# SYNTHESIS OF NANOSTRUCTURED CCTO & CCTO/MGTIO$_3$ COMPOSITE

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## Abstract

*The potential demand for miniaturization of electrical and electronic devices has raised a serious challenge for the development of capacitors with high dielectric constant and low loss. The high dielectric constant calcium copper titanate, $CaCu_3Ti_4O_{12}$(CCTO), and its isomorphs have attracted much attention for the development of promising capacitor materials for electronic industries. Being lead-free, it is environment-friendly possessing high dielectric constant which is nearly temperature independent in the range 100–600K.$CaCu_3Ti_4O_{12}$ (CCTO) is a novel material with high $\varepsilon_r$and high tanδ.One of the main problems of CCTO is the relatively high dielectric loss (tan δ) at room temperature which makes CCTO not attractive for practical applications.*

*In this work CCTO & $MgTiO_3$ were synthesized via co-precipitation method using surfactant, the samples were sintered at 800$^oC$ & 600$^oC$ respectively. The composites of CCTO/$MgTiO_3$ (2%, 4% & 6%)were prepared by using mixed oxide technique. The characterization for phase identification was done by using X-Ray diffraction, for surface morphology scanning electron microscope was used. XRD results showed the formation of CCTO & $MgTiO_3$ phase with few impurities.*

***Keywords:*** *$CaCu_3Ti_4O_{12}$ (CCTO), $MgTiO_{3,}$ Coprecipitation, Dielectric properties, XRD, SEM.*

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## 1. INTRODUCTION

Lead free dielectric materials possessing huge dielectric constant & good thermal stability have gained considerable attention for their practical applications in cellular phones, global positioning systems, resonators, filters, capacitors and memory devices (B. Renner et.al. 2004). There is a huge desire for miniaturization of electrical and electronic devices, material possessing high dielectric constant are required for miniaturization.$CaCu_3Ti_4O_{12}$(CCTO) has gained interest because of its very high (~$10^4$) dielectric constant, CCTO shows perovskite-related structure (with general formula, $ABO_3$) in which $Ca^{2+}$ and $Cu^{2+}$ share the A-site (M.A. Subramanian et.al. 2000; B. Bochu et.al. 1979). The size difference between $Ca^{2+}$& $Cu^{2+}$ causes the $TiO^6$ octahedral to undergo substantial tilting, leading to a bcc supercell of space group Im3 in which the $Ti^{4+}$ ions occupy centrosymmetric position in the octahedral sites. The angle of tilt is sufficiently large such that the $Cu^{2+}$ions occupy an essentially square-planer environment (T.B.Adams et.al. 2006).$BaTiO_3$ and $SrTiO_3$ based ferroelectricmaterials exhibit high $\varepsilon_r$but these materials are temperature dependent which is not desirable from the device points of view [X.J. Chou et al. 2007; C.Zhao et al. 2007). On the other hand, $CaCu_3Ti_4O_{12}$ (CCTO) ceramic has high $\varepsilon_r(10^4 – 10^5)$ independent of frequency ($10^2$ – $10^6$ Hz) & temperature (100- 600K) which is required for microelectronic applications. CCTO is usually prepared by the conventional solid-state reaction method from metal oxides at huge temperature with several intermediate grindings (T.B. Adams et al. 2002; D.C. Sinclair et al. 2002) but the disadvantages of solid state reaction method are chemical inhomogeneity and coarse.

Particle size of the powder. Unfortunately, the CCTO ceramic with high dielectric constant shows high dielectric loss that limits its practical applications. Intrinsic and extrinsic effects were suggested to be the cause that gives rise to very high $\varepsilon_A$ values. The extrinsic effect is widely accepted. (R. Schmidt et al. 2012; P. Thongbai et al. 2013; N. Sangwong et al. 2013). The underlying mechanism for the giant dielectric response is the internal barrier layer capacitor (IBLC) structure of a heterogeneous microstructure.

In this work, we synthesized CCTO and $MgTiO_3$byCo-precipitation method using surfactant and then composite of CCTO/$MgTiO_3$ by using mixed oxide technique.The microstructure and surface morphology was done by using XRD and SEM. Dielectric properties were measured by using Novotherm alpha-a high performance frequency analyser.

## 2. MATERIALS AND METHODS

All the chemicals used in the present investigation were of analytical grade. The raw materials used are salts of Ca, Cu & Ti, surfactant& AZS.

## 2.1 Synthesis of CCTO &$MgTiO_3$

Calcium copper titanium oxide is synthesized by using co-precipitation method. Initially the stoichiometric amount of salts of calcium (solution 1) and copper (solution 2) & surfactant (solution 3) added to water separately and stirred slowly till they get dissolved. The titanium precursor is prepared by adding titanium to IPA and stirred till the clear solution is obtained (solution 4). Then later solution 2, solution 3 and solution 4 was added drop wise by burette to solution 1 slowly and stirred for few minutes (solution 5). Later the proportionate amount of AZS is added to the above solution 5 slowly drop by drop to form the precipitate and then the solution is filtered and the obtained precipitate is dried at $100^0$C &sintered at $800^o$C.

