

Preparation and Dielectric properties of CCTO and CCTO/MgTiO₃ Nanocomposite

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ABSTRACT: The materials possessing high dielectric constant are widely used in microelectronic devices such as resonators, capacitors and others microelectronic devices where high dielectric constants allow smaller capacitive components, thus contributing to the decrease in size of electronic devices. Calcium Copper Titanate, CaCu₃Ti₄O₁₂ (CCTO) possess high dielectric constant, which has attracted much attention for the development of capacitors materials for electronic industries. The purpose of this work was to study the effect of MgTiO₃ addition to CCTO. In this work the nano-powders of CCTO & MgTiO₃ were prepared by Co-precipitation method using surfactant. The powders were subjected to muffle and microwave furnace sintering. CCTO/MgTiO₃ composites were prepared by using mixed oxide technique. High temperature and longer time in conventional heating increases the production cost of the materials. In order to retain or reduce the cost, microwave sintering is being developed as a new tool for high temperature processing of materials. The microstructure, structural morphology of the powder & composite has been studied by using XRD and SEM. The dielectric properties of CCTO & CCTO/MgTiO₃ composites were investigated using Novotherm alpha-a high performance frequency analyser. Dielectric properties of CCTO and CCTO/MgTiO₃ were measured. Frequency dependence of the dielectric constant and dielectric loss were studied.

KEYWORDS: CCTO, MgTiO₃, Co-precipitation method, nanoparticles, mixed oxide technique, XRD, SEM, Dielectric properties.

I. INTRODUCTION

Nano sized materials exhibiting high dielectric constant are centre of attraction. There is a huge demand for miniaturization of electrical and electronic devices. The material possessing huge dielectric constant are required for miniaturization. Electroceramic materials possessing high dielectric constant are widely used in technological applications such as for cellular phones, capacitors, resonators and filters [1]. Recently lead free Calcium copper titanate has gained considerable interest due to its unusually high dielectric permittivity ($\epsilon_r \sim 10^4 - 10^5$) which is temperature independent in the range 100–600 K [2–3]. The giant dielectric responses in CCTO is due to extrinsic mechanism caused by internal barrier layer capacitance (IBLC) associated with the grain boundaries, twin boundaries, dislocation networks and Schottky barriers or interfacial polarization effect [4–6]. CCTO belongs to a family of oxides of the type ACu₃Ti₄O₁₂. It was first reported by Subramanian et al. Unfortunately, the CCTO ceramic with giant dielectric constant exhibits higher dielectric loss that limits its practical applications. Therefore, some methods like substitutions and insulating doping have been conducted to reduce the dielectric loss. The dielectric constant (ϵ_r) and loss tangent ($\tan\delta$) of CCTO are strongly dependent upon processing conditions such as sintering temperature [7], cooling rate and partial pressure of sintering atmosphere [8,9]. Solid-state reaction method is generally used to prepare CCTO with starting materials, CaCO₃, CuO and TiO₂, in stoichiometric ratio at high temperature. The disadvantage of this method is mixtures are calcined for long duration with several intermediate grindings. It requires tedious work, relatively long reaction time and high temperature condition. High temperatures needed for solid-state compound formation, give rise to poor sintering behavior, inhomogeneous microstructures, possibly abnormal grain growth, and lack of control of cation stoichiometry.

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Due to these reasons there is an urge to find out different synthesis techniques which use low temperature & short time to synthesize these materials. Different techniques like sol-gel process [10], co-precipitation [11], pyrolysis [12], microwave heating [13], polymerized complex method [14] etc. To improve the dielectric properties of CCTO different dopants such as La [15, 16], Al [17], Nb [18], and Mn [19, 20], have been introduced. Addition of insulating oxides such as ZrO_2 [21], SiO_2 , $Cr_2O_3-Nb_2O_5$, and $CaTiO_3$, have also been added to $CaCu_3Ti_4O_{12}$ ceramics to reduce the dielectric losses. However, the results are mostly not desirable. Hence, further efforts are needed to improve the dielectric properties of $CaCu_3Ti_4O_{12}$ ceramics for future applications. Several unit cells of CCTO are shown in Fig 1. CCTO is made up of Ca^{+2} , Cu^{+2} and O_3 , in which Ca^{+2} are located in A site, O_3 site is occupied by oxygen & Cu^{+2} are situated in B site as shown in the below figure.

