000^\circ\text{C}/5\text{h}$ (fig. 3-a). As for the pellets sintered at $1140^\circ\text{C}/5\text{h}$ the microstructure shows an increase in grain size where the small grains range from 10 to $20\ \mu\text{m}$ and the large grains attain a size of about $40\ \mu\text{m}$ (Fig.3-b).

The chemical analysis of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ made by an energy dispersive spectrometer (EDS) inside the grain (G) and at the grain boundaries (G. B.) is shown in table (1). The table shows that the analysis is close to the stoichiometric ratio of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. The EDS analysis inside the grain show slightly CuO-deficient and Cu/Ca ratio is 2.94. The Cu/Ca ratio at the grain boundary is 3 which is slightly higher than Cu/Ca ratio inside the grain. Normal grain growth was observed at $\text{Cu}/\text{Ca} \leq 2.9$ ⁽¹⁹⁾, while abnormal grain growth was observed at $\text{Cu}/\text{Ca} \geq 2.95$, since CuO promotes densification via liquid phase sintering⁽²⁰⁻²²⁾. Moreover, it was reported that CuO segregates at the grain boundaries even at stoichiometric composition ($\text{Cu}/\text{Ca} = 3$)^(8 & 18). Kim *et al.*⁽¹⁹⁾ analyzed the distribution and amount of intergranular liquid phase by TEM analysis. However, it was difficult to quantify the total amount of intergranular liquid by observing a very small area of the TEM specimens.

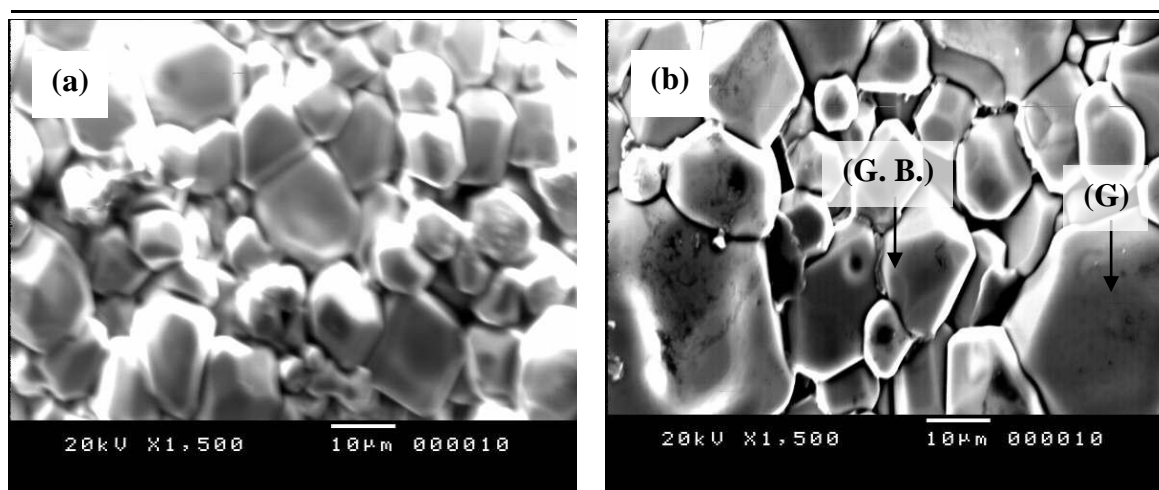


Fig3. SEM micrograph of CCTO pellet sintered at; (a) 1050°C and (b) 1140°C for 5h.

Table1. The percentage of component elements determined by EDS.

Element	Grain (G) Atomic %.	Grain boundary (G. B.) Atomic %.
Ca	4.61	4.89
Cu	13.56	14.68
Ti	19.15	20.02
O	62.68	60.41

The frequency dependence of the dielectric constant (ϵ') and the loss tangent ($\tan \delta$) of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramic sintered at 1090 °C are shown on Fig. (4). Dielectric constant (ϵ') of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics sintered at 1090 °C (Fig. 4-a) indicates weak frequency dependence in the range of 100 Hz to 1 MHz at room temperature and at 100 °C with a giant dielectric constant of about 10^4 . As the measuring temperature increases the giant dielectric constant increases to be more than 10^9 at 300 °C and frequency 100 Hz. Figure (4-b) shows that, dielectric loss ($\tan \delta$) of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ is also of weak frequency dependence in the range of 100 Hz to 1 MHz at room temperature and at 100 °C. As the measuring temperature increases the dielectric loss increases and becomes more frequency dependent. The dielectric loss ($\tan \delta$) slightly increases from about 0.3 to about 0.5 when the measuring temperature increases from room temperature to 100 °C at low frequency. A further increase in the dielectric loss ($\tan \delta$) takes place when the measuring temperature increases above 100 °C.

