Influence of Nb and Zr co-doping on the structural, morphological and dielectric properties of CaCu$_3$Ti$_4$O$_{12}$ ceramics

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Abstract. In this work, CaCu$_3$Ti$_{3.8-x}$Nb$_{0.2}$Zr$_x$O$_{12}$ (where x=0.0, 0.05, 0.1, 0.2) ceramics were made using the normal solid-state reaction method to assess the influence of Nb$^{5+}$ & Zr$^{4+}$ co-doping on the structure, morphology and electrical properties of CaCu$_3$Ti$_4$O$_{12}$ ceramics. Reitveld refinement by Fullprof package was done to achieve the structural information. No phase transformation was observed upon doping. The CCTNZO ceramics occupied a fine-grained microstructure with grain sizes ranges from 0.26-0.33 μm. Furthermore, grain size uniformity was enhanced with gradual doping of Zr$^{4+}$ ion. within the meantime, the CCTNZO ceramics unfolds extensive durability of dielectric constant over a good range of frequency and also shows a lower loss factor. Doping resulted during a gradual decrease in grain sizes and a dielectric loss at low and high frequency. It had been found that 10% of Zr doped CCTNZO ceramics has the very best dielectric constant (3655) at 0.1 kHz. Meanwhile, rock bottom dielectric loss of 0.241 at 0.1 kHz was observed for 20% Zr doped CCTNZO ceramics.

Keywords: Structural stability; Uniform grain size; Co-doping; Dielectric constant; Dielectric loss

1. Introduction
“Researchers have found that the CCTO ceramics showed tremendous lofty dielectric constant of 100,000 at low temperature and little temperature dependence from 100 to 400 K” [1]. “Moreover, CCTO ceramics has nearly frequency independent dielectric constant beneath 106 Hz, that is wished for several microelectronic appliances” [2]. Besides, materials having extensive dielectric constant over both wide temperature range and frequency range would extremely contribute to the miniaturization of memory storage devices and capacitors [3]. “The CCTO ceramics are much impressionable to several parameters, which can affect its dielectric properties. “Mass research has been equipped to define the premodial of the enormous dielectric property of CCTO ceramics” [4, 5]. CCTO belongs to the family of a double perovskite group with space group Im3 [6]. “The dielectric loss of CCTO ceramics is 0.5 at 1 kHz, which is extremely high” [7]. It's highly necessary to understand the explanation for high loss factor in CCTO ceramics and find an efficient way to reduce it. “Several well-known methods are established to mitigate the loss factor of Calcium copper Titanate ceramics by doping, substitution, two-phase composite processes” [7]. As of now, several researchist have effectively employed these methods like CCTO doped with Cr$_2$O$_3$ [8], CCTO doped with La [9], CCTO/CaTiO$_3$ composite [10], etc.
Elements with ionic charges +3 like Bi$^{3+}$, La$^{3+}$, Nd$^{3+}$, etc. are used as donors for A site, whereas elements having ionic charges +5 or +6 like Nb$^{5+}$, Ta$^{5+}$, Sb$^{5+}$, W$^{6+}$, etc. are often used as donor for Ti ions [7]. The surplus charge at A site creates (Ca$^{2+}$) vacancies and excess charges at B site (Ti$^{4+}$), generally creating vacancies. Sintering time increasing may create both more oxygen vacancies also as space charges [11]. Sulaiman, Muhammad Azwadi et al. reported that 1% of Nb-doped CCTO ceramics produced by a standard solid-state reaction method gives the very best dielectric constant with a high dielectric loss. The Dielectric loss was minimized when 3% of Nb was utilized in CCTO [7]. Hong et al. reported that 20% of Nb-doped CCTO ceramics has the very best dielectric constant and highest dielectric loss value [12]. W. L. Li et al. reported that doping with Zr$^{4+}$ simultaneously decreases dielectric loss [13]. Single element doping may be a common approach, but the effect of doping is uncertain. A couple of works are found on co-doping in CCTO ceramics. H.A. Ardakani et al. investigated that Cr & La co-doped CCTO ceramics could reduce dielectric loss to an excellent extent [14], A.K Thomas et al. reported that dielectric constant increased with co-doping of La at A site and Nb at B site [6]. It is considered that doping simultaneously at A site and B site or only A site or only B site is worth it in improving the dielectric constant with a big reduction in dielectric loss.

