Complex impedance and electrical conduction analysis of Ho$_2$O$_3$ doped CaCu$_3$Ti$_4$O$_{12}$ NTC ceramics

Guang-Tan Miao*, Zhen-Jie Wang*, Peng Li*, Ji-Gong Hao*, Wei Li*, Juan Du*, Wei-Fang Han*, Chun-Ming Wang*, Guo-Rong Li* and Peng Fu*a,b

*School of Materials Science and Engineering, Liaocheng University, Liaocheng, PR China; †School of Physics, State Key Laboratory of Crystal Materials, Shandong University, Jinan, PR China; ‡The State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Science, Shanghai, PR China

ABSTRACT

The structure and electrical properties of CaCu$_3$Ti$_4$O$_{12}$ (CCTO) ceramics doped with xHo$_2$O$_3$ synthesized by solid-phase reaction method were systematically studied. Insights from X-ray diffraction (XRD) measurements indicate the existence of a primary phase of CCTO in all samples. Ho$_2$O$_3$ dopant was found to inhibit grain growth and thus leading to a reduced grain size of ceramics. Moreover, the distribution of resistivity with temperature revealed the manifestation of a negative temperature coefficient (NTC) effect in the samples. More specifically, the resistivity ($\rho_{25}$) values of obtained ceramics configurations decreased from 8.54 × 10$^9$ to 1.76 × 10$^8$ Ω cm with increasing Ho$_2$O$_3$ doping content. In addition, thermal constant ($B_{20/35}$) of all samples was higher than 4000 K. Electrical properties analysis disclosed that electron hopping process is main conduction mechanism within CCTO-based ceramics. In addition, insights from complex impedance spectra revealed the existence of grain boundaries with resistance higher than grains resistance. This effect is strongly connected with the manifestation of electrical relaxation procedures within grain boundaries. Our outcomes verify that both the structural configuration and the electrical performance of the CCTO-based ceramics can be tuned directly and effectively by incorporating Ho$_2$O$_3$ dopant.

1. Introduction

NTC thermistor is a type of important electronic component due to its functional characteristic since its resistivity reduced by elevating the temperature. Such types of materials are widely used in temperature control and in-situ measurement of mechanical devices. Traditional NTC thermistors exhibit the spinel-type (AB$_2$O$_4$) structure that mainly consists of transition metal elements (such as Mn, Co, and Ni et al.) [1–3].

The performance of NTC thermistors is determined by two quite important parameters: the electrical resistivity (ρ) and the thermal constant (B). However, spinel-type NTC thermistors display relative high B values that are always coupled with higher ρ and vice versa, which is detrimental for their applications [4]. Additionally, they exhibit poor electrical stability due to the decomposition-related processes of the spinel structure, which induced serious problems during the device operation at temperatures above 300°C [5]. The above-mentioned issues render imperative the need to explore new NTC thermistor configurations with good stability and suitability for a wide temperature range. Along these lines, ceramics with perovskite structure (ABO$_3$) arise as a promising solution since they exhibit good structural stability due to the reduced cations interchange rates at high temperatures [6]. Such types of materials with perovskite structure including Bi$_{0.2}$Sr$_{0.5}$La$_{0.3}$TiO$_3$ [6], YC$_{0.5}$Mn$_{0.5}$O$_3$ [7], BaBiO$_3$ [8], Bi$_{0.3}$Ba$_{0.3}$FeO$_3$ [9], CCTO [10] exhibit also distinct NTC characteristics and as a result have been extensively studied in recent years.

As far as the CCTO-based ceramics are concerned, the inherent colossal dielectric permittivity $\varepsilon'$ values (approximately 10$^8$–10$^9$), as well as the excellent non-ohmic properties, render them promising candidates for capacitors with high dielectric constant and protection against overvoltage events [11]. In general, the internal barrier layer capacitor approach is suitable for interpreting the anomalous dielectric behavior of the CCTO-based ceramics [12–14]. Although CCTO ceramics exhibit huge $\varepsilon'$ values, the high loss tangent (tanδ) limits their widespread applications. Moreover, numerous synthesis processes have been considered in order to optimize the dielectric characteristics of CCTO-based ceramics, such as sol–gel deposition [15] and spark-plasma sintering [16]. Additionally, high dielectric constant and low loss were obtained in similar material configurations by doping single Zn$^{2+}$ ion or (Y$^{3+}$, Mg$^{2+}$) and (Zr$^{4+}$, Nb$^{5+}$) ion pair [17–19]. Thus, the
local microstructures and electrical properties of CCTO-based ceramics can be significantly regulated by the doping approach.