Figure (5) shows the frequency dependence of dielectric properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramic sintered at 1140°C in the frequency range of 100 Hz to 1MHz. The dielectric constant shows significant frequency dependence at all measuring temperatures. The giant dielectric constant is significantly higher than that of the $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramic sintered at lower temperature (1090°C). This increase in the dielectric constant of the sample sintered at 1140°C may be attributed to the presence of semiconducting secondary phases⁽²³⁾, such as CuO or Cu_2O . Since the conductivity of Cu_2O ($\approx 10^{-3} \Omega^{-1} \text{cm}^{-1}$) is much higher than that of CuO ($\approx 10^{-5} \Omega^{-1} \text{cm}^{-1}$)⁽²³⁾, the giant dielectric constant for the sample sintered at 1140 °C is much higher than that in the samples sintered at 1090 °C due to the transformation of the secondary phase of CuO to Cu_2O upon increasing the sintering temperature.

The dielectric loss ($\tan \delta$) of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ samples sintered at 1140 °C is also weak frequency dependent in the range of 100 Hz to 1 MHz at room. While at 100 °C the dielectric loss slightly decreases with increasing frequency up to 1MHz then tends to increase. The samples sintered at 1140°C were found to give a higher dielectric loss than the samples sintered at 1090 °C. The dielectric loss noticeably increases by increasing the measuring temperature from room temperature to 100 °C. A significant increase in the dielectric loss takes place by further increase in measuring temperature.

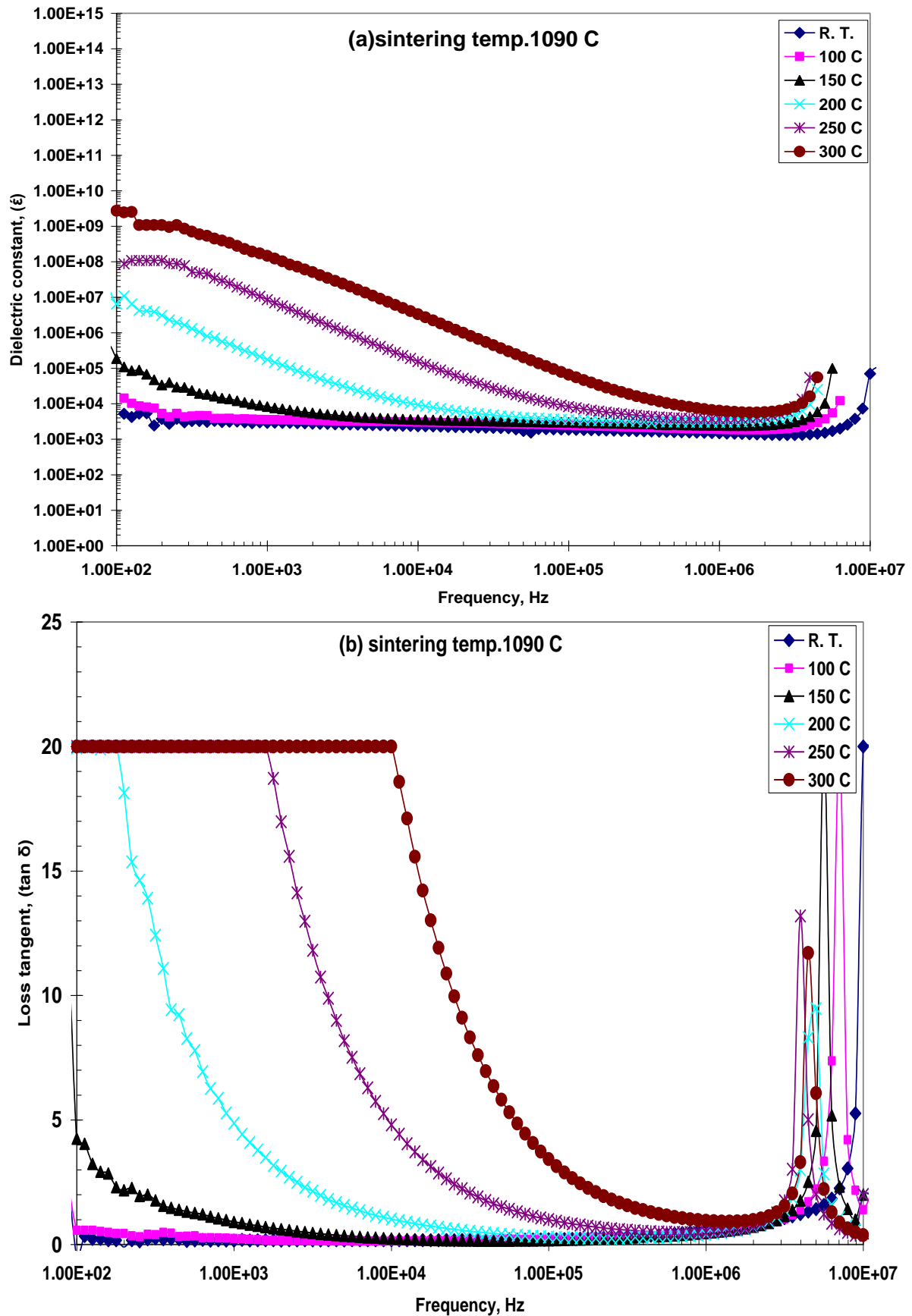


Fig4. Frequency dependence of dielectric properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics sintered at 1090°C at different measuring temperatures, (a) dielectric constant and (b) loss tangent factor.

