SYNTHESIS AND ANALYSIS OF CALCIUM COPPER TITANATE CERAMICS

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Abstract

Calcium copper titanate ceramics were synthesized by solid-state reaction method. The structural and microstructural properties of sample powder were examined by X-ray diffraction (XRD) and scanning electron microscope (SEM). The capacitance, resistance and dissipated factor of ceramics were measured at frequency range 1 kHz to 25 kHz by LCR meter. The average dielectric constant, of ceramics (at 850˚C for 5h different heat treatment four times) were found to be 94.4,99.4,112.7 and 133.7 in the frequency range from 1kHz to 25kHz. The values of the dielectric loss and conductivity of samples were calculated.

Keywords: Ceramics, X-ray diffraction, SEM, Dielectric constant, Dielectric loss, Conductivity.

Introduction

High dielectric constant materials have numerous important applications in electric devices such as multilayer capacitors, dielectric resonators and capacitating material at microwave frequency, etc. In recent years, high dielectric ceramics had been developed for microelectronics (Marter. Su, 12, 2006). Titanates as members of perovskite structure family are widely used as ferroelectric materials with superior dielectric properties(Omar A. A. An , Abdelal2014).

The vast majority of a ferroelectric material is used commercially in the form of polycrystalline ceramics. Ferroelectric materials offer a wide range of useful properties for the electronic engineer to exploit the field .Ferroelectric mainly has two characteristics, asymmetry and high dielectric constants several ceramic materials with ferroelectric properties(N Tripathy, K C Das, S P Ghosh, G Bose and J P Kar .2016).

Ceramics can be made with different techniques. Out of then solid-state reaction technique have some advantages over other techniques such as low cost and good compositional homogeneity. The properties of materials largely depend on the method of preparation, method treatment and usually modified by the formation of the solution and doping with other additive oxides(K-H FELGNER, H.T.KAMMER.2001).

In this research, $CaCu_3Ti_4O_{12}$ powder was synthesized by the solid-state route. The structural properties of powder was carried out by X-ray diffraction. The microstructure of powder was examined by scanning electron microscope (SEM). The capacitive properties of ceramics were measured by LCR meter with varying frequencies. The high dielectric constant, dielectric loss and conductive of samples were calculated.

Sample Preparation

$CaCO_3$, TiO_2, and CuO were mixed by the stoichiometric formula. The mixture powder and acetone (100 ml) were milled by magnetic stirring for six hours. This powder of mixing and milling repeated two times to obtain a homogeneous powder. The homogeneous powder and

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acetone (100ml) were mixed and ground by agate motor for five hours. The fine powder was obtained. The fine powder was calcinated at $850\,^{\circ}C$ (five hours) for four different times. The four different powder was checked by X-ray diffraction (XRD). $CaCu_3Ti_4O_{12}$ pellets were produced using PVA as a binder and applying pressure of 15 ton/cm^2. The pellets were heated at $700\,^{\circ}C$ for one hour. The $CaCu_3Ti_4O_{12}$ ceramics were obtained. Each pellet of diameter and the thickness are 10mm and 3 mm. The block diagram of the sample preparation and the photo of the samples were shown in Figure 1 and Figure 2.
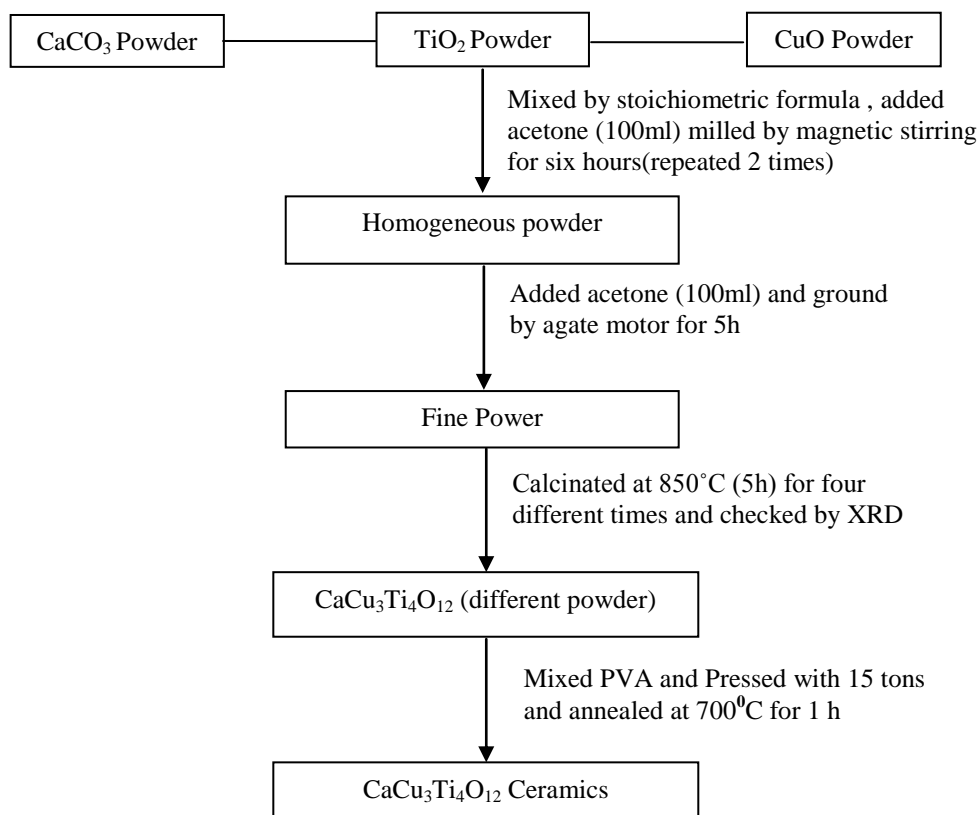
CaCO₃ Powder	TiO₂ Powder	CuO Powder