Meanwhile, the semiconducting and the impedance performance of CCTO ceramics have been also preliminarily studied. The impedance spectrum for CCTO ceramics reveals that the grain exhibits a semiconductivity pattern, while the grain boundary possesses insulating properties [20]. This implies this type of material displays a certain conductivity pattern within a specific temperature range. The established conduction mechanism model of CCTO-based ceramics stems from the cation-related non-stoichiometry theoretical approach, proposed by Li et al. [21]. Considering that CCTO ceramics behave as n-type semiconductors by assembling a big amount of available free electrons in the conduction band, renders them attractive for active material within the NTC thermistors. In addition, the electrical performance of CCTO ceramics can be tuned directly by following a doping strategy with Zr, La, Y and Mn, as was reported by B. Zhang et al. [22–24].

Although the implementation of the NTC effect by employing CCTO ceramics has been previously reported, a detailed study of the underlying conduction mechanisms is still missing. In this work, we present a thorough study on the doping effect of CCTO-based ceramics with $\text{Ho}_2\text{O}_3$ and the concomitant impact on the local microstructure and electrical properties. In addition, fruitful insights are attained by elaborating on the physical conduction mechanisms, whereas the impedance spectroscopy studies divulged the role of the electrical relaxation effects on the total conduction pattern.

2. Experimental procedures

In order to fabricate the $x\text{Ho}_2\text{O}_3$-(1-x)CCTO (x = 0, 0.01, 0.03, 0.05) ceramics through the solid-phase method the following starting powders were used: CaCO$_3$ (99%, Sinopharm), TiO$_2$ (98%, Sinopharm), CuO (99%, Sinopharm), Ho$_2$O$_3$ (99%, Aladdin). The starting powders were weighed stoichiometrically and subsequently ball-milled for 16 h by using alcohol as grinding media. Afterward they were dried and calcined at 850°C for 6 h. The calcined mixtures were ball-mixed for 16 h and powders were pressed into disks of 15 mm in diameter with PVA. Subsequently, the disks were sintered at 1100°C for 2 h after removing the binder at 610°C. Finally, the silver paste coated on the surface of the polished samples was thermal annealed at 620°C for 20 min.

The phase structure of the Ho-CCTO ceramics was characterized by performing 2$\theta$ scanning from 20° to 70° by using an X-ray diffractometer (Ultima IV, Rigaku Co., LTD, Japan). Field-emission scanning electron microscopy (SEM, Zeiss, merlin compact, Germany) was employed to perform the morphology of the surface and fracture, while the elemental distribution was detected by carrying out energy-dispersive X-ray spectroscopy (EDS, IE250X-Max50, Oxford, UK). X-ray photoelectron spectroscopy (XPS, K-Alpha+, Thermo fisher Scientific, USA) measurements were carried out to determine the valence state of the elements. Electrical resistance measurements were conducted within the temperature from 20°C to 300°C by a multimeter (Keithley Instruments Inc., USA) with a heat source. In addition, the dielectric characteristics, modulus and complex impedance distributions of all samples were examined by employing the Broadband Dielectric/Impedance Spectrometer (Concept80, Novocontrol Inc., Germany).

3. Results and discussion

Figure 1(a) illustrates the XRD patterns for the $x\text{Ho}_2\text{O}_3$-(1-x)CCTO ceramics. All diffraction peaks in Figure 1(a) can be matched with the standard CCTO configuration (JCPDS 75–2188), indicating that all samples possess a pure perovskite structure with a space group of Im-3 [25]. As it is depicted in Figure 1(b), the (220) diffraction peak of the $x\text{Ho}_2\text{O}_3$-(1-x)CCTO ceramics shift toward to higher angles with increasing Ho$_2$O$_3$ addition, indicating that the occupation of Ca$^{2+}$ (0.99 Å) by Ho$^{3+}$ (0.901 Å). The extracted analysis reveals that Ho$^{3+}$ ions have fully entered the CCTO lattice as $x \leq 0.03$;

Figure 1. XRD patterns of the $x\text{Ho}_2\text{O}_3$-(1-x)CCTO ceramics: (a) 2$\theta$ = 20–70°; (b) 2$\theta$ = 33–35.5°.
however, the (220) diffraction angle is not increasing further more for the $x\text{Ho}_2\text{O}_3$-(1-$x$)CCTO ceramics as $x > 0.03$. This result indicates that the doping amount of $\text{Ho}_2\text{O}_3$ is not larger than 0.03.

Figure 2 depicts the SEM micrographs for the $x\text{Ho}_2\text{O}_3$-(1-$x$)CCTO ceramics. The results signify that the microstructures of the pure CCTO and $\text{Ho}_2\text{O}_3$ doped samples are significantly different. Moreover, it can be observed that coarse grains are embedded within smaller grains matrix in the pure CCTO ceramic, which could be related to its liquid phase sintering mechanism at high temperatures [26]. In addition, the inhibitory effect of the $\text{Ho}_2\text{O}_3$-based doping on the abnormal grain growth effect of the host ceramic can be also observed. A declined trend of the average grain size and a more uniform distribution can be detected by increasing the $\text{Ho}_2\text{O}_3$ concentration, which could originate from the implementation of the solute drag mechanism [27]. Zn/Al doping has a similar effect on CCTO-based ceramics [28]. A detailed analysis of the elemental distribution of 0.03$\text{Ho}_2\text{O}_3$-0.97CCTO samples is presented in Figure 3, where the samples’ fracture section was taken into account. Additionally, the relevant intensity profile shows the characteristic peaks of Cu, Ca, Ti and Ho detected with no additional peak as an impurity phase. The EDS analysis results of section profiles revealed the homogeneous distribution of the following elements: Ca, Ti, Cu, O and Ho, which confirm the stoichiometric nature of the sintered sample.