$MgTiO_3$ was prepared by using co-precipitation method. Initially the stoichiometric amount of salts of magnesium (solution 1) & surfactant (solution 2) added to water separately and stirred slowly till they get dissolved. Thetitanium precursor is prepared by adding titanium to IPA and stirred till the clear solution is obtained (solution 3). Then later solution 2, solution 3 and solution 1 was added drop wise by burette to solution 1 and stirred for few minutes (solution 4). Then the proportionate amount of AZS is added to the above solution 4 slowly drop by drop to form the precipitate and then the final contents are stirred and the solution is filtered and the precipitate is dried at $80^0$C and sintered at $600^o$C.

## 2.2 Synthesis of CCTO/$MgTiO_3$ Composite

For the preparation of CCTO/$MgTiO_3$ composite the as prepared CCTO and $MgTiO_3$ were mixed by using mixed oxide technique by using different dopant concentration i.e. 2%, 4% and 6% mixing of this powders in pestle and mortar and then dried at $80^o$C. This powders were pressed into pellets & the dielectric properties of the samples were measured using Novotherm alpha-a high performance frequency analyser. The crystalline phase of the sample was analysed using X-Ray powder diffraction. The Microstructures of the sample were examined by using a SEM.

## 3. RESULTS & DISCUSSION

### 3.1 XRD Analysis

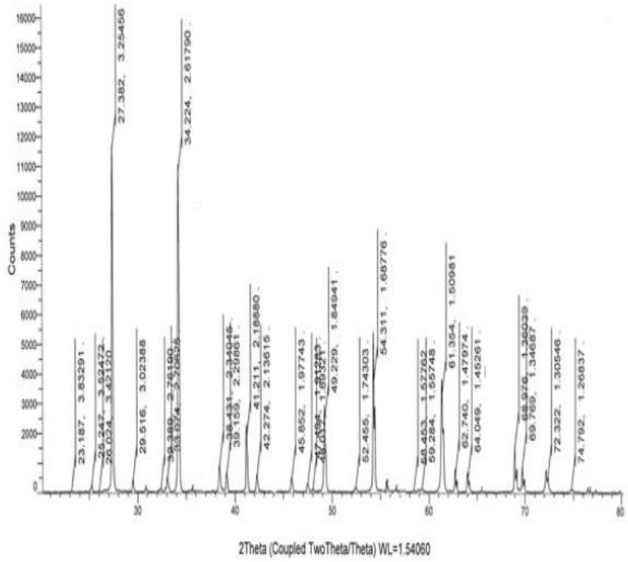


**Fig 1:** XRD patterns of CCTO

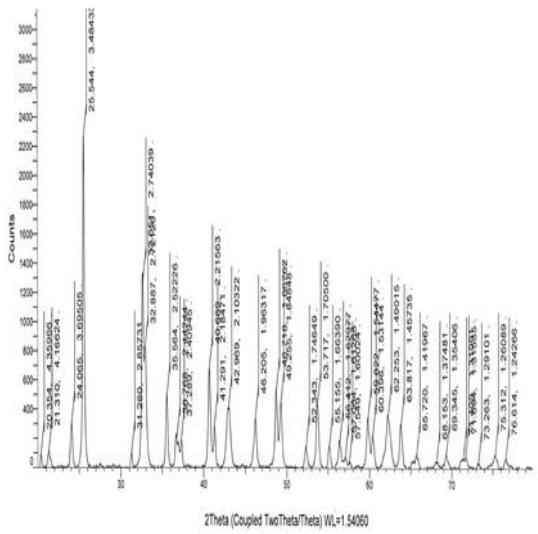


**Fig 2:** XRD patterns of $MgTiO_3$

Fig 1 shows the XRD patterns of CCTO samples. The sample showed the formation of CCTO phase the 2θ values was matched with the standard CCTO ICDD data (00-056-0767). Along with the CCTO phase secondary phases of CuO, $CaTiO_3$& $TiO_2$ were formed. The secondary phases formed were matched with the standard ICDD data (ICDD-00-005-0661),(ICDD-00-022-0153) & (ICDD-00-015-0875) respectively.

Fig 2 represents the XRD patterns of $MgTiO_3$ samples. The 2θ values matched with the standard $MgTiO_3$ ICDD data (00-006-0494). The secondary phases formed were matched with the standard $MgTi_2O_5$ ICDD data (00-035-0792), MgO (00-002-0829). The crystalline size of the CCTO & $MgTiO_3$ were in the range of 25-32nm.

## 4. MORPHOLOGICAL STUDIES

The morphological studies of CCTO and $MgTiO_3$ Nano powders are observed from SEM. Fig. 3(a) & 3(b) shows SEM image of CCTO&$MgTiO_3$ sample. The SEM images shows the formation of rod like structures &small grains like structure.