In this present study, Nb & Zr co-doped CCTO ceramics were yielded using the traditional solid-state reaction method to enhance dielectric constant property. Several dopants percentages were used to minimize dielectric loss. The dielectric constant and dielectric loss were measured during a wide selection of frequencies. However, the effect of simultaneous partial substitution of Nb & Zr at B site has not been reported yet. This study will present the effect of partial substitution of Nb & Zr co-doped CCTO ceramics on the structural, morphological, and dielectric properties.

2. Materials and Method
Conventional solid-state reaction way was accustomed to produce monocrystalline samples of CaCu$_3$Ti$_{3-x}$Nb$_x$Zr$_x$O$_{12}$, where $x = (0.00, 0.05, 0.10, 0.20)$ ceramics. The samples are named CCTNZO-0, CCTNZO-5, CCTNZO-10 & CCTNZO-20 because of the 0%, 5%, 10%, and 20% replacement of Ti-sites respectively. Pure raw materials of CaCO$_3$, CuO, TiO$_2$, Nb$_2$O$_5$, ZrO$_2$ were used with ≥ 99.9% purity and supplied by Merck Specialties, India. The desired powders were weighed with an accurate ratio and circumstantially kneading by ball milling with high pure ethanol for 20 hrs. to keep up a consistent solution. After that, an oven was used to dry the liquid solution at 100°F for 24 hrs. to induce the powder, and then the powder was hand-milled thoroughly to avoid lump formation. Then calcination was administered at 860°C for two hrs. Then, the obtained powder was again hand-milled and pressed into pellet (13 mm diameter and 2 mm thickness) with an appropriate binder named PVA. Sintering was administered at 1020°C for 2 hrs. at ambient pressure. XRD analysis was performed using Bruker Advanced Diffractometer (Germany) to spot the possible synthesized phases. Rietveld refinement was done using Fullprof software to urge detailed the structural information. Scanning electron microscope was administered to watch surface morphology and particle sizes of the samples. The Linear intercept method was applied to calculate the grain size and Image J software was used to determine grain size distribution. Dielectric constant was measured with an Impedance analyzer.

3. Results and discussion
3.1 Structural analysis
X-ray diffraction analysis was performed to collect information about structure. Figure 1 exhibits the XRD pattern alongside the magnified pattern at 31-39 degrees. The XRD curves are well-matched with the peaks of CaCu$_3$Ti$_{3-x}$O$_{12}$ (CCTO). 0%, 5%, 10%, 20% Zr doped CCTNO (Nb-doped CCTO) are denoted by CCTNZO-0, CCTNZO-5, CCTNZO-10 & CCTNZO-20 respectively. The magnified portion in figure 1 starting from 31-39 degrees shows an entire merging of (202) peak from CCTNZO-0 to CCTNZO-20.” All the peaks in figure 1 are indexed considering body-centered cubic with the space group Im3” [12].

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Figure 1: X-ray diffraction pattern of various percentage doped CCTNZO ceramics (left) at room temperature and magnified XRD pattern at 31-39° (right)

Fullprof software was used to further explore the information about structure. Figure 2 shows the possible structural refinement and curve fitting using the software. Hence, 20% substitution reveals no secondary phases. Refined structural information are enlisted in Table 1 which is in consistent with JCPDS #75-2188. Calculated lattice constant shows increment with increasing doping percentage.

Figure 2: Stacking Reitveld refined graphs of CCTNZO ceramics
Table 1: Structural parameters of CCTNZO- (0, 5, 10, 20) ceramics obtained by Reitveld Refinement

| Parameters      | CCTNZO-0  | CCTNZO-5  | CCTNZO-10 | CCTNZO-20 |
|-----------------|-----------|-----------|-----------|-----------|
| Lattice parameters | a = 7.3918Å  | a = 7.4018Å  | a = 7.4029Å  | a = 7.4030Å  |
|                 | V= 403.8709 Å³ | V= 405.5152 Å³ | V= 405.7047 Å³ | V= 405.7239 Å³ |
| Density         | 6.225 g/cm³  | 6.210 g/cm³  | 5.5057 g/cm³  | 5.866 g/cm³  |
| Rexp            | 13.7       | 13.6       | 7.34       | 9.86       |
| GoF             | 1.3        | 1.6        | 1.6        | 1.4        |

From Figure 3 it is often seen that increasing dopant percentage causes a gradual increment in lattice parameters. The explanation behind increasing lattice constant could also be ascribed to the difference in ionic radius between Ti and Zr ions (r(Ti⁴⁺) =0.605 Å and (r(Zr⁴⁺) =0.80 Å” [12]. Moreover, the Goodness of fit (GoF) indicating the reliability of our refinement.