Figure 4 reveals the DC resistivity vs. temperature plot of the $x\text{Ho}_2\text{O}_3$-(1-$x$)CCTO ceramics. Table 1 lists the detailed resistivity values at 20°C ($\rho_{20}$) and 75°C ($\rho_{75}$). An exponential decrease of resistivity as a function of the temperature can be confirmed, indicating the manifestation of the typical NTC response. As can be ascertained from Table 1, the resistivity values $\rho_{20}$ decreased from the value of $8.54 \times 10^5$ to $1.76 \times 10^5$ $\Omega$ cm by enhancing the doping amount of $\text{Ho}_2\text{O}_3$. The resistivity distribution pattern of the NTC ceramics can be interpreted by considering the impact of both grain size and carrier concentration [9]. More specifically, from the SEM analysis, it can be concluded that elevating the $\text{Ho}_2\text{O}_3$ doping concentrations makes the grain size distribution more uniform. The grain size in pure CCTO presents a bimodal distribution, with large grains surrounded by small grains. Simultaneously, small-sized grains occupy a larger proportion of the number. The inhomogeneous microstructure in the pure CCTO ceramic could accelerate the electron scattering events in the grain boundary area, resulting thus in a higher resistivity value [29]. Furthermore, $\text{Ho}_2\text{O}_3$ could also play the role of donor dopant and introduce electrons into the system through the following reaction:

\[ \text{Ho}^{3+} + \text{Ca}^{2+} \rightarrow \text{Ho}^{2+}_{\text{Ca}} + e'. \]

As a result, an elevated carrier concentration will be attained which lowers the energy barrier height for electron hopping and induce the resistance to decrease. Similar results have been reported regarding the modification of the electrical properties in CCTO-based ceramics with Y$^{3+}$ doping [22].

Figure 5 shows the distribution between $\ln \rho$ and $1000/T$ for the $x\text{Ho}_2\text{O}_3$-(1-$x$)CCTO ceramics. The linear relationship between them indicates the manifestation of a thermally activated conduction process of carriers that can be well fitted by Arrhenius expression:

\[ \rho = \rho_0 \exp(E_a/kT) \]

(1)

Figure 2. SEM images of the $x\text{Ho}_2\text{O}_3$-(1-$x$)CCTO ceramics: (a) $x = 0$; (b) $x = 0.01$; (c) $x = 0.03$; (d) $x = 0.05$. 
where $\rho_0$, $k$ and $T$ represent the inherent factor of material, the Boltzmann constant and the absolute temperature, respectively. Table 1 depicts a decrease of activation energies ($E_a$) values of the $x$Ho$_2$O$_3$-(1-$x$) doped CCTO-based ceramics from 0.5346 to 0.3845 eV by increasing the doping content, which probably originates from the elevated concentration of charge carriers.

As far as the NTC thermistors are concerned, the

![Figure 3. SEM, elements mapping and relevant intensity profile for the cross-section of the 0.03Ho$_2$O$_3$-0.97CCTO ceramic.](image)
B value is also a quite important parameter that reflects their sensitivity within a certain temperature range. \( B_{20/75} \) can be obtained according to the equation:

\[
B_{20/75} = \frac{\ln(\rho_{20}/\rho_{75})}{1/T_{20} - 1/T_{75}} \tag{2}
\]

As can be ascertained from Table 1, the values of the \( B_{20/75} \), \( \rho_{20} \), and \( \rho_{75} \) are in the range of 4258–5954 K, \( 1.76 \times 10^5 – 8.54 \times 10^6 \) Ω cm and \( 1.70 \times 10^2 – 3.44 \times 10^5 \) Ω cm, respectively. The \( B \) values of most commercial NTC thermistors is in the range of 2000–6000 K [30], so the \( B \) value of Ho\(_2\)O\(_3\) doped CCTO ceramics meet commercial requirements. The relatively moderate values of both \( \rho \) and \( B \), in conjunction with the good linear dependence of \( \rho \), as can be confirmed from Figure 5, indicate that Ho\(_2\)O\(_3\) modified CCTO ceramics is a great candidate for temperature control applications within a wide-temperature range.

