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# Dielectric properties of CaCu₃₋ₓMgₓTi₄O₁₂ (x=0.20 & 0.50) material synthesized by the semi-wet route for energy storage capacitor

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## Abstract

Dielectric properties of high percentage Mg doped $CaCu_3Ti_4O_{12}$, $CaCu_{3-x}Mg_xTi_4O_{12}$ (x=0.20 & 0.50) ceramics carried out. They were synthesized by the semi-wet route using a solution based citrate–nitrate method along with inexpensive solid $TiO_2$ powder. X-ray diffraction analysis reveals that the ceramics form single phase when sintered at 950 ºC for 12h. SEM analyses show the smooth surfaces of grains with a spherical appearance. The grains of CCMTO2 and CCMTO5 ceramics were found to be in the size range of 1-5 μm and 1-3 μm, respectively. Dielectric studies show that the CCMTO2 ceramic has higher value of dielectric constant and lower dielectric loss in comparison to that of CCMTO5.

*Keywords*: Ceramics; Oxides; Chemical synthesis; Calcium copper titanate;

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## 1. Introduction

It is well known that $CaCu_3Ti_4O_{12}$ (CCTO) perovskite oxide possess high dielectric constant with good thermal stability [1]. Several other ceramic materials such as hexagonal $BaTiO_3$ and (Li, Ti) doped NiO etc. possessing colossal high dielectric constant are also reported [2, 3]. CCTO with very high dielectric constant in the range, $10^4$-$10^5$, at radio frequency and below near room temperature shows a good temperature stability over a wide temperature range from 100-600 K [4,

5]. Also, its cubic structure (a=7.391 Å) remains unchanged, suggesting thereby that no structural phase transition occurs. There are several explanations for the origin of colossal dielectric property of CCTO but the intrinsic or extrinsic effects are the most important among them. While the intrinsic model is attributed to local dipole moments related to off–canter displacement of Ti ions [6], the evidences of the extrinsic model come from impedance spectroscopy measurements [7], first-principle calculations [8], infrared measurements [9], in-homogeneity morphology analysis [10], the electrode polarization effect [11], and the heat treatment effects [12-14]. However, the internal barrier layer capacitor (IBLC) model representing semiconducting grains and insulating grain boundaries [15] has been widely accepted for the abnormal dielectric response in CCTO. The origins of semi-conductive grains and highly resistive grain boundary were not established, but two models, oxygen loss and oxygen stoichiometric have been proposed. The dielectric response of this material was found to be very sensitive to the microstructure (such as grain size) and processing condition [16] as well as doping [17, 18]. There are many examples for doping effects of different ions in the literature such as substitution of Mn, Zn and Mg for Cu [19-24], La for Ca [25, 26], W for Ti site [27]. In the present paper, the high percentage of Mg substituted CCTO, $CaCu_{3-x}Mg_xTi_4O_{12}$ (x=0.20 & x=0.50) ceramics were synthesized by the semi-wet route. The resulting ceramic shows higher $Mg^{2+}$ solubility in $CaCu_{3-x}Mg_xTi_4O_{12}$ system x $\leq$ 0.50 due to diffusion of metal cations at atomic scale than other solid state ceramic routes reported earlier [28-29].

## 2. Experimental

Analytical grade chemicals Ca $(NO_3)_2.4H_2O$, $Cu(NO_3)_2.3H_2O$, $Mg(NO_3)_2.2H_2O$, $TiO_2$ and citric acid, having purity of ~ 99.5% were used as starting materials for synthesizing $CaCu_{3-x}Mg_xTi_4O_{12}$ (where x= 0.20 and 0.50) abbreviated as CCMTO2 and CCMTO5, respectively. Aqueous solutions of calcium nitrate, copper nitrate and magnesium nitrate, in stoichiometric amount, were mixed in a beaker and calculated amounts of solid $TiO_2$ and aqueous citric acid were added to the mixture. The heterogeneous solution was heated on a hot plate using a magnetic stirrer at 70-80 ºC to evaporate water and dried at 100-120 ºC in hot air oven for 12 h to yield a blue gel. The gel was calcined in air at 800 ºC for 6 h in a muffle furnace. The resultant mixtures were converted into fine powder using a pestle and mortar and then it was used to make cylindrical pellets using hydraulic press. The pellets were sintered at 950 ºC for 12 h in air. The crystalline phases of the sintered ceramics were identified using an X-ray Diffractometer (Rich-Siefert, ID-3000) employing Cu-K$_\alpha$ radiation. The particle size was examined using high resolution transmission electron microscope (FEI Technai F30). The microstructures of the fractured surface were examined using a Scanning Electron Microscope (JEOL JSM5410) attached with EDX analyser. The dielectric and impedance measurements were made using pellets, both surfaces of which were polished and coated with silver paint, by the impedance analyzer (HP 4294 A).