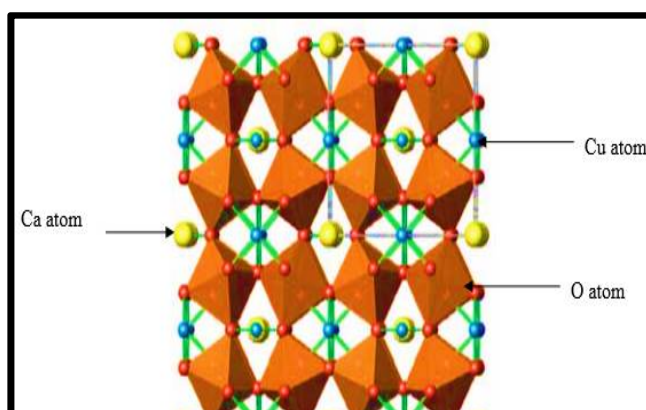


Fig 1: Several unit cells of $CaCu_3Ti_4O_{12}$

II. MATERIALS AND METHODS

Materials

All the chemicals used were of analytical grade. The chemicals used were salts of Ca, Cu & Ti, surfactant & AZS.

Synthesis of CCTO

Initially standard aqueous solution of Ca, Cu were prepared by dissolving in distilled water and stir till it gets dissolved (step 1). And then titanium precursor was prepared by dissolving in IPA and stirred (Step 2). Next step surfactant is mixed in water and stirred till it gets dissolved (step 3). And step 3 is added to step 1 and stir for about 20 mins. And then add Step 2 to step 1 and stir it for few mins. AZS was added slowly to the solution and stir the final contents for 1 hr then filtration of the solution is done, and drying of precipitate at $100^\circ C$ for 1 hr. And sintered in microwave and muffle furnace at $800^\circ C$ for 1hr and then allow it to cool.

Synthesis of $MgTiO_3$

Initially standard aqueous solution of Mg were prepared by dissolving them in distilled water and stir them until it gets dissolved (step 1). And then titanium precursor was prepared by dissolving in IPA and stirred (Step 2). Next step surfactant is dissolved in water till it gets dissolved (step 3). And step 3 is added to step 1 and stir for about 20 mins. And then add Step 2 to step 1 and stir it for few mins. AZS was added slowly to the solution and stir the final contents for 1 hr. Then filtration of the solution is done, and drying of precipitate at $80^\circ C$ for 1 hr. And sintered in microwave and muffle furnace at $600^\circ C$ for 1hr and then allow it to cool.

Synthesis of CCTO/ $MgTiO_3$ composite

The composites of CCTO/ $MgTiO_3$ were prepared by using mixed oxide technique by using different dopant concentration i.e. 2%, 4% and 6% mixing of these powders in pestle and mortar and then drying at $100^\circ C$ for 1hr. And

then this powders were pressed into pellets and then the dielectric properties of this samples were measured using Novotherm alpha-a high performance frequency analyser.

III. EXPERIMENTAL RESULTS

The crystal structure and morphology of the samples were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The dielectric properties of the CCTO and CCTO/MgTiO₃ composite was measured using Novotherm alpha-a high performance frequency analyser frequency range 1Hz-10000 KHz, respectively.

XRD ANALYSIS

Fig 2 (a) & (b) shows the XRD patterns of Microwave and muffle sintered CCTO samples, the diffraction patterns were recorded in the range of 20°- 80° at a rate of 2° per minute. The 2θ values were matched with the standard CCTO ICDD data (00-056-0767).