### Table 1. Electrical parameters for the xHo\(_2\)O\(_3\)–(1-x)CCTO samples.

| \( x \) | \( \rho_{20}(\Omega \text{ cm}) \) | \( \rho_{75}(\Omega \text{ cm}) \) | \( E_a(\text{eV}) \) | \( B_{20/75}(\text{K}) \) | \( E_{\text{relax}}(\text{eV}) \) |
| --- | --- | --- | --- | --- | --- |
| 0.00 | \( 8.54 \times 10^6 \) | \( 3.44 \times 10^5 \) | 0.5346 | 5954 | 0.6200 |
| 0.01 | \( 3.58 \times 10^6 \) | \( 2.31 \times 10^5 \) | 0.4974 | 5081 | 0.5628 |
| 0.03 | \( 6.92 \times 10^5 \) | \( 6.96 \times 10^4 \) | 0.4263 | 4258 | 0.5234 |
| 0.05 | \( 1.76 \times 10^5 \) | \( 1.70 \times 10^4 \) | 0.3845 | 4333 | 0.5755 |

Figure 4. The DC resistivity as a function of temperature for the xHo\(_2\)O\(_3\)–(1-x)CCTO ceramics.

Figure 5. Relationship between ln\( \rho \) vs. 1000/T of the xHo\(_2\)O\(_3\)–(1-x)CCTO ceramics.
XPS was used in order to clarify the valence states of various elements in the ceramics, and the XPS spectra of Cu 2p, O 1s and Ti 2p of xHo$_2$O$_3$-(1-x)CCTO ceramics illustrated in Figure 6(a-c). Figure 6(a) depict the high-resolution XPS spectra of Cu 2p, while by employing Gaussian-Lorentzian profile fitting, the peak of Cu 2p$_{3/2}$ can be individually resolved into two components and attributed to the existence of Cu$^{2+}$ and Cu$^+$ [31]. Moreover, as can be observed from Figure 6(c), the Ti 2p$_{3/2}$ signal can be well fitted by considering the manifestation of two peaks, which signify the existence of Ti$^{4+}$ and Ti$^{3+}$ [15]. More importantly, the peak fitting results show that the concentration percentages of Cu$^+$ and Ti$^{3+}$ increase with the increase of Ho$_2$O$_3$ doping content. The increase of electron carriers promotes the conversion of Cu$^{2+}$ to Cu$^+$ and Ti$^{4+}$ to Ti$^{3+}$. By considering the chemical environment of the detected signal of O 1s (Figure 6(b)), the fitting peaks are assigned to both lattice oxygen with low binding energy and oxygen vacancy with high binding energy. Similar to other perovskite structure compounds, the creation mechanism of oxygen vacancies in CCTO ceramics is associated with the oxygen deficiency in making ceramics [32]. Additionally, it can be observed that the oxygen vacancy concentration decreases when x = 0.05, which may be due to excessive Ho$_2$O$_3$ doping inhibiting oxygen deficiency.

According to the literature [4], the conduction mechanisms of thermistors are closely associated with electron hopping processes between different valence states that are induced by the cations’ formation. The coexistence of the following cations: Cu$^+/Cu^+$, Ti$^{4+}/Ti^{3+}$ in XPS analysis verifies this assumption, which are prerequisites for the hopping-based electron transport. Li et al. [21] reported that in terms of CCTO-based ceramics with semi-conducting characteristics, double-charged Cu$^{2+}$ cations will be reduced to single charged Cu$^+$ during the sintering process, while

![Figure 6](image_url)
the loss of charge is compensated by Ti\(^{4+}\) occupying Cu site, which resulting in the creation of the following formula: \(\text{Ca}(\text{Cu}_{2/3}^+\text{Cu}_{1/3}^+\text{Ti}^{4+})\text{Ti}_4\text{O}_{12}\). On the other hand, the electrons in the Cu\(^{+}\) state will hop to the Ti 3d orbit and reduce part of Ti\(^{4+}\) to Ti\(^{3+}\) as the cooling process occurs, which can be described by: Cu\(^{+}\) + Ti\(^{4+}\) → Cu\(^{3+}\) + Ti\(^{3+}\). Due to Ho\(_2\)O\(_3\) doping will induce the creation of more electrons, which can trigger the sub-sequent reactions: Cu\(^{2+}\) + e' → Cu\(^{+}\), Ti\(^{4+}\) + e' → Ti\(^{3+}\). XPS results show that Ho\(_2\)O\(_3\) doping increases the Cu\(^{+}\) and Ti\(^{3+}\) concentration, thus an enhanced concentration of heterovalent ion pairs is anticipated to take place that could significantly influence the electrical conduction process. This assumption is consistent with the observed result that the monotonous decrease of the measured resistivity values by increasing the concentration of Ho\(_2\)O\(_3\).