Mixed by stoichiometric formula , added acetone (100ml) milled by magnetic stirring for six hours(repeated 2 times)

Homogeneous powder

Added acetone (100ml) and ground by agate motor for 5h

Fine Power

Calcinated at 850°C (5h) for four different times and checked by XRD

$CaCu_3Ti_4O_{12}$ (different powder)

Mixed PVA and Pressed with 15 tons and annealed at $700\,^{0}C$ for 1 h

$CaCu_3Ti_4O_{12}$ Ceramics

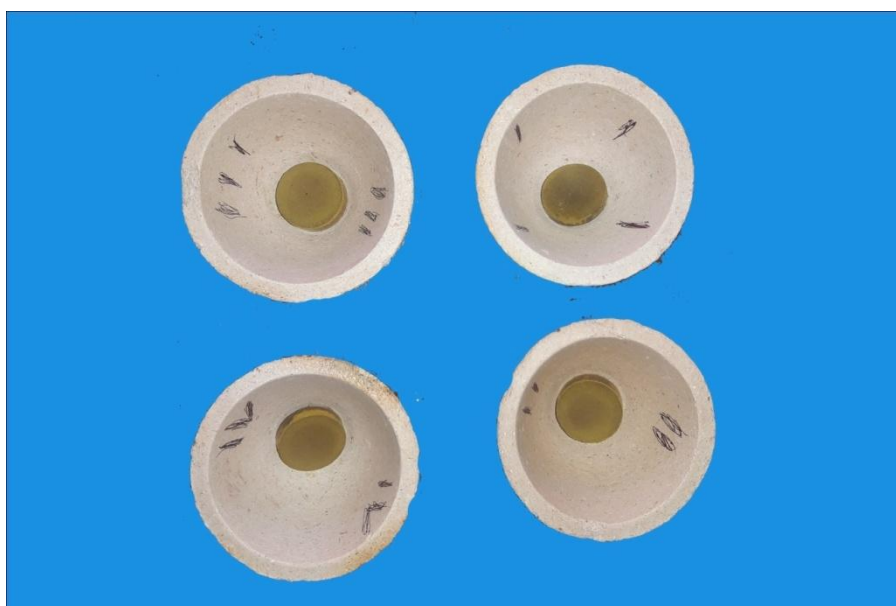**Figure 1** The block diagram of the preparation for $CaCu_3Ti_4O_{12}$ ceramics

Figure 2 The photo of $CaCu_3Ti_4O_{12}$ ceramics at 850°C for 5h, 4 different heat treatments.