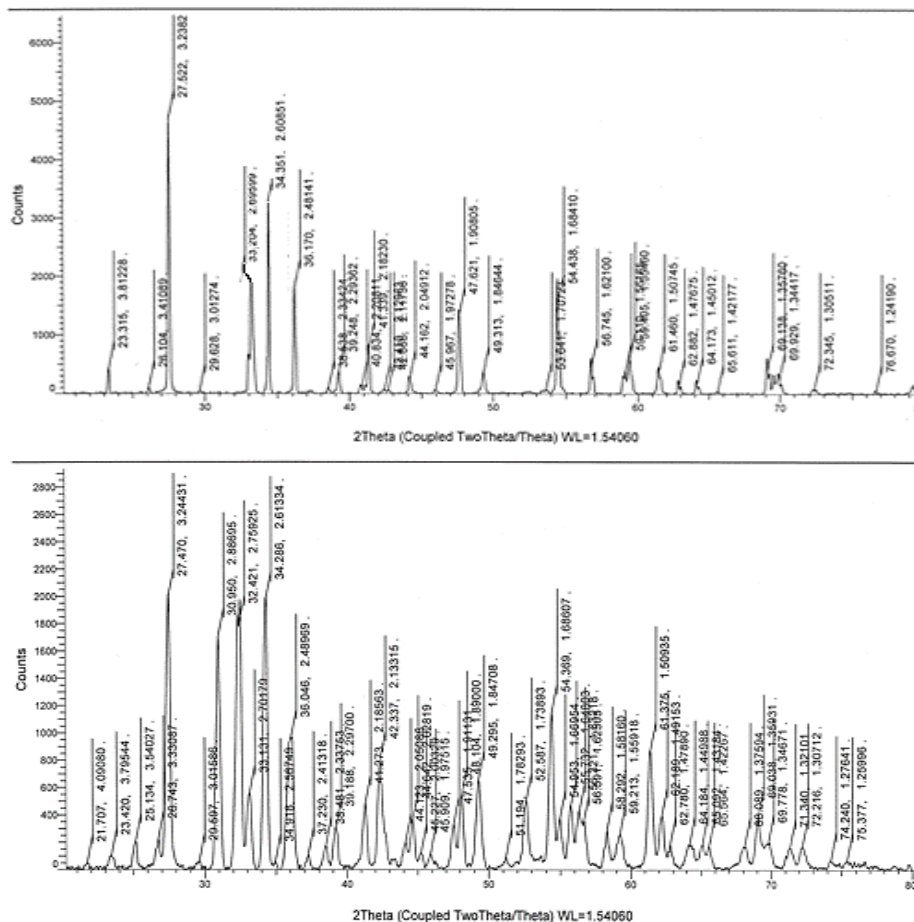


Fig 2: XRD patterns of CCTO (a) Microwave furnace (b) Muffle furnace

Along with the CCTO phase secondary phases of CuO, CaTiO₃& TiO₂ were observed. The secondary phases formed were matched with the standard ICDD data (ICDD-00-005-0661), (ICDD-00-022-0153) & (ICDD-00-015-0875) respectively. The lattice constant and volume of cubic unit cell of the both sintered samples i.e MF and MW furnace matched with the standard values of lattice constant and volume i.e a=7.38693Å, V=403.081Å³ respectively.

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Fig 3 (a) & (b) represents the XRD patterns of Microwave and muffle sintered MgTiO₃ samples. The 2θ values matched with the standard MgTiO₃ ICDD data (00-006-0494).