## 3. Results and discussion

XRD patterns of CCMTO2 and CCMTO5 electro-ceramics sintered at 950 ºC for 12h are shown in Fig.1. X-Ray data were indexed on the basis of a cubic unit cell similar to un-doped CCTO (JCPDS 75-2188), which confirm the formation of its single phase. The lattice parameters determined by the least square refinement method using most intense (220) diffraction peak, are 7.394 and 7.400 Å, respectively for CCMTO2 & CCMTO5. There is no evidence of the presence

of secondary phase. XRD patterns show the presence of split peaks for the reflections at 400, 422 and 440. This may be due to presence of Cu-K$\alpha_2$ along with Cu-K$\alpha_1$ in the X-ray radiations used for the diffraction studies.
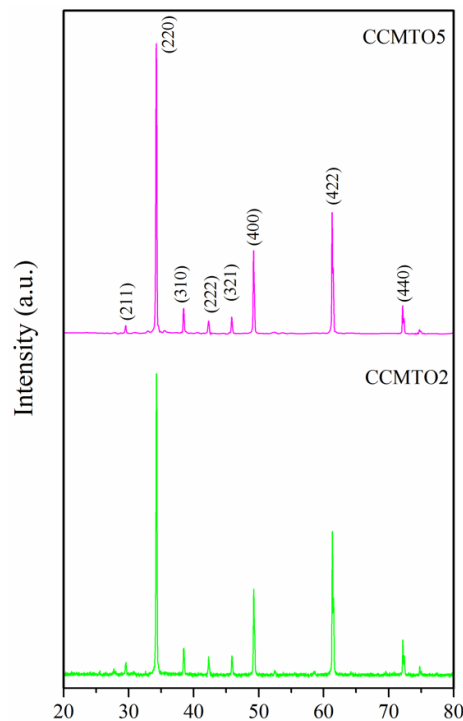


Fig. 1 X-ray powder diffraction patterns of CaCu$_{3-x}$Mg$_x$Ti$_4$O$_{12}$ (x=0.20 & 0.50) sintered at 950 °C for 12h.

Fig. 2 (a, b) shows a representative bright field TEM image and corresponding selected area electron diffraction patterns (SAED) of the CCMTO2 ceramic. The particle size was found to be in the range of 70±12 nm. In addition, the SAED pattern 2 (b) confirmed the presence of single-phase polycrystalline material. The diffraction patterns have been indexed on the basis of cubic crystal structure with (220) plane. The additional spots observed in the SAED patterns are from adjacent grains and sub-grains due to their orientation in diffraction directions.
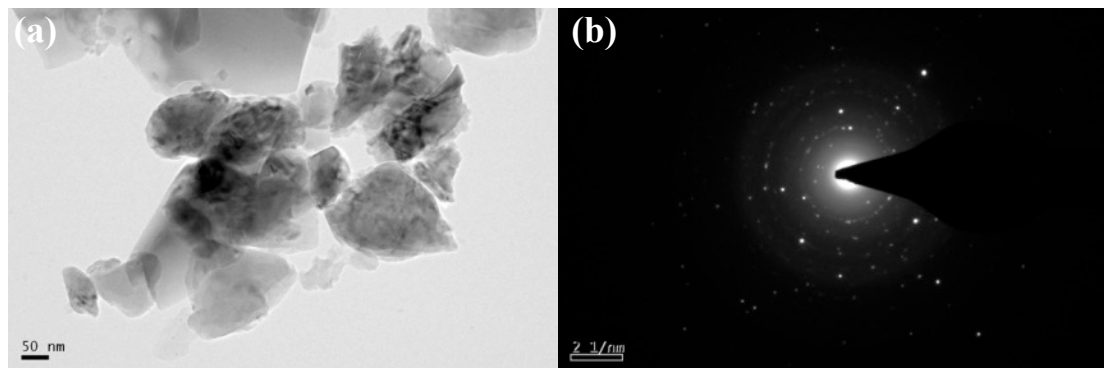


Fig. 2 (a) Bright field TEM images (b) Corresponding selected area diffraction pattern (SAED) of CCMTO2 sintered at 950°C for 12h.

