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DIELECTRIC PROPERTIES OF $(CaCu_3Ti_4O_{12})_{1-X}(Fe_3O_4)_X$

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ABSTRACT
The dielectric properties of $CaCu_3Ti_4O_{12})_{1-x}(Fe_3O_4)_x$ (x = 0, 0.01, and 0.05) have been studied. We found that with only 1% mixing of Fe_3O_4, ε' dramatically decreases from 10^4 to 65. The values of activation energy (E_a) and characteristic frequency (f_o) of $(CCTO)_{1-x}(Fe_3O_4)_x$ system are calculated by the Arrhenius fitting. These samples $(CCTO)_{1-x}(Fe_3O_4)_x$ (x = 0, 0.01, 0.05) exhibit two activation energies, one is at around room temperature (which we called high temperature, HTR), the other is at low temperature (LTR), but it should be noticed that the $(CCTO)_{0.99}(Fe_3O_4)_{0.01}$ has two activation energies in low temperature range (LTR).
Keywords: Activation Energy, Arrhenius Fitting, Dielectric Properties, High Dielectric Constant, $CaCu_3Ti_4O_{12}$
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INTRODUCTION

The $ACu_3Ti_4O_{12}$ and $ACu_3Ti_3FeO_{12}$ families were investigated in 1967,[1] their structure was determined in 1979.[2] Oxides of the $ACu_3Ti_4O_{12}$ variety are known for their high dielectric constants-most notably Calcium Copper Titanate (CCTO). CCTO exhibits a remarkable dielectric constant of approximately 12,000 at 1 kHz, maintaining exceptional stability across a temperature range of 100 K to 300 K. In 2000, Subramanian et al. reported that CCTO possesses a high dielectric constant and noted the absence of a ferroelectric phase transition down to 35K.[3] Sinclair *et al.*[4] performed impedance spectroscopy experiments, demonstrating electrical heterogeneity in CCTO ceramics, with insulating grain boundaries and semi-conducting grains present. They came to the conclusion that the dielectric giant phenomenon is caused by an IBLC at the grain boundary rather than some inherent property of the crystal's structure. The IBLC explanation is currently largely accepted.[5,6] The increased dielectric constant that occurs at low temperatures may be due to a dynamic deceleration of dipolar oscillation inside nanoscale domains, according to an optical test on a CCTO-based single crystal performed by C.C. Homes *et al.*[7] in 2001. Research on novel ferroelectric materials has persistently garnered attention since the identification of ferroelectricity in Rochelle salt single crystals[8] and its later expansion into polycrystalline ceramics of barium titanate in the mid-1940s. The advancement of novel ceramic processing and thin film technology has resulted in materials being utilised across a broad spectrum of industrial and commercial applications. The applications of these materials encompass high dielectric constant capacitors, radio and communication filters, ultrasonic motors, thin film capacitors, and ferroelectric thin film memory. This research examines the influence of magnetite's dielectric characteristics in $(CaCu_3Ti_4O_{12})_{1-x}(Fe_3O_4)_x$ samples for x values of 0, 0.01, and 0.05.

Material and Methods

Ceramics of $(CaCu_3Ti_4O_{12})_{1-x}(Fe_3O_4)_x$ were synthesised by solid-state reaction and sintering techniques. High-purity precursor powders of $CaCO_3$, CuO, and TiO_2 were directly amalgamated in the requisite stoichiometric ratios and milled in an agate mortar with acetone. After the amalgamated powder had been ground to a suitable consistency, it was heated in a crucible. Starting at room temperature, the air was

heated to 850 °C at a rate of 5 °C/min. This was maintained for 12 hours. Then, the temperature was cooled from 850 °C to room temperature again at a rate of 5 °C/min. Subsequent to the initial heating process, the powders were re-ground with Fe_3O_4 in varying stoichiometric ratios. Following the second grinding, ceramic pellets of the composition $(CaCu_3Ti_4O_{12})_{1-x}(Fe_3O_4)_x$ (where x = 0, 0.01, and 0.05) were produced and subjected to heating once again under the same protocol, with the previous heating temperature of 850 °C adjusted to 1050 °C. The final step in measuring the dielectric constant was to smooth and uniformly polish each disc sample before coating it with silver paint and a thin conducting wire.

