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Dielectric Properties of $CaCu_3Ti_4O_{12}$ Ceramics by Modified Solid State Reaction Method of Preparation

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Abstract: ***In this work, an attempt has been made to study dielectric properties of $CaCu_3Ti_4O_{12}$ ceramics. For this, $CaCu_3Ti_4O_{12}$ was prepared by a modified solid state reaction method. The dielectric constant (ε') and dielectric loss (tan δ = ε''/ε') were measured within the frequency range from 10^2 Hz to 10^6 Hz and the temperature ranging from 30°C to 300°C using HP 4192A LF Impedance Analyzer. The results showed that the dielectric constant and dielectric loss of the sample are frequency dependent and temperature dependent. Dielectric constant and dielectric loss increases with decreasing frequency and increasing temperature due to interfacial polarization. The ceramics were prepared to use as an active dielectric medium in polymer composites.***

Key Word: $CaCu_3Ti_4O_{12}$, dielectric constant (ε') dielectric loss (tan δ = ε''/ε')

Introduction: Dielectric materials with high dielectric constant, good thermal stability and lead free have particularly attracted ever-increasing attention for their practical applications in micro-electronics [1]. Calcium copper titanate ($CaCu_3Ti_4O_{12}$), a perovskite-like (ABO_3) body-centered cubic oxide has attracted great attention for its giant dielectric constant, since its discovery by Subramaniam et. al. [2]. In $CaCu_3Ti_4O_{12}$, Ca and Cu ions reside at the A-sites, while Ti cations occupy the B-site. $CaCu_3Ti_4O_{12}$ shows great promise in dielectric applications owing to its essentially temperature and frequency independent dielectric constants ranging from about 10,000 for polycrystalline powders to 100,000 for single crystals [3]. $CaCu_3Ti_4O_{12}$ does not undergo any structural change over the large temperature range 100 to 600K although its dielectric constant abruptly decreases to less than 100 below 100K, showing a Debye-like relaxation. This excellent property renders this material particularly attractive for a wide range of applications [4]. In this paper, we report the dielectric properties of $CaCu_3Ti_4O_{12}$ by a modified solid state reaction method.

Experimental: $CaCu_3Ti_4O_{12}$ (CCTO) polycrystalline ceramics were prepared by solid-state reaction. Powders of CaO (99.95%), CuO (99.9%), and TiO_2 (99.7%) were used as starting materials. Stoichiometric amounts were weighed and mixed by ball milling in a rubber lined mill with zirconia balls, for 24 hours. The ball milled powder is then sieved using a 5 μm mesh. The sieved powder was compacted lightly in a crucible made of high grade alumina. Since the particle size of the constituent oxides plays a major part in the physical properties of the ceramic, therefore sieved powder was again sieved before compaction and sintering[5]. The gas, thus flushing out any traces of atmospheric oxygen. This is modified solid state reaction mentioned in the mixed powders were poured in a crucible and then calcined in air at 1100°C for 10 hours. The calcined powders were again milled and then sieved. They were pressed in a vanadium steel die with a 25 ton force acting on 2 cm^2 area, into pellets of cylinder shape with appropriate thickness, 4% by weight of the powder, poly vinyl alchohol was added as binder to form pellets. The pellets were sintered at 1250°C for 11 hours and then cooled to room temperature in the furnace. The sintering was done in an inert atmosphere. The inert atmosphere was maintained by continuously supplying Argon context. The crystal structures of the sample were examined by X-ray diffraction (XRD). The dielectric properties of the sample were determined using the HP 4192A LF Impedance Analyzer in the frequency range from 10 Hz to 10^6 Hz at 30^0C and 50°C – 300°C in the intervals of 50°C.

Results and Discussion: Table 1 and 2 shows the values of the dielectric constant and dielectric loss for $CaCu_3Ti_4O_{12}$ measured at 30^0C to 300^0C. From the table, it is clear that the values of both dielectric constant and dielectric loss increase as temperature increases, however as frequency increases, the values of dielectric constant and dielectric loss decrease.

Table-1: Dielectric constant (ε') for $CaCu_3Ti_4O_{12}$ measured at different temperatures

Frequency (Hz)	Dielectric Constant (ε') of $CaCu_3Ti_4O_{12}$						
	Temperature (^{0}C)						
	30^{0}C	50^{0}C	100^{0}C	150^{0}C	200^{0}C	250^{0}C	300^{0}C
100	177	181	218	443	695	715	1080
1000	139	140	184	234	432	399	459
10000	123	121	133	165	238	309	311
100000	120	119	121	134	154	198	256
1000000	110	109	111	124	144	164	240

Table-2: Dielectric loss (tan δ = ε''/ε') for $CaCu_3Ti_4O_{12}$ measured at different temperature

Frequency (Hz)	Dielectric Loss (tan δ = ε''/ε') of $CaCu_3Ti_4O_{12}$						
	Temperature (^{0}C)						
	30^{0}C	50^{0}C	100^{0}C	150^{0}C	200^{0}C	250^{0}C	300^{0}C
100	2.457	2.240	2.200	1.650	6.800	45.450	166.666
1000	0.474	0.500	0.430	0.641	1.440	8.470	38.120
10000	0.081	0.086	0.203	0.272	0.640	1.290	5.850
100000	0.011	0.010	0.0325	0.141	0.240	0.480	0.929
1000000	0.0036	0.0027	0.0063	0.044	0.190	0.230	0.400