Results and Discussion

Structural characterization

The XRD (X-ray diffraction) patterns of the powder samples were shown in figure2. From the XRD all profiles, the maximum intensity occurred at (220) plane. The average lattice constants of samples at (220) peak are calculated to be a =b= 7.3820 Å, 7.3861 Å, 7.3819 Å, 7.3790Å from the refinement of the XRD data. The structure of the samples was matched with cubic. The crystallite size was calculated by the Scherrer equation (Kittel, C.1956). The average crystallite sizes of samples were 1.008 nm, 1.067 nm, 1.107 nm, and 1.099 nm. The XRD pattern of samples at 850˚C(5h) for four different heat treatments were shown in Figure (3.a), (3.b), (3.c), and (3.d).
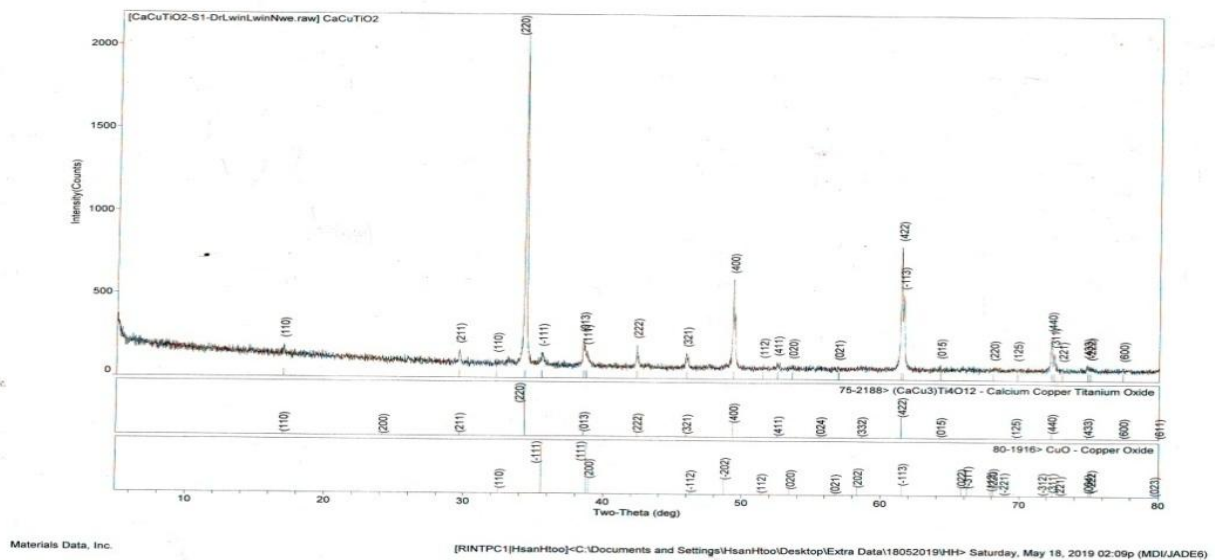

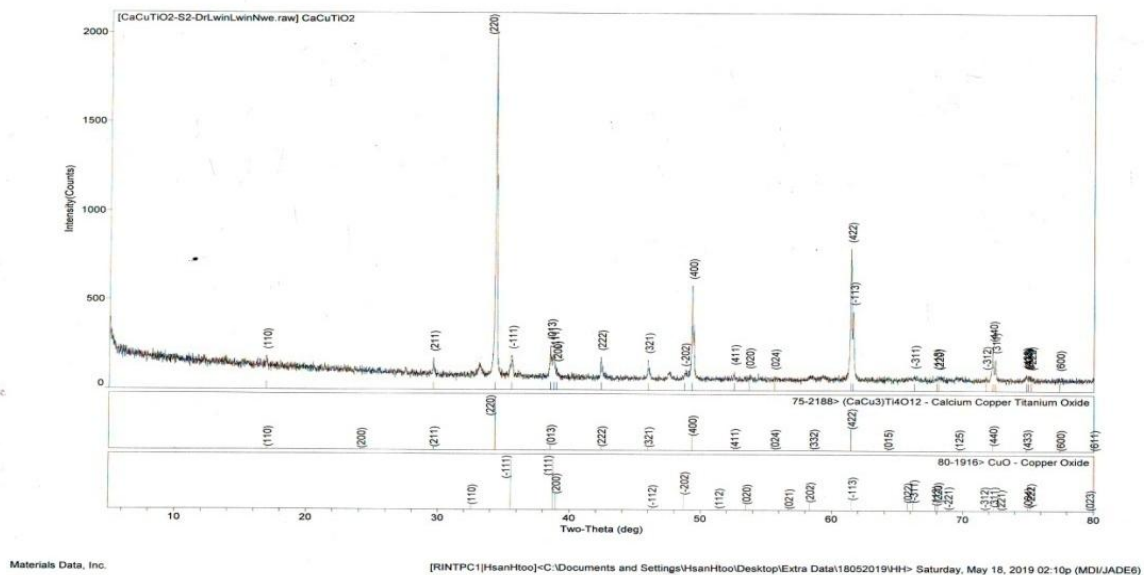**Figure 3 (a)**The XRD patterns of $CaCu_3Ti_4O_{12}$ powder at 850˚C for 5h,(heat treatments 1 times)