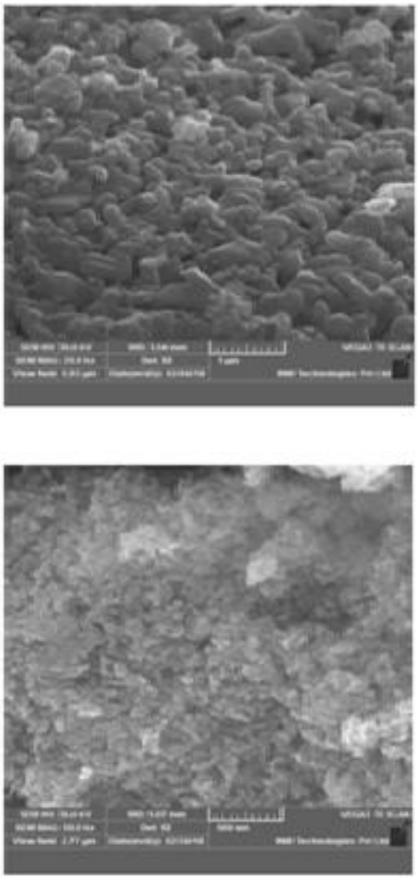

**Fig 3** SEM images of CCTO & $MgTiO_3$

## 5. DIELECTRIC MEASUREMENTS

The dielectric properties of the samples were measured using Novotherm alpha-a high performance frequency analyser at Room temperature & frequency range of 1Hz & 10000 kHz respectively. Frequency dependence of dielectric contant & loss is shown in the Fig4. So many theories have been proposed to describe the abnormal dielectric properties of CCTO but the IBLC mechanism has been widely accepted (Yan, L et al. 2006).

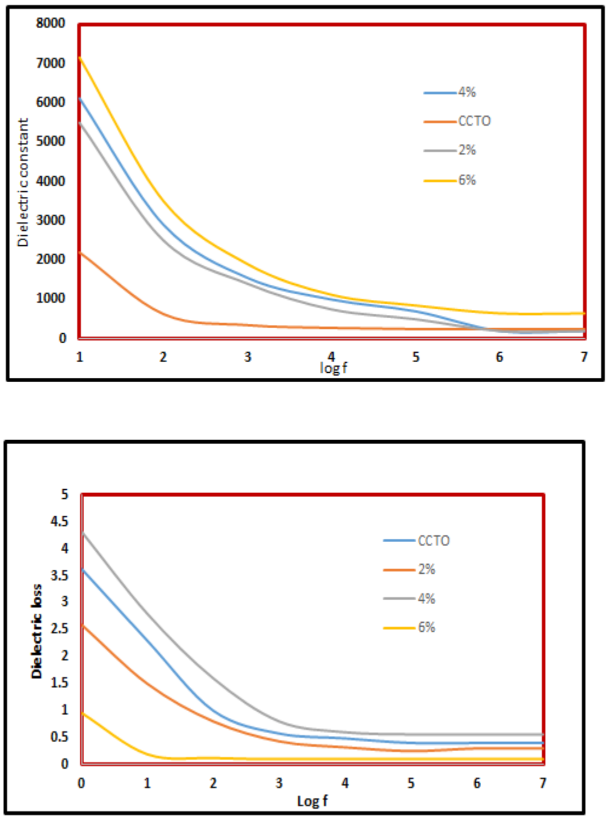


**Fig 4** frequency dependence of CCTO, CCTO/$MgTiO_3$ (a) $\varepsilon_r$ (b) tanδ

Fig 4 shows Frequency dependence of dielectric contant of CCTO, CCTO/$MgTiO_3$ (2%, 4%, and 6%). Fig shows the addition of $MgTiO_3$ has increased the dielectric constant. The dielectric constant is 2200, the addition of $MgTiO_3$ increased the dielectric constant from 2200-7160 respectively. From the above figure we can see that the dielectric constant increases with increase in temperature & drastically decreases as the frequency increase and approaches a constant value at $10^7$Hz.From fig it is seen that the dielectric loss is decreased with increase in frequency and approaches a constant value in the higher frequency region. The dielectric loss of CCTO is found to be 3.64, as the addition of $MgTiO_3$is increased the dielectric loss also increasedthe dielectric loss are affected by the presence of secondary phases.

## 6. CONCLUSION

Calcium copper titanium oxide and magnesium titanium oxide nanoparticles were prepared by Co-precipitation method using surfactant & sintered at 800°C & 600°C in Microwave furnace. Composites of CCTO/$MgTiO_3$ (2%, 4% and 6%)were prepared by mixed oxide technique. The crystalline size of the CCTO & $MgTiO_3$ were in the range of 25-32nm respectively. The Frequency dependence of $\varepsilon_r$&tanδ of CCTO & CCTO/$MgTiO_3$ were studied. Dielectric constant and dielectric loss increased as the addition of $MgTiO_3$increased. For efficient capacitors high dielectric constant &low dielectric loss are the important parameters.

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