X-ray Diffraction

Crystallographic data for all materials were acquired using a powder X-ray diffractometer equipped with Cu Kα radiation, utilising a scanning rate of approximately 1° in 2θ per minute.

Microstructure Investigation

In order to compare the size and morphology of the grains across different samples, multiple scales of FESEM (field emission scanning electron microscopy) images were acquired. These photographs facilitate the comparison of the dimensions and border contours of the grains.

Dielectric Properties Measurement

A small wire was attached to both sides of each sintered pellet to serve as an electrode, and the pellets were evenly coated with silver paste. Placing the sample under an electric lamp for about an hour allowed the silver paste to cure gradually. The samples are housed in a container constructed from a vacuum pipe, allowing for immersion in liquid nitrogen. An alternating voltage was provided, and thereafter, capacitance and conductivity values were evaluated at various temperatures ranging from 320 K to 80 K, in increments of 10 K. The voltage source frequency ranges from 20Hz to 1MHz, and the real and imaginary dielectric constants, as well as the loss tangent, were measured.

RESULTS AND DISCUSSION

$CaCu_3Ti_4O_{12}$

X-ray Diffraction pattern of $(CaCu_3Ti_4O_{12})_{1-x}(Fe_3O_4)_x$; (a) x = 0, (b) 0.01, and (c) 0.05 is shown in Fig.-1 with Miller indices of the peaks. The lattice constants deduced from the X-ray pattern for all the samples are similar, with a = 7.386 Å. The compound has a perovskite-like structure, without any impurity. Figure-2 shows the FESEM plot of CCTO sintered at 1050 °C; almost every grain has very sharp grain boundaries. A recent study on CCTO indicates that microstructures significantly enhance dielectric permittivity, as demonstrated in the latter portion of the manuscript.The dissipation factor D and the actual component of the dielectric constant as a function of temperature (sometimes referred to as loss "tanδ") of $CaCu_3Ti_4O_{12}$ (CCTO) is illustrated in Fig.-3.

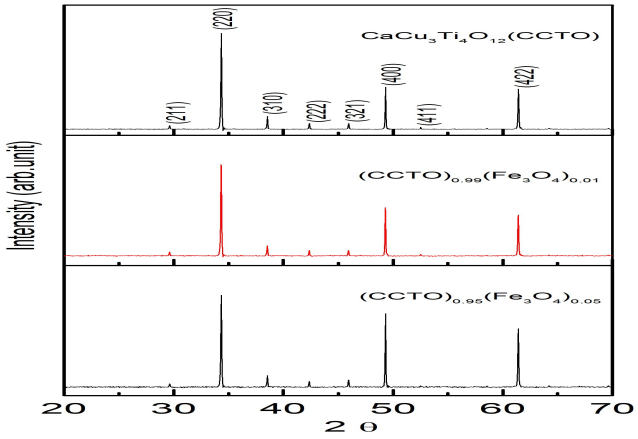

Fig.-1: X-ray diffraction pattern of the $(CaCu_3Ti_4O_{12})_{1-x}(Fe_3O_4)_x$ (x=0, 0.01 and 0.05) compound with Miller indices of the peaks

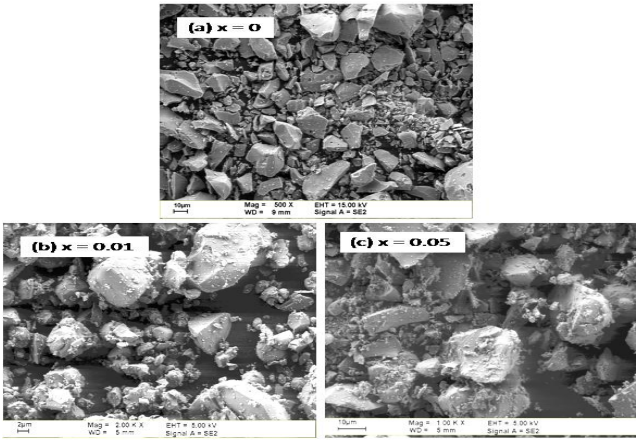

Fig.-2: FESEM photo of the $(CaCu_3Ti_4O_{12})_{1-x}(Fe_3O_4)_x$ (x=0, 0.01 and 0.05) compound