Figure 3(b) The XRD patterns of $CaCu_3Ti_4O_{12}$ powder at 850˚C for 5h, (heat treatments 2 times)

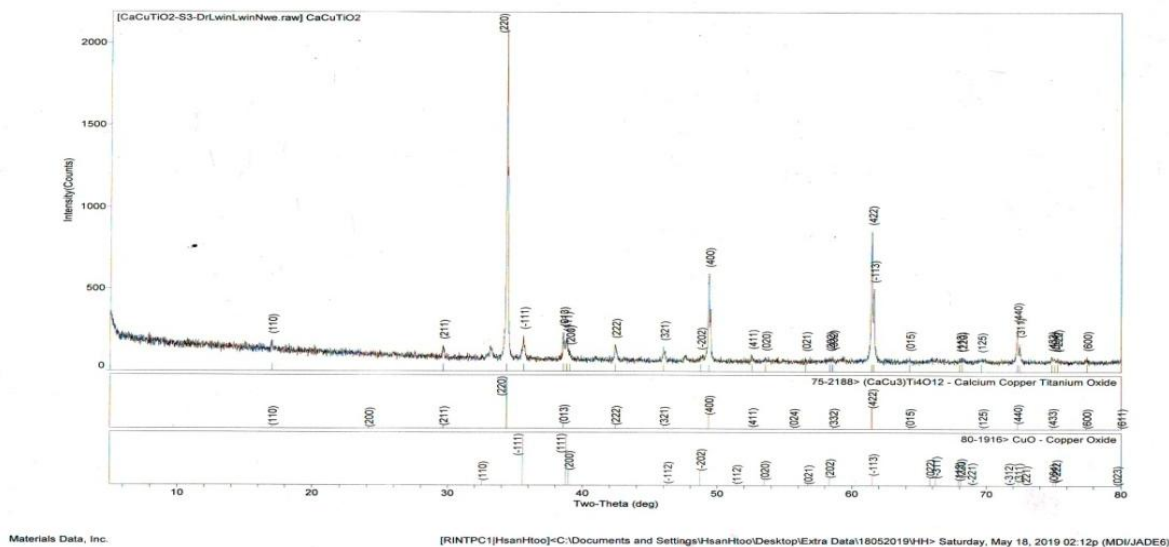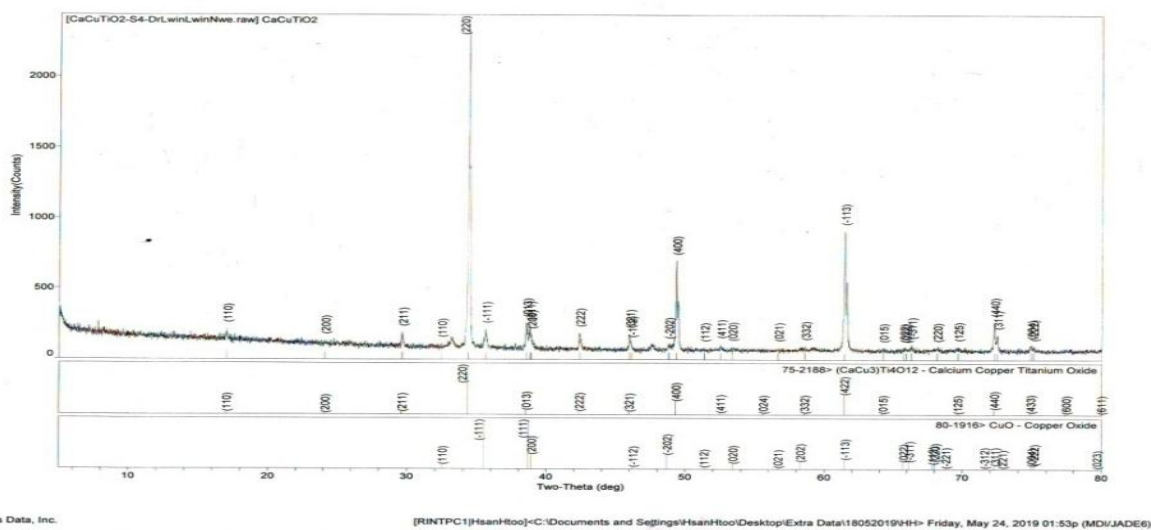**Figure 3(c)** The XRD patterns of $CaCu_3Ti_4O_{12}$ powder at 850°C for 5h, (heat treatments 3 times)