**Figure 7(a-d)** shows the frequency dependent dielectric constant (\(\varepsilon'\)) of the \(x\text{Ho}_2\text{O}_3\)-(1-\(x\))CCTO ceramics measured at various temperatures. The slight decreases of \(\varepsilon'\) value with the increase of frequency can be ascertainment. The space charge polarization

**Figure 7.** Relationship between dielectric constant (\(\varepsilon'\)) vs. frequency for the \(x\text{Ho}_2\text{O}_3\)-(1-\(x\))CCTO samples at different temperatures: (a) \(x = 0\); (b) \(x = 0.01\); (c) \(x = 0.03\); (d) \(x = 0.05\); (e) the \(\varepsilon'\) and \(\tan \delta\) of the \(x\text{Ho}_2\text{O}_3\)-(1-\(x\))CCTO as functions of frequency measure at 20°C.
effect causes dielectric dispersion in the low-frequency zone ($< 10^3$ Hz), which could lead to a relatively high value of $\varepsilon'$. However, the step-like decrease of $\varepsilon'$ by elevating the temperature indicates the thermally activated dielectric relaxation process [31]. The presence of the dielectric relaxation phenomenon within the measured frequency range (1–10$^6$ Hz) can be interpreted by considering the Maxwell-Wagner polarization effect [33], which is caused by the electrical inhomogeneity of the charge carriers of $x$Ho$_2$O$_3$-(1-x)CCTO ceramics. Furthermore, the $\varepsilon'$ value in the low-frequency zone ($< 10^3$ Hz) slightly decreases by elevating the temperature, which could be assigned to the weak electrical inhomogeneity caused by the grain boundary resistance ($R_{gb}$) being comparable to the grain resistance ($R_g$) [34].

The $\varepsilon'$ and tan $\delta$ as functions of frequency of $x$Ho$_2$O$_3$-(1-x)CCTO ceramics measured at 20°C are presented in Figure 7(c). It is interesting to notice that all samples possess a giant $\varepsilon'$ value within the measured frequency range. Additionally, the $\varepsilon'$ and tan $\delta$ increase by enhancing the Ho$_2$O$_3$ doping content, which could be correlated with the generation of free electrons that are induced by Ho doping. These electrons can be subsequently confined by the related clusters to enhance the dielectric response [35].

The Nyquist plots of the $x$Ho$_2$O$_3$-(1-x)CCTO ceramics at selected temperatures are shown in Figure 8. It is well-established that CCTO ceramics possess various electrically inhomogeneous phases. For the Nyquist plots, the grain boundary-related electrical behavior is represented by the low frequency arc while the grain-related electrical response is manifested by the high frequency arc. Furthermore, the observed single recessed semicircle shapes suggest that the grain as well as grain boundary in the ceramics may possess similar relaxation times [36]. Additionally, the contribution of the grains to the electrical response becomes more pronounced as the Ho$_2$O$_3$ content increases. The semicircle’s centers lie below the x-axis, indicating the manifestation of non-Debye relaxation [34]. Moreover, it can be ascertained that the intercept of the semicircle ($R_{total}$) at the low-frequency range decreases as the temperature rises, which is a typical response of the NTC effect.

In order to further examine the contribution of both grain boundaries and grains to the total resistance, the Zview software was employed to fit the complex impedance spectrum of $x$Ho$_2$O$_3$-(1-x)CCTO ceramics at the temperature value of 20°C. The equivalent circuit is composed of two in series connected subcircuits that include a resistor and constant phase element (CPE), which are parallelly connected (Figure 9 inset) [37]. CPE has previously been used to describe the non-ideal relaxation of ceramic materials explained by the expression [38]:

![Figure 8. Nyquist plots for the $x$Ho$_2$O$_3$-(1-x)CCTO samples measured at a few selected temperatures: (a) $x = 0$; (b) $x = 0.01$; (c) $x = 0.03$; (d) $x = 0.05$.](image-url)
Figure 9. \(R_{gb}\) and \(R_g\) of samples at 20°C as a function of \(\text{Ho}_2\text{O}_3\) content and simplified equivalent circuit of samples.

\[
Z_{\text{CPE}} = A^{-1}(i\omega)^{-n}
\]  
(3)