Figures 1 and 2 represent the dielectric constant and dielectric loss of $CaCu_3Ti_4O_{12}$ ceramics measured at different temperatures. The sample exhibits giant dielectric constant (1080) at low frequency for 300°C. As frequency increase, dielectric constant drastically decreases and approaching a constant value at 10^6Hz. The increase of dielectric constant as frequency decreases could possibly be due to interfacial polarization. The charge carriers may be blocked at the electrode interface under the influence of an electric field. It has been reported that $CaCu_3Ti_4O_{12}$ ceramics consist of insulating grain boundaries and semiconducting grains. The charge carriers accumulated at the interface between semiconducting grains and insulating grain boundaries resulted in an increase in the dielectric constant. This is in concordance with Inter Layer Barrier Capacitor (ILBC) model[6]. Dielectric loss factor of the sample exhibits dc conduction losses. It shows the dielectric loss of $CaCu_3Ti_4O_{12}$ drastically decreases with increasing frequency. The dielectric loss increases with temperature from 30°C to 300°C. The frequency and temperature effect on the dielectric loss illustrates the interfacial polarization of the grain boundaries within the sample. The dielectric constants of $CaCu_3Ti_4O_{12}$ at selected frequencies such as 10^2 Hz, 10^3 Hz, 10^4 Hz, 10^5 Hz and 10^6 Hz with respect to temperature (30°C–300°C) are given in Figure 3. It exhibits the temperature dependence of $CaCu_3Ti_4O_{12}$. The dielectric constant of $CaCu_3Ti_4O_{12}$ increases with increasing temperature. The increment of dielectric constant is low from 30°C–250°C especially during higher frequencies. This means that there exists mechanical limitation where lack of interfacial polarization occurs at higher frequencies. The large variation from 250^{0}C to 300^{0}C at low frequencies is due to the increase in interfacial polarization. Figure 4 shows that the dielectric loss drastically increases as the temperature increases.

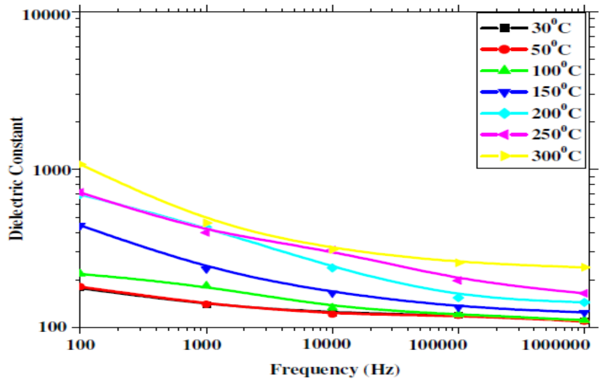

Figure-1: Dielectric constant of $CaCu_3Ti_4O_{12}$ measured at different temperature

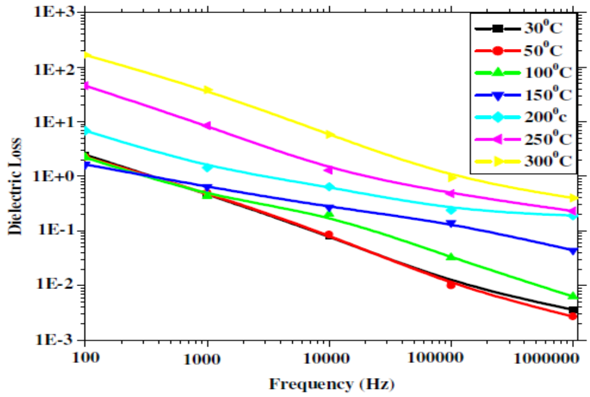

Figure-2: Dielectric Loss of $CaCu_3Ti_4O_{12}$ measured at different temperatures

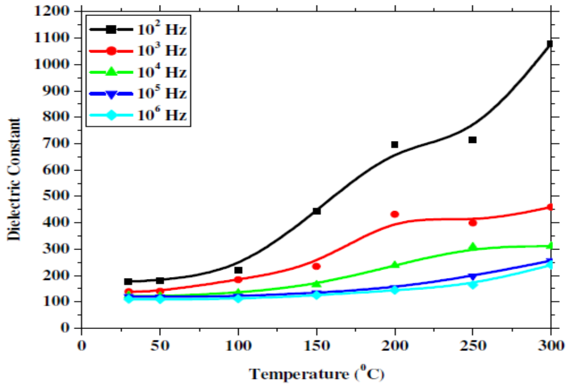

Figure-3: Dielectric constant of $CaCu_3Ti_4O_{12}$ with respect to temperature at selected frequencies

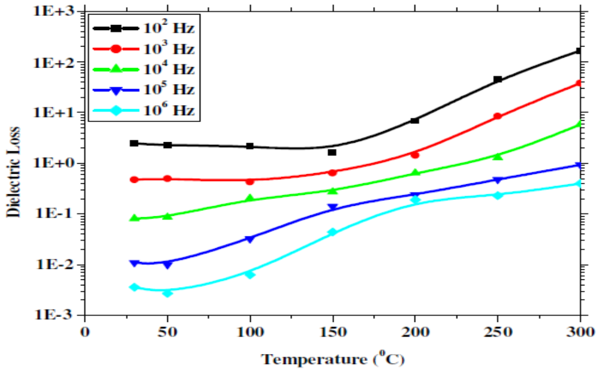

Figure-4: Dielectric Loss of $CaCu_3Ti_4O_{12}$ with respect to temperature at selected frequencies

Conclusions:

From the experimental results, $CaCu_3Ti_4O_{12}$ with high dielectric constant was successfully prepared via modified solid state reaction method. It can be observed that the dielectric properties of $CaCu_3Ti_4O_{12}$ ceramics are very sensitive to processing[7]. The dielectric constant and dielectric loss decrease with an increase in frequency. The dielectric constant and dielectric loss increase with an increase in temperature.

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