Figure 3 (d) The XRD patterns of $CaCu_3Ti_4O_{12}$ powder at 850°C for5h,(heat treatments 4 times)

Surface morphology analysis

Figure 4. showed the scanning electron microscope (SEM) images of $CaCu_3Ti_4O_{12}$ powder with the same temperature (850°C) for five hours, four different heat treatment times. The measurement was performed by 15 kV (accelerating voltage) and 50 mA (beam current). From the SEM images, the average grain sizes of sample powers were 0.143μm, 0.268μm, 0.314μm, and 0.342μm respectively.
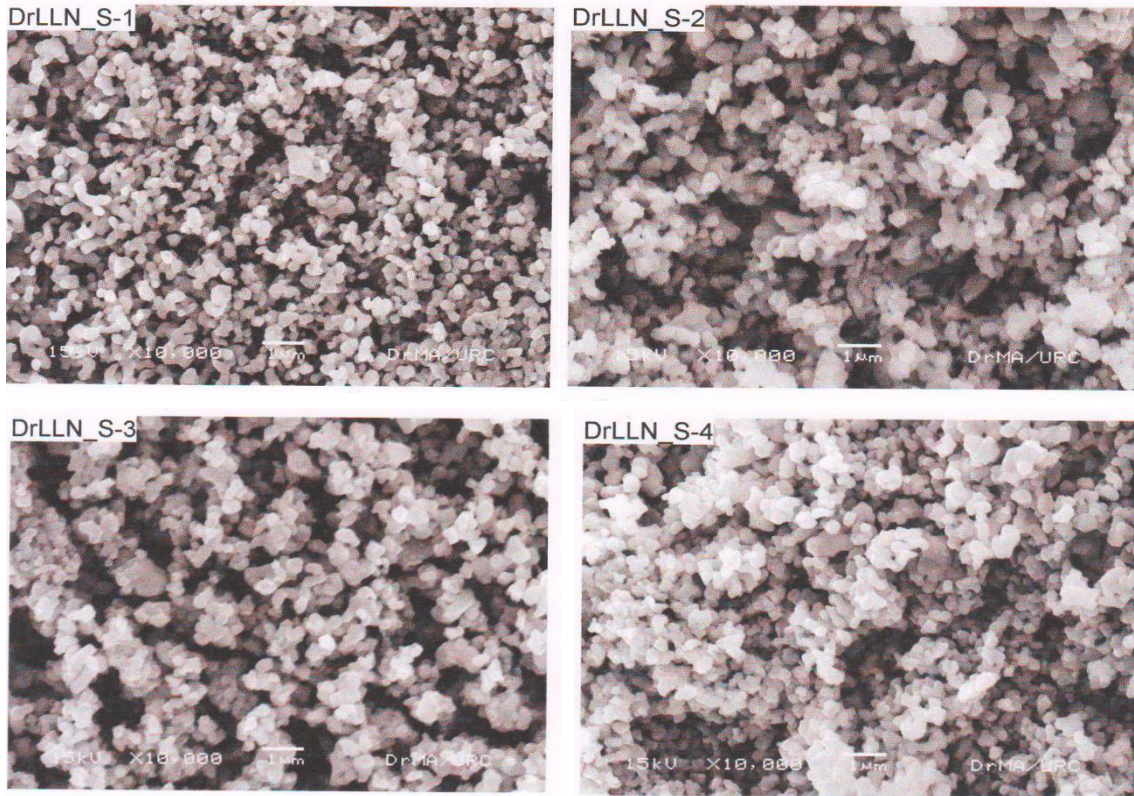
Figure 4 The SEM images of $CaCu_3Ti_4O_{12}$ powder at 850˚C for 5h, 4 different heat treatments