The microstructures of the CCMTO2 and CCMTO5 electro-ceramics are shown in Fig. 3. The grain size range of CCMTO2 and CCMTO5 are 1-5 μm and 1-3 μm, respectively. The CCMTO ceramics with x = 0.20 and 0.50 exhibit dense microstructure with abnormally large grains with very small grains segregating at grain boundaries. The grains of both ceramics have smooth surfaces associated with a spherical appearance. The CCMTO2 displayed the significant feature that the grains are surrounded by secondary phase of CuO along with some amount of Mg and Ti present at grain-boundaries. The presence of CuO rich phase formation of insulating grain boundary layers can be regarded as a predominant reason for the high dielectric permittivity.
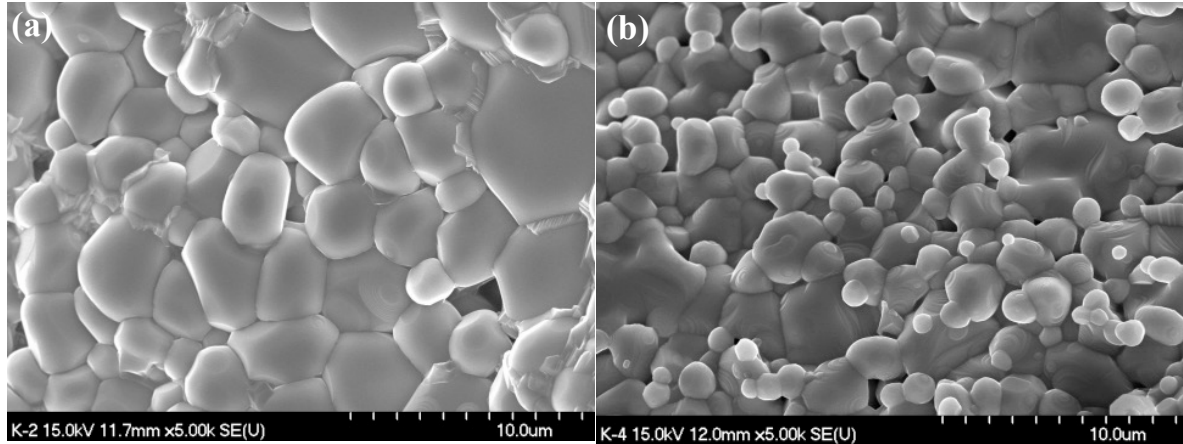


Fig. 3 SEM micrographs of (a) CCMTO2 and (b) CCMTO5 sintered at 950ºC for 12h.

The atomic percentage data of grains and grain-boundaries for CCMTO2 composition were also obtained by Energy dispersive X-ray (EDX) analysis. The atomic percentage of elements Mg, Ca, Ti and Cu, at grains 2.34, 12.41, 48.83 and 36.43 and at grain-boundaries 1.32, 6.93, 24.90 and 66.86, respectively. The EDX data of grain-boundary shows the copper rich phase with Mg & Ti content grain-boundary. The presence of rich CuO phase at the grain-boundaries suggests that the grain boundary effects are responsible for the enhanced dielectric permittivity [30, 31].