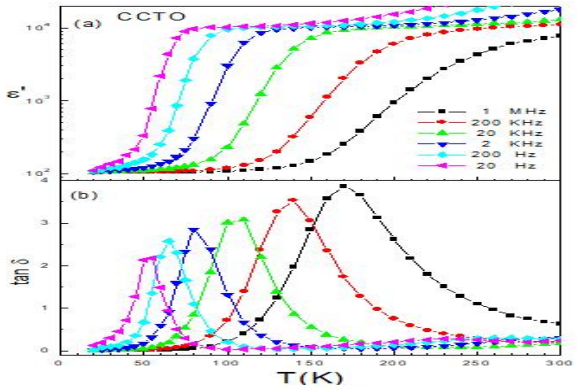

Fig.-3: (a) Shows that the Actual Component of the Dielectric Response of CaCu3Ti4O12 Varies with Temperature (CCTO) Over Various Frequencies Ranging from 20 Hz to 1 MHz, Sintered at 1050 °C. (b) Illustrates the Temperature Dependency of the Loss Tangent (tanδ) of CCTO at Identical Frequencies

The (T) indicates a substantially low-frequency dielectric constant (on the order of 10^4) that remains nearly constant at 2 KHz across the temperature range of 100 K to 300 K; however, as the temperature decreases, it diminishes to approximately 100. The temperature dependence of loss tanδ demonstrates Debye-like relaxation behaviour, with the typical relaxation frequencies approximately adhering to the Arrhenius equation.The loss tanδ and relative dielectric constant are frequency dependent. CCTO samples from 230 K to 300 K and from 70 K to 170 K are shown in Fig.-4 and Fig.-5, respectively.

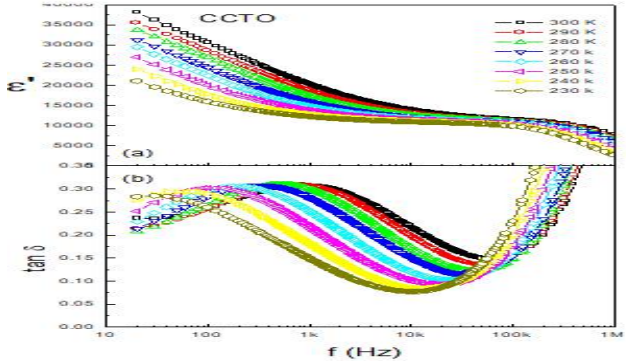

Fig.-4: (a)The frequency dependence of the real part of the dielectric response ε' of CCTO at different temperature between 230K and 300K, (b) The frequency dependence of the loss tanδ of CCTO at the same temperature

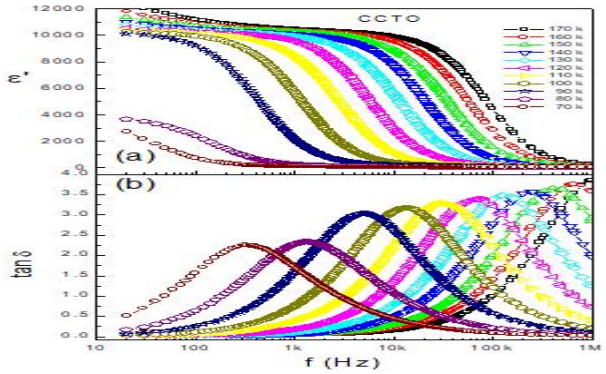

Fig.-5: (a)The frequency dependence of the real part of the dielectric response ε' of CCTO at different temperature between 70K and 170K, (b) The frequency dependence of the loss tanδ of CCTO at the same temperature