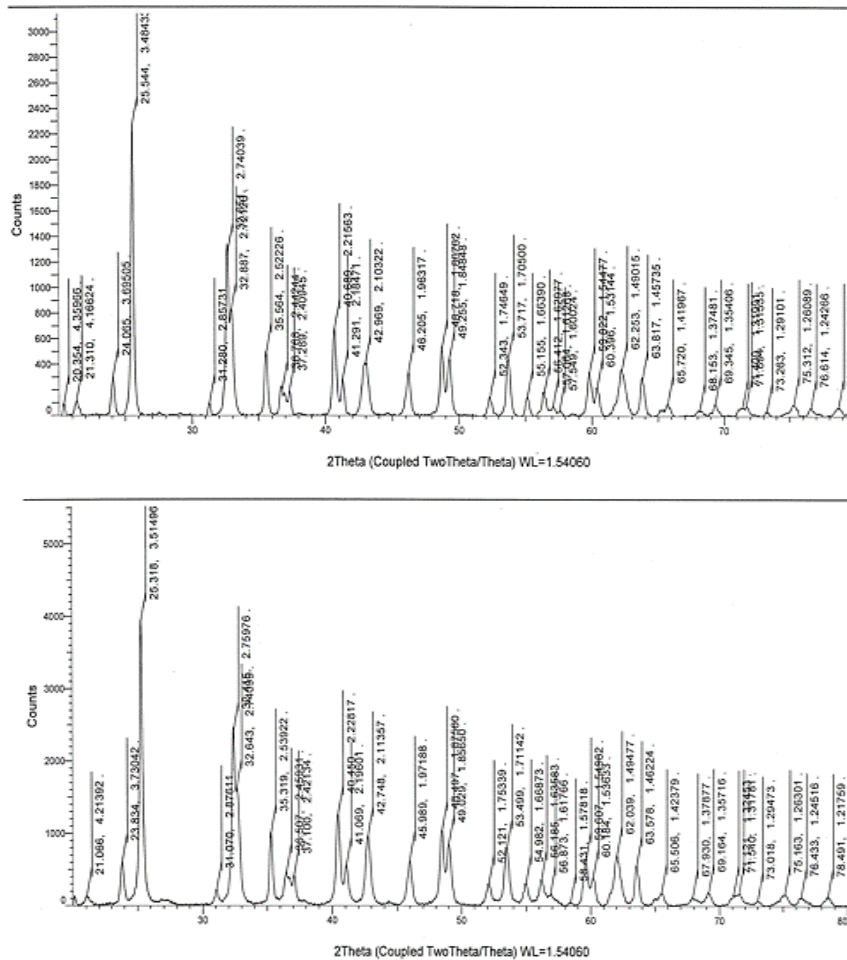


Fig 3: XRD patterns of MgTiO₃ (a) Microwave furnace (b) Muffle furnace

The secondary phases formed were matched with the standard MgTi₂O₅ ICDD data (00-035-0792), Mg₂TiO₄ (00-025-1157). The volume of the unit cell & lattice constant of the MF and MW sintered samples matches with the standard values of lattice constant & volume. $a = 5.0540(2) \text{ \AA}$, $c = 13.8956(9) \text{ \AA}$ and $V = 307.38(3) \text{ \AA}^3$. The crystalline size of the CCTO & MgTiO₃ were in the range of 25-32nm respectively.

SEM Analysis

The morphological studies of CCTO and MgTiO₃ Nano powders are observed from SEM images. SEM analysis is an important characterisation technique for topographic study of the sample. Fig. 4(a) & (b) represents the SEM image of Microwave and Muffle sintered CCTO sample. And From Fig. 4(c) & (d) represents the SEM image of Microwave and Muffle sintered MgTiO₃ sample.

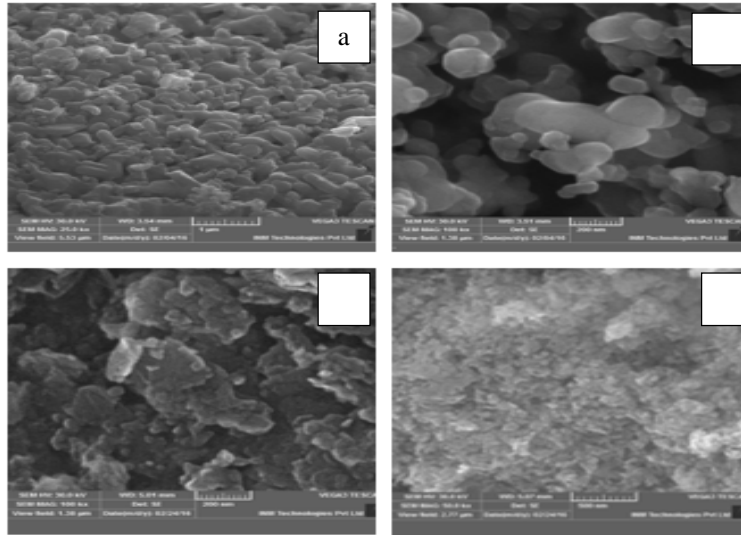
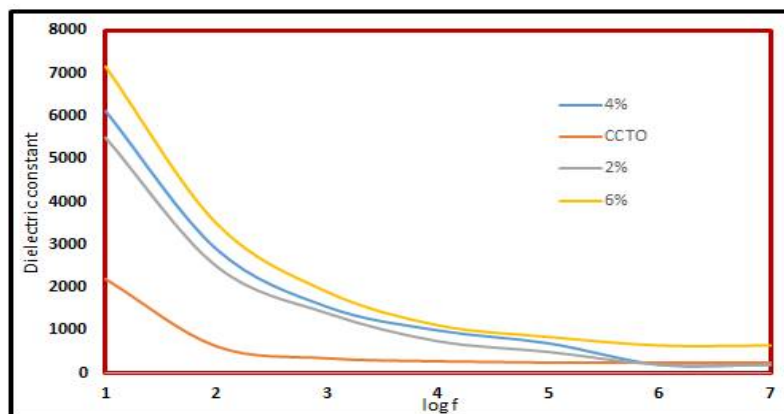