where \(\omega\) is the angular frequency of the alternating current. Use the \(R_g/\text{CPE}_1\) and \(R_{gb}/\text{CPE}_2\) components to fit the left and right sides of the frequencies marked by the arrow in Figure 8 respectively, and finally perform a full-spectrum fitting over the entire frequency range. Figure 8 shows that the impedance spectra experimental data (black symbol) of \(x\text{Ho}_2\text{O}_3(1-x)\text{CCTO}\) ceramics at 20°C is in good agreement with the fitting results (orange line), and the error rates of the \(R_g\) and \(R_{gb}\) values are less than 5%. Figure 9 depicts the \(R_g\) and \(R_{gb}\) fitted values as functions of \(\text{Ho}_2\text{O}_3\) doping concentration, where a clear decrease in both the \(R_{gb}\) value (from 840 kΩ to 14 kΩ) and the \(R_g\) value (from 82 kΩ to 5.3 kΩ) by increasing \(\text{Ho}_2\text{O}_3\) concentration can be observed. Besides, the values of both fitting parameters \(R_{\text{total}}\) and \(R_{gb}\) are in the same order of magnitude, while \(R_g\) is much smaller than \(R_{gb}\). From these results, we can draw the conclusion that the electrical response of CCTO ceramics can be directly tuned by adjusting the content of \(\text{Ho}_2\text{O}_3\). Additionally, the different contribution of \(R_{gb}\) and \(R_g\) on the resistance distribution are captured by the IBLC model and play an important impact on dielectric properties [39]. It needs to be emphasized that the presence of electrical heterogeneous phases within composite dielectrics will cause interface polarization, which leads to the implementation of the Maxwell-Wagner relaxation [40,41].

Figure 10 shows the frequency dependences of the real part of the impedance (\(Z'\)) obtained at selected temperatures. Due to the accumulation effect of space charges, the \(Z'\) value at the temperature of 20°C is very high and stable in the low-frequency range (<10¹ Hz), while it decreases rapidly as the frequency shifts toward higher values.

Figure 10. Variations of real part of the impedance (\(Z'\)) as a function of the temperature for the \(x\text{Ho}_2\text{O}_3(1-x)\text{CCTO}\) ceramics at several representative temperatures: (a) \(x = 0\); (b) \(x = 0.01\); (c) \(x = 0.03\); (d) \(x = 0.05\).
Moreover, the magnitude of Z' of each component decreases with increasing the temperature, suggesting an enhancement of the AC conductivity. Additionally, the shift of the Z' plateau in the low-frequency region to a higher value by increasing the temperature provides a piece of strong evidence in the manifestation of frequency-dependent relaxation [42]. Finally, the Z' responses at all temperature ranges are merged to a line in the higher frequency zone, which could originate from the reduction of the potential barrier induced by the release of space charges [43]. Furthermore, the Z' value decreases by enhancing the content of Ho2O3, probably due to the elevated electron concentration.

Figure 11 illustrates the frequency-dependent imaginary part of the impedance (Z'') at selected temperatures. The Z'' curve at each temperature will reach its maximum value (Z''\text{max}) at the relaxation frequency (fβ). The existence of a sole peak for all curves at a lower frequency represents that the materials are governed by a single relaxation process, which is closely related to the grain boundary effect [20]. In addition, Z'' decreases by increasing the temperature and shift toward higher frequencies, indicating the decrease of the relaxation time (τ). Moreover, from the extracted data it is concluded that the Z''\text{max} signal also decreases by increasing the Ho2O3 content, suggesting a clear reduction in Rgb (Z''\text{max} = Rgb/2) [44], which is similar to the fitting result presented in Figure 9.

The electrical modulus analysis is an effective method for investigating the electrode polarization effects as well as identifying the bulk (grain and grain boundary) conduction properties. The M'' spectra for the xHo2O3-(1-x)CCTO ceramics within the temperature range of 20–100°C are presented in Figure 12. For all samples, a discernible broadened peak (M''\text{max}) can be observed in the measured spectra for all the studied temperatures, indicating the expansion of the relaxation time for non-Debye response. M''\text{max} shifts to high-frequency zone implying the manifestation of a temperature dependent-relaxation mechanism. From these results, it’s apparent that the carriers hopping triggers the thermally activated relaxation process [45].

In order to further reveal the relaxation nature for the xHo2O3-(1-x)CCTO ceramics, the relationship between ln(τ) and 1000/T is plotted in Figure 13. The activation energy for the relaxation process (E\text{relax}) can be expressed from the Arrhenius law:

\[ \tau = \tau_0 \exp\left(-\frac{E_{\text{relax}}}{kT}\right) \]  

(4)

![Figure 11. Variations of imaginary part of the impedance (Z'') as a function of the temperature for the xHo2O3-(1-x)CCTO ceramics at several representative temperatures: (a) x = 0; (b) x = 0.01; (c) x = 0.03; (d) x = 0.05.](image-url)
where \(\tau_0\) denotes the pre-exponential factor, while \(\tau\) is determined from \(f\), at different temperatures by using the following relation: \(\tau = 1/2\pi f\). Table 1 lists the \(E_{\text{relax}}\) values in the range of 0.5755–0.6200 eV, which are consistent with the Maxwell-Wagner polarization phenomenon that is caused by the activation of oxygen vacancies \([46]\). CCTO-based ceramics can inevitably produce oxygen vacancies during the sintering process, as described by the following defect equation

\[
2O_2^0 \rightarrow O_2(g) + 2V_{\text{o}}^{**} + 4e^-
\]  

The values of \(E_{\text{relax}}\) are also closely associated with the energies required for the second ionization of oxygen vacancies \(V_{\text{o}}^{**}\). Generally, since the long-range migration of oxygen vacancies is easily inhibited by the presence of grain boundaries, the respective relaxation processes are dominated by space charge-related mechanisms \([47]\).