The Arrhenius fitting plots are shown in Fig.-6 (a) and Fig.-6 (b); two values of activation energy are available in the CCTO sample. One value is 291 meV between 230 K and 300 K, and the other is 83 meV between 70 K and 170 K. The frequency dependence of the imaginary part of the dielectric response of CCTO at various temperatures between 70 K and 170 K is shown in Fig. 7(a). By collecting the values of those peaks of in Fig.-7(a) and using the Debye model ($\omega_p \tau$ =1, $\omega_p$is the peak at ε'' and τ is the relaxation time. The rapid increase with decreasing temperature is suggestive of a thermally activated Arrhenius process. A linear regression of ln(τ) versus 1/T (see Fig.-7(b)) describes the data well, as indicated by the dotted line and yields activation energy E_a = 96 meV and τ_o = 2.4 ns.

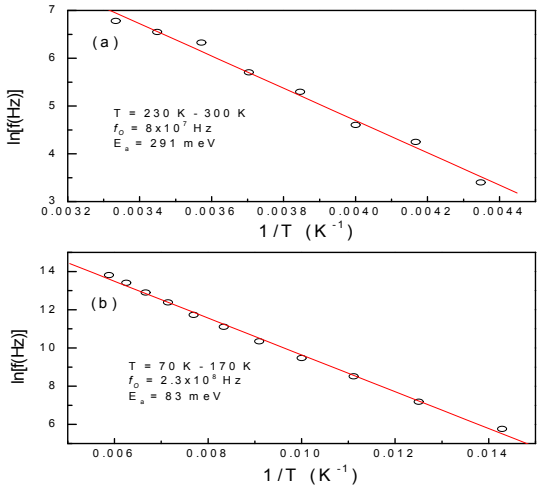

Fig.-6: (a) Arrhenius Plot for The Observed Relaxations of CCTO between 230 K and 300 K, (b) Arrhenius Plot for the Observed Relaxations of CCTO between 70 K and 170 K

$(CaCu_3Ti_4O_{12})_{0.99}(Fe_3O_4)_{0.01}$

The frequency dependence of the loss tanδ of the (CCTO) 0.99(Fe_3O_4)0.01 sample over the temperature range from 290 K to 320 K and from 130 K to 200 K is shown in Fig.-8 (a) and Fig.-9. (a), respectively. The peak of frequency of tan δ in Fig.-8 (a) shifts rightward as the temperature goes up. For each peak, the values of T and f were collected using the Arrhenius plots (see Fig.-8 (b)), with 1/T as the horizontal axis and ln f as the vertical axis. The activation energy of the sample was then determined to be 487 meV. The activation energy values for $(CCTO)_{1-x}(Fe_3O_4)_x$ are listed in Table-1. In contrast, two relaxation groups are shown by the loss tan δ in Fig.-9 (a). The values of these peaks were used to draw the Arrhenius plots (Fig.-9 (b), two values of activation energy are available in the sample. One value is 255 meV over the temperature range between 160 K and 200 K, and the other is 13.6 meV over the temperature range between 130 K and 160 K.

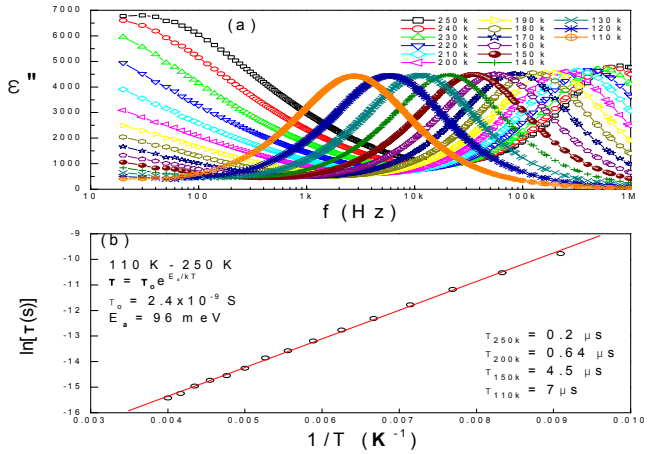

Fig.-7: (a) The frequency dependency of the Imaginary Part of the Dielectric Response of CCTO at different temperatures between 70K AND 170 K, (b) The log of the relaxation time τ versus 1/T, which shows activated behaviour