Fig 4: SEM images of CCTO (a) Muffle sintered (b) Microwave sintered & MgTiO₃ (c) Muffle sintered (d) Microwave sintered

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 constant & loss is shown in the Fig 5. Many theories have been proposed to describe the abnormal dielectric properties of CCTO the most widely accepted is the internal barrier layer capacitance mechanism [22]. The intrinsic dielectric response in CCTO is due to barrier layer capacitance related with grain boundaries which results in interfacial polarization. The giant dielectric constant is dependent on microstructure and the formation of internal boundary layer capacitance (IBLC) between the grains [23].



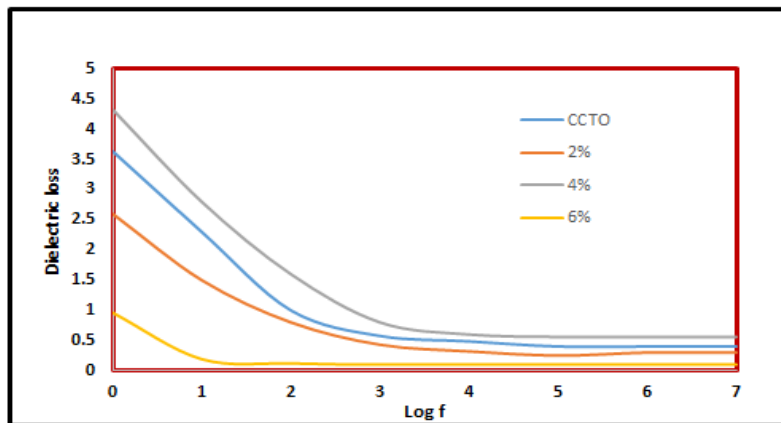


Fig 5: Dielectric constant & Dielectric loss of CCTO & CCTO/MgTiO₃ (2%, 4%, 6%)

Figure 5(a) represents the dielectric response of the CCTO and CCTO/MgTiO₃ composites against frequency at RT from the fig it can be seen undoped CCTO & CCTO/MgTiO₃ (2%, 4% and 6%) composites possess a dielectric constant of 2200, 5500, 6120 & 7160 respectively at low frequency and decreases slightly as the frequency increases and approaches a constant value. The decrease in dielectric constant as frequency increases is due to several polarization mechanisms. The space charge relaxation time & dipolar polarizations normally take part only at lower frequencies & the reduction in dielectric constant as frequency increases proposed that the dipole doesn't have enough time to respond to reversal field which occurs over a short period of time. Henceforth, it contributes to decrease in dielectric constant. As the concentration of MgTiO₃ is increased the dielectric constant is increased. Figure 5(b) represents the dielectric loss vs frequency of CCTO and CCTO/MgTiO₃ (2%, 4% & 6%) samples. The decrease in value of dielectric loss for composites of CCTO/MgTiO₃ depends on the amount of Magnesium titanate added to the CCTO. The values of dielectric loss of CCTO, CCTO/MgTiO₃ (2%, 4% & 6%) are 3.64, 2.6, 4 and 0.96 respectively. Composite of CCTO/MgTiO₃ (2%, 6%) reduced the dielectric loss from 3.64-2.6, 3.46-0.96. To understand the dielectric properties effectively it is necessary to prepare single phase MgTiO₃.

IV. CONCLUSION

Nanostructured powder of CCTO & MgTiO₃ were prepared by Co-Precipitation method using surfactant for controlling the grain growth. Mixed oxide technique was used for the preparation of CCTO/MgTiO₃ composite. The phase formation was confirmed by using XRD. The crystalline size were in the range of 25-32nm respectively. Dielectric properties of CCTO and CCTO/MgTiO₃ were carried out. As the concentration of MgTiO₃ the dielectric constant of the samples increased from 2200, 5500, 6120 & 7160 respectively. The CCTO/MgTiO₃ (2%, 6%), decreased the dielectric loss. From the above results it implies that the dielectric properties can be improved by synthesizing single phase CCTO and MgTiO₃ powder. For the efficient capacitor high dielectric constant & low dielectric losses are the vital parameters.