Measurement of LCR meter and calculations

The capacitive properties of samples were measured by using LCR meter with respect to frequency in the region (1 kHz-25 kHz). The dielectric constant, dielectric loss and conductivity of samples were calculated by using the following equations(1),(2) and (3).

$$C = \varepsilon_0 \varepsilon_r A/d \qquad (1)$$

Where, C= the capacitance, ε_0= the permittivity of free space, ε_r= the dielectric constant, d= the distance between the electrodes, A= the area of the electrodes

$$\tan\delta = D/\varepsilon_r \qquad (2)$$

Where, $\tan\delta$= the dielectric factor, D= the dissipation factor

$$\sigma = 1/\rho \qquad (3)$$

Where, σ= the conductivity of ceramic, ρ= the resistivity of ceramic

From the calculation results, it was found that the dielectric constant was higher in the lower frequency region. It decreases with increasing frequency and becomes almost nearly equal at a higher frequency region. It can be seen that the dielectric constant decreases with increasing frequency. It means that the dielectric constant of these samples was the strong function of frequency. The average dielectric constant of four samples in the range 1kHz to 25 kHz at room temperature found to be ε_r = 94.4, 99.4, 112.7, and 133.7 respectively. The dielectric loss of samples decreased with increasing frequency heat-treated times. The dielectric varying with increasing frequencies of $CaCu_3Ti_4O_{12}$ ceramics at 850˚C for 5h, 4 different heat treatments were shown in Figure 5.
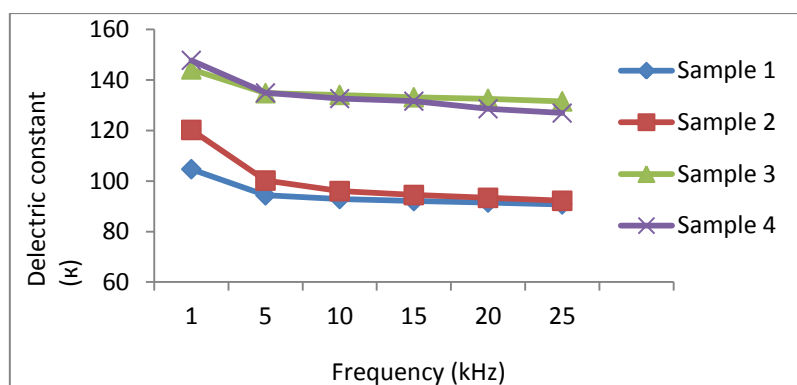
Figure 5 The dielectric varying with the frequency of $CaCu_3Ti_4O_{12}$ ceramics at 850°C (5h), 4 different heat treatments

The electrical conductivity of ceramics was calculated. The capacitive properties and conductivities of samples were shown in Table 1, 2, 3 and 4. The graph of conductivity with respect to frequency was shown in Figure 6. From the result and graph, the conductivity of samples increases with increasing frequency applied. It may be said that the possibility of the use of these materials in high-frequency device applications.

Table 1 The values of capacitive effect of $CaCu_3Ti_4O_{12}$ Ceramic at 850°C (5h) for one time

Frequency (kHz)	Capacitance (pF)	Dissipated factor(D)	Dielectric constant (ε_r)	Resistance (kΩ)	Tan δ (x10⁻³)	Conductivity (mho/m)
1 kHz	2.426	0.122	104.69	7347.00	1.170	0.052
5 kHz	21.87	0.048	94.35	633.55	0.510	0.603
10 kHz	2.152	0.038	92.88	263.52	0.410	1.450
15 kHz	2.134	0.032	92.07	129.79	0.350	2.943
20 kHz	2.120	0.027	91.49	101.46	0.300	3.765
25 kHz	2.103	0.026	90.76	78.39	0.290	4.873

Table 2 The values of capacitive effect of $CaCu_3Ti_4O_{12}$ Ceramic at 850°C(5h) for two times