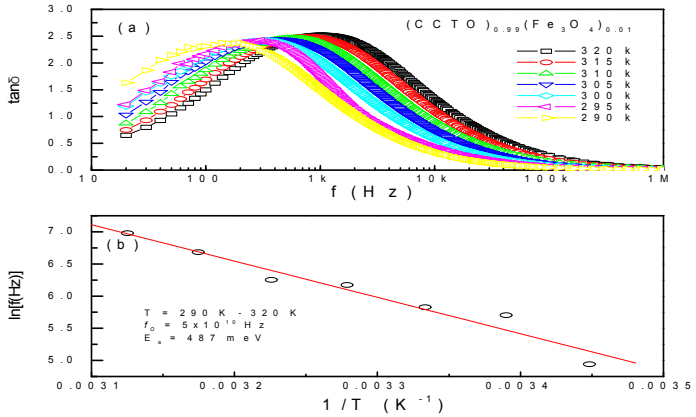

Fig.-8: (a) The frequency dependence of the loss tanδ for the $(CCTO)_{0.99}(Fe_3O_4)_{0.01}$ between 290K and 320K, (b) Arrhenius plot for the obsereved relaxations of $(CCTO)_{0.99}(Fe_3O_4)_{0.01}$ between 290K and 320K

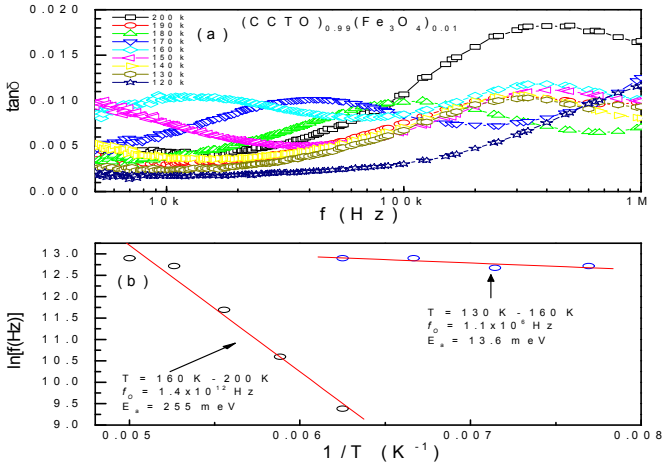

Fig.-9: (a) The frequency dependence of the loss tanδ for the $(CCTO)_{0.99}(Fe_3O_4)_{0.01}$ between 130K and 200K, (b) Arrhenius plot for the obsereved relaxations of $(CCTO)_{0.99}(Fe_3O_4)_{0.01}$ between130K and 200K

Table-1: Activation Energy Values of $(CCTO)_{1-x}(Fe_3O_4)_x$.

Arrhenius fitting results for $(CCTO)_{1-x}(Fe_3O_4)_x$				
	HTR		LTR	
ceramics	f_o (Hz)	E_a (meV)	f_o (Hz)	E_a (meV)
$CaCu_3Ti_4O_{12}$(CCTO)	$8x10^7$	291	$2.3x10^8$	83
$(CCTO)_{0.99}(Fe_3O_4)_{0.01}$	$5x10^{10}$	487	$1.4x10^{12}$	255
$(CCTO)_{0.95}(Fe_3O_4)_{0.05}$	$8.6x10^9$	473	$5.5x10^{12}$	274

CONCLUSION

The values of activation energy(E_a) and characteristic frequency(f_o) of $(CCTO)_{1-x}(Fe_3O_4)_x$ system are calculated by the Arrhenius fitting result listed in Table-4, in each sample of $(CCTO)_{1-x}(Fe_3O_4)_x$ (x = 0, 0.01, 0.05), two activation energy have been observed, one is at around room temperature (which we called high temperature, HTR), the other is at low temperature (LTR), but, it should be noticed that the $(CCTO)_{0.99}(Fe_3O_4)_{0.01}$ has two activation energies in low temperature range (LTR).

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

The present work is related to *SDG-9: Industry, Innovation, and Infrastructure*. All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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