![Figure 3: Lattice parameter Vs Co-dopants substitution](image)

3.2 Morphological analysis

The Scanning electron microscope observed the Surface morphology of CCTNZO ceramics, and therefore the micro images are shown in Figure 4. Careful observation depicts that CCTNZO-0 has larger size grain.

![Figure 4: Scanning electron micrographs of CCTNZO (0, 5, 10, 20) ceramics respectively](image)
Increasing the Zr percentage into CCTNZO ceramics causes grains to be core shell-like structure. Another clear visualization from the SEM micrographs suggests that increasing dopant percentage causes a consecutive reduction in average grain size. Li, W. L et al. also reported that the Zr dopant reduces grain size [13]. Hence, the grain size of CCTNZO ceramics is minimized, and grain size similarity is attained by a gradual increase in Zr dopant percentage. Linear intercept method was used to calculate the average grain size [16]. The grain size for CCTNZO-0, CCTNZO-5, CCTNZO-10 and CCTNZO-20 ceramics are 4.82 μm, 0.33 μm, 0.29 μm and 0.26 μm respectively. Figure 5 depicts the grain size distribution of CCTNZO-0, CCTNZO-5, CCTNZO-10 and CCTNZO-20 ceramics. The grain size distribution becomes narrower with increasing the dopant percentage.

\[ d = \frac{k \gamma}{\beta \cos \theta} \]  

(1)

Where \( \beta \) denotes the FWHM of the main diffraction peak, \( k \) is that the dimensionless constant with a typical value \( \approx 0.9 \), \( \lambda \) is that the wavelength of Cu K\(_{\alpha}\) radiation with the worth of 1.5406 Å, and \( \theta \) stands for the Bragg angle of the main peak. Calculated parameters are enlisted in Table 2. As smaller crystallite size results in higher diffusion and agglomeration, a decrease in particle size with Zr doping is justified by the decrease in corresponding crystallite size [17, 18].

| Name of the element | Average grain size (μm) | Crystallite size (μm) |
|---------------------|-------------------------|----------------------|
| CCTNZO-0            | 4.82                    | 0.058                |
| CCTNZO-5            | 0.33                    | 0.034                |
| CCTNZO-10           | 0.29                    | 0.031                |
| CCTNZO-20           | 0.26                    | 0.029                |

3.3 Dielectric property analysis

Figure 6 and Figure 7 exhibits the frequency depended dielectric constant (k) and dielectric loss (\( \tan \delta \)) respectively. The measured constant values of CCTNZO (0%, 5%, 10%, 20%) ceramics at 0.1 kHz are 7402, 3452, 3455, and 1597 respectively. Dielectric constant slowly reduces for all specimens with the increment of dopant percentage, and it becomes stable at a better frequency. This
sort of phenomenon is often justified in 2 ways. “Firstly, among the four sorts of polarization, only interfacial and dipolar polarization contribute at lower frequencies. In this way, there are fewer polarization contributors at higher frequencies, leading to low dielectric constant” [19]. “Secondly, following Maxwell-Wagner theory, space charges move and coagulate at grain boundaries if sufficient resistance is present. Nevertheless, at a higher frequency, space charges don't receive adequate time to coagulate at boundaries of grain and so collapse the dielectric properties” [20, 22]. The dielectric values are enlisted in Table 3. The grain size values can reveal the gradual decrement of dielectric constant values. Domain wall movement is simpler for larger grain, resulting in a rise in dielectric properties [21]. In other research, we've found this sort of property also [22]. Sem micrographs in figure 4 lucidly shows that partial substitution of Zr$^4+$ into Ti$^4+$ ion has an impression on decreasing grain size. Measured grain size is enlisted in Table 2 depicts, decreasing grain size with increasing Zr percentage causes a gradual decrease in dielectric constant. Table 2 depicts that CCTNZO-0 has the biggest grain size with the highest dielectric constant.