Plots of dielectric constant ($\varepsilon_r$) and dielectric loss (tanδ) as a function of temperature of CCMTO2 and CCMTO5 ceramics for few selected frequencies are shown in Figs. 4(a, b) and 5(a, b), respectively. It is apparent that both the ceramics exhibit high dielectric constant. The values of dielectric constant of these ceramics are higher than those of un-doped CCTO reported earlier [32]. The values of dielectric constant of CCMTO2 and CCMTO5 were found to be $\varepsilon_r \sim$ 32.5 x $10^3$ and 9.8 x $10^3$ at 1 kHz and at 453 K, respectively and decrease in the case CCMTO5 with very high percentage (x=0.50) magnesium concentration. The dielectric constant of CCMTO5 at 10 kHz remains almost constant in the temperature range 300- 500 K while in the case of CCMTO2 it increases with increasing temperature beyond 400 K. The dielectric loss (tan δ) values of both CCMTO2 and CCMTO5 ceramics show the temperature dependent dielectric relaxation between 350-500 K.
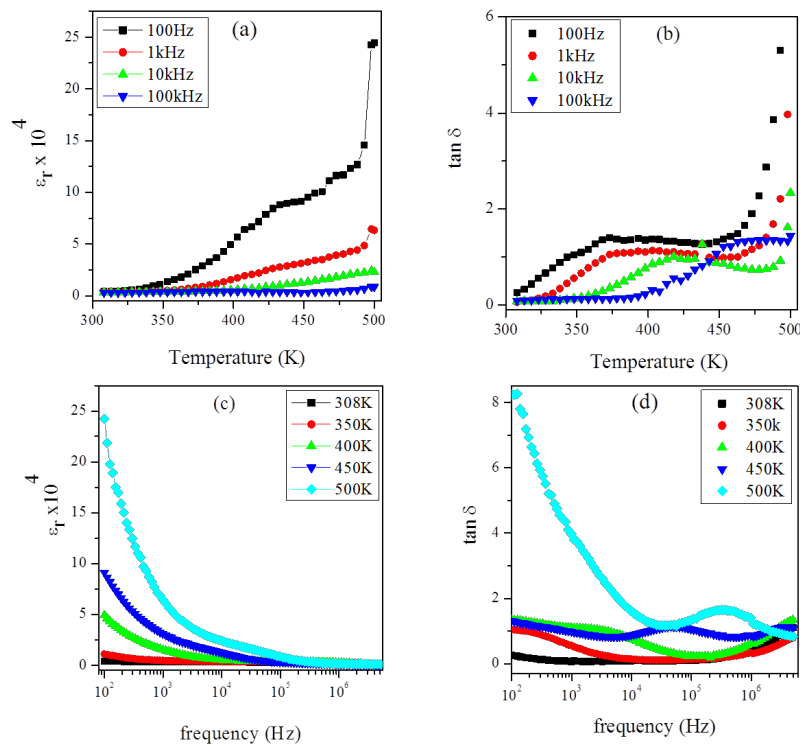
Fig. 4 Plots of (a) dielectric constant ($\varepsilon_r$) vs T (b) dielectric loss (tan$\delta$) vs T (c) dielectric constant ($\varepsilon_r$) vs $f$ (d) dielectric loss (tan$\delta$) vs $f$ for CCMTO2

Plots of dielectric constant ($\varepsilon_r$) and dielectric loss (tan$\delta$) as a function of frequency for CCMTO2 and CCMTO5 ceramics for few selected temperatures are shown in Fig. 4(c, d) and 5(c, d). The dielectric constant values for CCMTO2 & CCMTO5 ceramics decrease rapidly ($10^2$-$10^3$ Hz) and then remain nearly constant between 10 kHz –5 MHz. It is also noted that $\varepsilon_r$ values decrease with increasing frequency. The values of tan $\delta$ for the CCMTO2 and CCMTO5 at 453 K are 0.98 and 3.3, respectively at1 kHz. It is also observed from the figure that dielectric loss for both the ceramics show dielectric relaxation behaviour in low frequency range region (below than$10^3$ Hz) as well as in high frequency ranges (above$10^5$ Hz). The low frequency relaxation may be due to space charge polarization which arises when two phases of grain–grain boundaries of different electrical conductivity are in contact [33, 34]. The high frequency relaxation above $10^5$ Hz in these ceramics is probably due to the resonance effect arising from the stray inductance of the contacts [35].
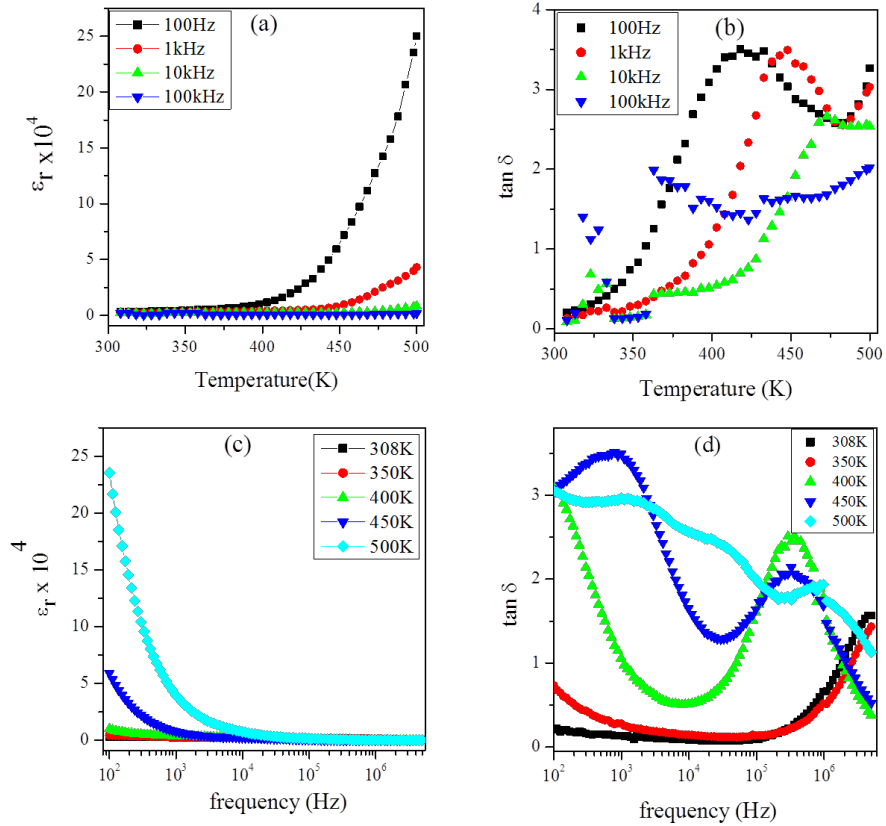
Fig. 5 Plots of (a) dielectric constant ($\varepsilon_r$) vs T (b) dielectric loss (tanδ) vs T (c) dielectric constant ($\varepsilon_r$) vs $f$ (d) dielectric loss (tanδ) vs $f$ for CCMTO5