4. Conclusions

The microstructure, NTC effect as well as relaxation behavior of \(x\text{Ho}_2\text{O}_3-(1-x)\text{CCTO}\) ceramics were investigated. XRD analysis proves that \(\text{Ho}^{3+}\) ions dissolve into the CCTO lattice and maintains the cubic perovskite structure. The average grain size of the samples was reduced by considering the impact of \(\text{Ho}^{3+}\) ions. Furthermore, all samples exhibit excellent NTC effect, while the incorporation of a small amount of \(\text{Ho}_2\text{O}_3\) yield in a clear reduction of the \(\rho_{20}\) values of CCTO from \(8.54 \times 10^6\) to \(1.76 \times 10^5\ \Omega\ cm\), whereas
the $B_{20/75}$ values ranged from 4258–5954 K. The electrons hopping between various oxidation energy states, induced by the formation of cation, was proposed as the prevailing conduction mechanism for the sintered sample. Significant insights were gained by analyzing the impedance spectra, confirming the grain boundary resistances were higher than the respective grain resistances. Moreover, the electrical relaxation behavior was induced by the presence of space charges at the interface of ceramics. From our analysis, we can draw the conclusion that the electrical properties for CCTO NTC ceramics could be significantly regulated by varying the $\text{HO}_2\text{O}_3$ content.

**Disclosure statement**

No potential conflict of interest was reported by the author(s).

**Funding**

This work was supported by the National Natural Science Foundation of China (Grant Nos. 51872166), Project funded by China Postdoctoral Science Foundation (Postdoctoral Research Foundation of China 2017M622196), the Opening Project of Key Laboratory of Inorganic Functional Materials and Devices, Chinese Academy of Sciences (Grant No. KLIFMD201705), Natural Science Foundation of Shandong Province of China (ZR2020ME035, ZR2020QE043, ZR2020QE044, ZR2020ME031, ZR2020ME033) and Innovation Team of Higher Educational Science and Technology Program in Shandong Province (2019JKA025).

**References**

[1] Guan F, Dang ZW, Wu YQ, et al. LaCo$_7$Fe$_3$O$_7$-NiMn$_2$O$_4$ supported NTC composite ceramics with a sandwich-like structure. J Eur Ceram Soc. 2021;41(8):4490–4495.

[2] Park K, Lee JK. Mn–Ni–Co–Cu–Zn–O NTC thermistor with high thermal stability for low resistance applications. Scripta Mater. 2007;57(4):329–332.

[3] Li HB, Zhang HM, Chang AM, et al. Fast response and high stability Mn–Co–Ni–Al–O NTC microbeads thermistors. J Am Ceram Soc. 2021;00:1–7.

[4] Li QX, Luo Y, Chen GH. Structural stability and electrical properties of Ba$_2$CoNb$_2$O$_6$-based negative temperature coefficient sensitive ceramics. Ceram Int. 2019;45(7):8145–8149.

[5] Raj NPMJ, Alluri NR, Chandrasekhar A, et al. Self-powered ferroelectric NTC thermistor based on bismuth titanate. Nano Energy. 2019;62:329–337.

[6] Liu T, Chen X, Zhang HM, et al. Fabrication of high-sensitivity Bi$_{0.2}$Ce$_{0.8}$Sr$_{1-x}$La$_3$Ti$_6$O$_{13}$ (0 < x < 0.05) ceramics for high-temperature NTC thermistors. J Alloy Compd. 2021;853:156749.

[7] Zhang B, Zhao Q, Chang AM, et al. Spark plasma sintering of MgAl$_2$O$_4$-Y$_2$O$_3$-Sm$_2$O$_3$ composite NTC ceramics. J Eur Ceram Soc. 2014;34(12):2989–2995.

[8] Qu JJ, Fei SL, Liu LX, et al. Effect of phase structures and substrate temperatures on NTC characteristics of Cu-modified Ba–Bi–O-based perovskite-type thermistor thin films. Mat Sci Semicon Proc. 2021;121:105375.

[9] Fu P, Miao GT, Yin M, et al. Structure and electrical properties of Bi$_{0.8}$Ba$_{0.2}$FeO$_{3}$–Y$_2$O$_3$ composite NTC ceramics. Mater Sci Eng B-Adv. 2019;249:114421.

[10] Chen XY, Zhang B, Li N, et al. New negative temperature coefficient ceramics in Zr-doped CaCu$_3$Ti$_{12}$O$_{12}$ system. J Alloy Compd. 2020;821:153476.

[11] Lee JW, Koh JH. Enhanced dielectric properties of Ag-doped CCTO ceramics for energy storage devices. Ceram Int. 2017;43(12):9493–9497.