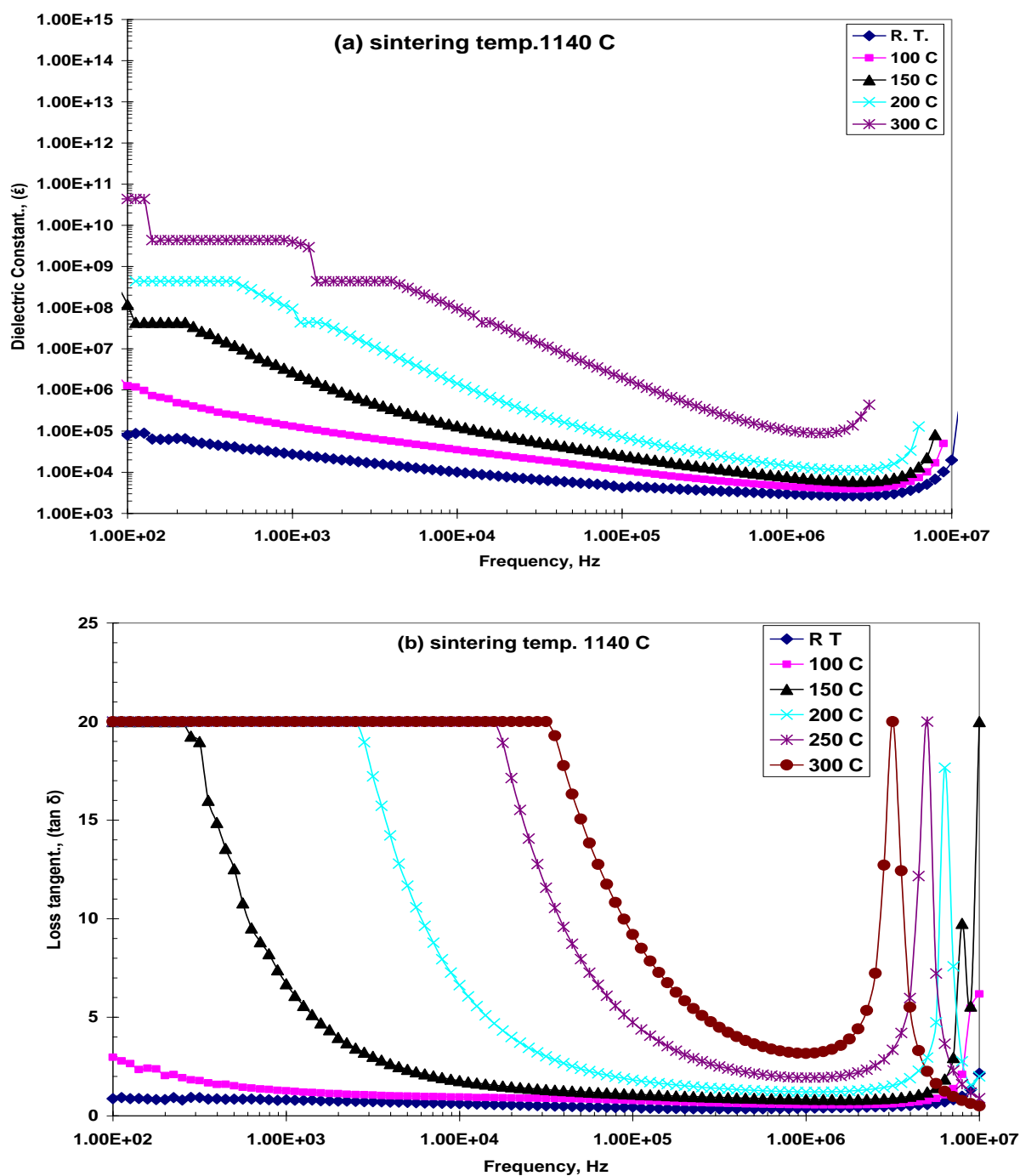


Fig5. Frequency dependence of dielectric properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics sintered at 1140°C at different measuring temperatures, (a) dielectric constant and (b) loss tangent factor.

4. CONCLUSION

Polycrystalline single phase of CCTO ceramics were successfully prepared by conventional solid-state reaction method. XRD patterns showed no change in the crystal structure phase for the two sintering temperatures. The SEM showed normal grain growth in CCTO samples sintered at 1090°C , while abnormal grain growth was observed in samples sintered at 1140°C . The chemical composition determined by EDS is close to the stoichiometric ratio of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. Dielectric constant (K') of CCTO ceramic sintered at 1090°C indicates weak frequency dependence in the range of 100 Hz to 1 MHz, and it becomes significantly frequency dependent when sintered at 1140°C . The dielectric constant value is about 10^4 for samples sintered at 1090°C while it is greater than 10^5 for samples sintered at 1140°C measured at room temperature and 100 Hz. The dielectric loss ($\tan \delta$) is about 0.3 for samples sintered at 1090°C while it is close to 1 for samples sintered at 1140°C .

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