The increase in dielectric constant by the substitution of Mg$^{+2}$ ions can be explained by the following mechanism: these ceramic materials are expected to loss of traces of oxygen during their sintering at high temperature in accordance with reaction given below [36];

$$O_o \leftrightarrow \frac{1}{2}O_2 + V_o^{\bullet\bullet} + 2e' \qquad (1)$$

where all the species are written in accordance with Kroger–Vink Notation of defects [37, 38]. Electrons released in the above reaction may be captured by Cu$^{2+}$ or Ti$^{4+}$ to produce Cu$^+$ or Ti$^{3+}$, respectively, as given below:

$$2Cu^{2+} + 2e^- \rightarrow 2Cu^+, \qquad (2)$$
$$2Ti^{4+} + 2e^- \rightarrow 2Ti^{3+}, \qquad (3)$$

The presence of Cu$^+$ and Ti$^{3+}$ in CCMTO ceramic was also reported by L. Ni et al. On increasing the Mg doping in CCTO, the ratio of Cu$^+$/Cu$^{++}$ and Ti$^{3+}$/Ti$^{4+}$ also increases and this was confirmed by X-ray photoelectron spectroscopy (XPS) studies [39, 40]. The formation of Cu$^+$ and $V_o^{\bullet\bullet}$ may be suggested in accordance with the following equation (7):

$$3Cu_{cu}^x + O_O^x \xrightarrow{MgO} Mg_{Cu}^x + 2Cu_{cu}' + V_o^{\bullet\bullet} + CuO + \frac{1}{2}O_2 \qquad (4)$$
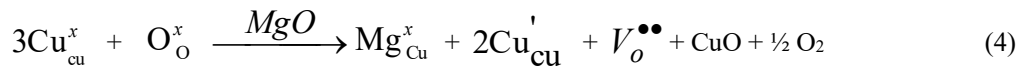
On substitution of one $Mg^{2+}$ cation at $Cu^{2+}$ site converted two $Cu^{2+}$ in to two $Cu^+$ ions at its lattice sites. In this process replaced $Cu^{2+}$ combine with vacated $O^{2-}$ ions and form CuO which segregated at grain boundary. The presence of CuO phase at grain-boundary was also supported by SEM and EDX analyses. These results conclude that on Mg doping in CCTO, oxygen vacancies and ratio of $Cu^+/Cu^{++}$ and $Ti^{3+}/Ti^{4+}$ ions increase. Therefore, the above results are responsible for high dielectric constant in Mg doped CCMTO2 and CCMTO5.

## 4. Conclusions

We have successfully synthesized high percentage Mg substituted CCTO, $CaCu_{3-x}Mg_xTi_4O_{12}$ (x= 0.20 & 0.50) ceramics at relatively low temperatures and short heat treatment duration. XRD patterns indicate that the ceramics form single phase. The SEM morphology shows the grains have smooth surfaces associated with a spherical appearance. The dielectric measurements show that $CaCu_{3-x}Mg_xTi_4O_{12}$ (x= 0.20 & 0.50) ceramics exhibit higher values of dielectric constant $\varepsilon_r \leq 10^3$.

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