REFERENCES

- [1] B. Renner, P. Lunkenheimer, M. Schetter, A. Loidl, A. Reller, S.G. Ebbinghaus, J. Appl. Phys, Vol 96, no. 8, pp 4400, 2004.
- [2] P.Liu, Y.He, G.Q.Zhu, X.B.Bian, "Influence of Nb doping on the dielectric properties of CaCu₃Ti₄O₁₂ ceramics," Acta Physica Sinica, Vol. 56, pp. 5489- 5493, 2007.
- [3] C.C.Home, T.Vogt, S.M.Shapiro, S.Wakimoto, A.P.Ramirez, "Optical responses of high-dielectric constant perovskite related oxide," Science, Vol.293, pp.673-676, 2001.
- [4] D C Sinclair, T B Adams, F Morrison and A R West Appl. Phys. Lett, Vol 80, pp 2153, 2002.
- [5] S Aygun, X Tan, J P Maria and D P Cann Proc 204th Electrochem. Soc. Meeting Orlando, Florida, 2003.
- [6] L He, J B Neaton, D Vanderbilt and M H Cohen Phys. Rev. B 67 012103, 2003.
- [7] D. Capsoni, M. Bini, V. Massarotti, G. Chiodelli, M.C. Mozzatic, C.B. Azzoni, J. Solid State Chem., Vol 177, pp 4494-4500, 2004.

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(An ISO 3297: 2007 Certified Organization)

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- [8] T.T. Fang, H.K. Shiau, J. Am. Ceram. Soc, Vol 87, pp 2072–2079, 2004.
- [9] P. Jha, P. Arora, A.K. Ganguli, Mater. Lett., Vol 57, pp 2443–2446, 2003.
- [10] Sun DL, Wu AY, Yin ST, J Am Ceram Soc 91:169, 2008.
- [11] Barbier B, Combettes C, Fritsch SG, Chartier T, Rossignol F, Rumeau A, Lebey T, Dutarde E, J Eur Ceram Soc 29:731, 2009.
- [12] Masingboon C, Thongbai P, Maensiri S, Yamwong T, Seraphin S, Mater Chem Phys 109:262, 2008.
- [13] Liu J, Sui Y, Duan C, Mei WN, Smith RW, Hardy JR, Chem Mater 18:387, 2006.
- [14] Yu H, Liu H, Luo D, Cao M, J Mater Process Technol 208:145, 2008.
- [15] L.X. Feng, X.M. Tang, Y.Y. Yan, X.Z. Chen, Z.K. Jiao and G.H. Cao: Phys. Status Solidi A, pp 203, R22, 2006.
- [16] S.H. Jin, H.P. Xia and Y.P. Zhang: Ceram. Inter, Vol35, pp 309, 2009.
- [17] S.W. Choi and S.H. Hong: J. Am. Ceram. Soc, Vol 90, pp 4009, 2007.
- [18] S.H. Hong, D.Y. Kim, H. M. Park and Y.M. Kim: J. Am. Ceram. Soc, Vol 90, pp 2118, 2007.
- [19] W. Kobayashi and I. Terasaki: Physica B, Vol 771, pp 329-333, 2007.
- [20] M. Li, A. Feteira, D.C. Sinclair, A.R. West: Appl. Phys. Lett., Vol 88, 2006.
- [21] E.A. Patterson, S. Kwon, C.C. Huang, D.P. Cann: Appl. Phys. Lett., Vol 87, 2005.
- [22] Y. Yan, L. Jin, L. Feng, and G. Cao, "Decrease of dielectric loss in giant dielectric constant $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics by adding CaTiO_3 ," Materials Science and Engineering B: Solid-State Materials for Advanced Technology, vol. 130, no. 1–3, pp. 146–150, 2006
- [23] L. A. Ramajo, M. A. Ramirez, P. R. Bueno, M. M. Reboledo, and M. S. Castro, "Dielectric behaviour of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ - Epoxy composites," Materials Research, vol. 11, no. 1, pp. 85–88, 2008.