![Figure 6: Frequency depended Dielectric constant values of CCTNZO ceramics at room temperature](image)

**Table 3:** Dielectric constant and Dielectric loss of CCTNZO (0, 5, 10, 20) ceramics

| Name of the element | Dielectric Constant (k) | Dielectric loss (Tanδ) |
|---------------------|-------------------------|------------------------|
|                     | 0.1 kHz | 1 MHz | 0.1 kHz | 1 MHz |
| CCTNZO-0            | 7402    | 33    | 0.369   | 1.21   |
| CCTNZO-5            | 3652    | 19    | 0.282   | 0.51   |
| CCTNZO-10           | 3655    | 44    | 0.270   | 0.49   |
| CCTNZO-20           | 1597    | 10    | 0.241   | 0.60   |

Whereas, the dielectric loss of CCTNZO (0%, 5%, 10%, 20%) ceramics are within the extent between 0.241-0.369 at 0.1kHz, which is within the tolerance limit. Figure 7 depicts that Nb-doped CCTO and
Nb & Zr doped CCTNZO ceramics show different defect chemistry. The sole exception is that CCTNZO-0 ceramics show an enormous dispersion at 10 kHz, as pointed that at this frequency extent sufficient volume of space charges did not ensue the channel of the electrical field [23]. Several mild arors are seen within the range between 100-1000 kHz. Several other parameters such as internal stress, domain density, etc. needed to be taken into account for an extra detailed clarification of this dielectric loss tangent (Tanδ) behavior [21]. Above all, doping Zr ions into CCTNO ceramics can increase the frequency fixity also as decrease the loss factor, and this broaden fixity is conductive to be applied in microelectronics devices [24]. “Q.G Chi et al. reported that mixed valent structure and oxygen vacancies should be the elemental root of huge dielectric constant for CCTO ceramics. The dielectric relaxation mechanism of CCTO ceramics are often illustrated by losing of O₂ during its sintering at heat in accordance with reaction” [25].

![Figure 7: Frequency depended Dielectric loss of CCTNZO ceramics at room temperature](image)

\[ O_2 = \frac{1}{2} O_2 + V_{O'} + 2e^- \]  
\[ \text{Cu}^{2+} \text{or Ti}^{4+} \text{capture those released electrons from equation 1 to generate Cu}^+ \text{or Ti}^{3+} \text{as follows,} \]  
\[ 2\text{Cu}^{2+} + 2e^- = 2\text{Cu}^+ \]  
\[ 2\text{Ti}^{4+} + 2e^- = 2\text{Ti}^{3+} \]  
As Ti\(^{4+}\) with 3d\(^0\) configuration is in its most stable state, the probability of formation of Ti\(^{3+}\) is negligible. On the opposite hand, Cu\(^+\) having 2d\(^{10}\) configuration is stable state of Cu due to noble gas configuration. Cu\(^+\) ions on Cu\(^{2+}\) site will bear an efficient charge. These may produce dipoles with V\(O'\). “These dipoles can alteration their orientation because of either floating of electron among Cu\(^+\) and Cu\(^{2+}\) or jumping of O\(^2-\) ions through vacant oxygen sites round the CuO\(_4\) square or TiO\(_6\) octahedral giving uprising to orientation polarization” [24].” “Q.G Chi et al. reported that prime frequency dielectric relaxation of CCTO ceramics is induced by mixed valent structure of Cu\(^+\)/Cu\(^{2+}\) and Ti\(^{3+}\)/Ti\(^{4+}\) [24]. Furthermore, CCTNZO ceramics have an equivalent mechanism of dielectric relaxation. Doping Zr\(^{4+}\) on Ti\(^{4+}\) site, oxygen vacancy formation is suppressed as follows;

\[ \text{ZrO}_2 + 2V_{(\text{O}_2 - \text{ZrTi})} + 2O_0 \]  
This will alleviate the creation of Cu\(^+\) and V\(O'\). The partial substitution of Zr\(^{4+}\) on Ti\(^{4+}\)curtails the coagulation of Cu\(^+\) and V\(O'\) also as inhibits forming the mixed valent structure in CCTNZO ceramics and reduces the dipolar polarization leading to curtailing dielectric loss [24].
4. Conclusion
In precis, traditional solid-state reaction method was used to produce the Nb and Zr co-doped CCTO ceramics. Structural study reveals no accompanying phase has arrived with the rise of Zr\textsuperscript{4+} doping from 5% to 20%. Although Nb & Zr co-doping produced an equivalent cubic structure with space group Im\overline{3}, Lattice parameters increased with co-doping. Reitveld refinement confirms the structural stability. Co-doping features a far-reaching effect on grain growth. The microstructural analysis predicts that Zr\textsuperscript{4+} might act as a grain growth inhibitor. Thus, diminished grain size and narrow size distribution are observed. Significant decrease in dielectric loss observed for CCTNZO ceramics with increasing doping percentage. 10% doping causes significant improvement both in dielectric constant & dielectric loss. Finally, though doping has made significant improvements within the dielectric constant and dielectric loss within the lower frequency, it's going to not be fit use in higher frequency devices.

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