Frequency (kHz)	Capacitance (pF)	Dissipated factor(D)	Dielectric constant(ε_r)	Resistance (kΩ)	Tan δ (x10⁻³)	Conductivity (mho/m)
1 kHz	2.786	0.175	120.22	5886.67	1.456	0.065
5 kHz	2.322	0.158	100.19	2395.95	1.577	0.159
10 kHz	2.225	0.103	96.02	581.40	1.073	0.657
15 kHz	2.189	0.079	94.46	428.28	0.836	0.892
20 kHz	2.163	0.066	93.34	278.20	0.707	1.373
25 kHz	2.136	0.058	92.17	201.69	0.629	1.894

Table 3 The values of capacitive effect of CaCu₃Ti₄O₁₂Ceramic at 850°C (5h)for three times

Frequency (kHz)	Capacitance (pF)	Dissipated factor(D)	Dielectric constant(ε_r)	Resistance (kΩ)	Tan δ (x10^{-3})	Conductivity (mho/m)
1 kHz	3.341	0.221	144.17	6097.83	1.533	0.063
5 kHz	3.123	0.039	134.77	507.28	0.280	0.753
10 kHz	3.107	0.028	134.08	154.19	0.209	2.477
15 kHz	3.085	0.024	133.14	120.67	0.180	3.166
20 kHz	3.071	0.023	132.52	79.24	0.174	4.821
25 kHz	3.040	0.022	131.52	56.46	0.166	6.766

Table 4 The values of capacitive effect of CaCu₃Ti₄O₁₂Ceramic at 850°C(5h) for four times

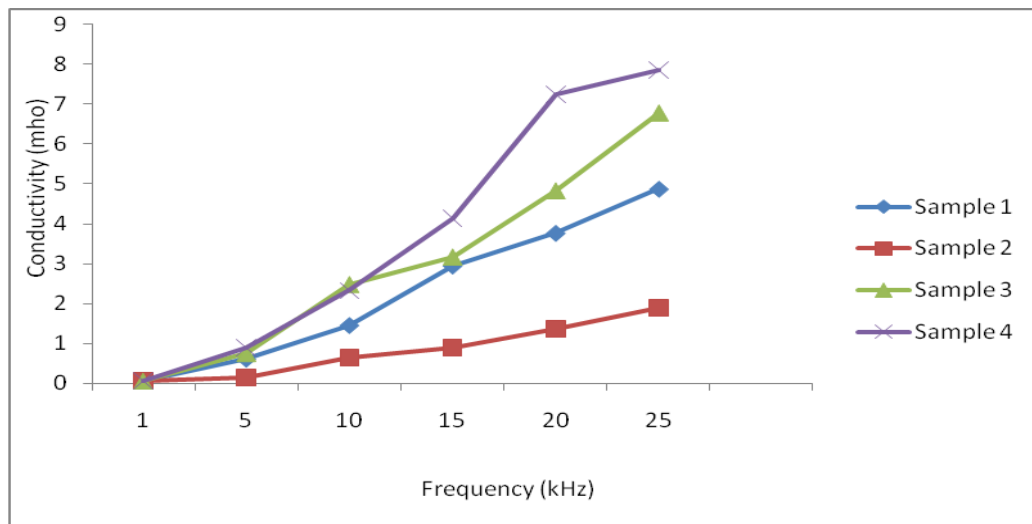| Frequency (kHz)	Capacitance (pF)	Dissipated factor(D)	Dielectric constant(ε_r)	Resistance (kΩ)	Tan δ (x10^{-3})	Conductivity (mho/m)
1 kHz	3.424	0.122	147.76	5567.20	0.825	0.069
5 kHz	3.125	0.051	134.87	425.95	0.378	0.897
10 kHz	3.073	0.039	132.62	146.12	0.294	2.328
15 kHz	3.049	0.032	131.59	92.09	0.234	4.148
20 kHz	2.979	0.026	128.57	62.82	0.202	7.232
25 kHz	2.941	0.023	126.89	48.65	0.181	7.852

Figure 6   The conductivity vary with the frequency of CaCu₃Ti₄O₁₂ ceramics at 850°C (5h), 4 different heat treatments

Conclusion

CaCu₃Ti₄O₁₂ ceramics were synthesized by a solid-state reaction method. The cubic structure of ceramics was confirmed by XRD patterns. The formation of microstructures with the well-defined grain size of samples was determined by the SEM result. Samples were free crack. The dielectric constant of samples with a frequency increase in heat treatment times. If the temperature of heat-treated and time taken may be increased, the dielectric constant of samples will be increased

Acknowledgments

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