[12] Sinclair DC, Adams TB, Morrison FD, et al. CaCu$_3$Ti$_{12}$O$_{12}$: one-step internal barrier layer capacitor. Appl Phys Lett. 2002;80(12):2153.

[13] Taylor NT, Davies FH, Davies SG, et al. The fundamental mechanism behind colossal permittivity in oxides. Adv Mater. 2019;31(15):1904746.

[14] Bovtun V, Petzelt J, Kempa M, et al. Wide range dielectric and infrared spectroscopy of (Nb plus In) co-doped rutile ceramics. Phys Rev Mater. 2018;2(7):075002.

[15] Lin H, Xu WT, Zhang HT, et al. Origin of high dielectric performance in fine-grain-sized CaCu$_3$Ti$_{12}$O$_{12}$ materials. J Eur Ceram Soc. 2020;40(5):1957–1966.

[16] Manière C, Riquet G, Marinell S. Dielectric properties of flash spark plasma sintered BaTiO$_3$ and CaCusTi$_{12}$O$_{12}$. Scripta Mater. 2019;173:41–45.

[17] Boonlakhorn J, Chanlek N, Manyam J, et al. Structural and dielectric properties, and nonlinear electrical properties of the CaCu$_3$Zn$_2$Ti$_{12}$O$_{12}$ ceramics: experimental and computational studies. Ceram Int. 2021;47(16):22390–22396.

[18] Boonlakhorn J, Putasaeng B, Kidkhunthod P, et al. Improved dielectric properties of (Y + Mg) co-doped CaCu$_3$Ti$_{12}$O$_{12}$ ceramics by controlling geometric and intrinsic properties of grain boundaries. Mater Design. 2016;92:494–498.

[19] Mao P, Wang JQ, Xiao P, et al. Colossal dielectric response and relaxation behavior in novel system of Zr$^{4+}$ and Nb$^{5+}$ co-substituted CaCu$_3$Ti$_{12}$O$_{12}$ ceramics. Ceram Int. 2021;47(1):111–120.

[20] Kumara V, Pandey S, Kumar A, et al. Investigation of dielectric, magnetic and impedance spectroscopic properties of CaCu$_3$Mn$_2$Ti$_{12}$Mn$_2$O$_{12}$ (x = 0.10) nano-ceramic synthesized through semi-wet route. J Mater Res Technol. 2020;9(6):12936–12945.

[21] Liu J, Subramanian MA, Rosenfeld HD, et al. Clues to the giant dielectric constant of of CaCu$_3$Ti$_{12}$O$_{12}$ in the defect structure of “SrCu$_3$Ti$_{12}$O$_{12}””. Chem Mater. 2004;16(25):5223–5225.

[22] Chen XY, Zhang B, Chang AM. New negative temperature coefficient ceramics in Ca$_{1-x}$Y$_x$Cu$_3$Ti$_{12}$Zr$_{0.1}$O$_{12}$ system. J Mater Sci-Mater El. 2020;31(2):1745–1751.

[23] Jia XM, Zhang B, Chang AM. New negative temperature coefficient ceramics in La-doped La-doped CaCu$_3$Ti$_{12}$O$_{12}$ system. J Mater Sci-Mater El. 2019;30(11):10217–10223.
[24] Zhang B, Zhao Q, Chang AM, et al. New negative temperature coefficient thermistor ceramics in Mn-doped CaCu$_3$Mn$_{1-x}$Ti$_x$O$_{12}$ (0≤x≤1) system. Ceram Int. 2014;40(7):11221–11227.

[25] Du GP, Wei FB, Li W, et al. Co-doping effects of A-site Y$^{3+}$ and B-site Al$^{3+}$ on the microstructures and dielectric properties of CaCu$_3$Ti$_{1-y}$O$_{12}$ ceramics. J Eur Ceram Soc. 2017;37(15):4653–4659.

[26] Löhner R, Bartsch H, Schmidt R, et al. Microstructure and electric properties of CaCu$_3$Ti$_4$O$_{12}$ multilayer capacitors. J Am Ceram Soc. 2015;98(1):141–147.

[27] Boonlakhorn J, Srepusharawoot P, Thongbai P. Distinct roles between complex defect clusters and insulating grain boundary on dielectric loss behaviors of (In$^{3+}$/Ta$^{5+}$) co-doped CaCu$_3$Ti$_4$O$_{12}$ ceramics. Results Phys. 2020;16:102886.

[28] Xu C, Zhao XT, Ren LL, et al. Enhanced electrical properties of CaCu$_3$Ti$_4$O$_{12}$ ceramics by spark plasma sintering: role of Zn and Al co-doping. J Alloy Compd. 2019;792:1079–1087.

[29] Guan F, Dang ZW, Huang SF, et al. LaCr$_{1-x}$Fe$_x$O$_3$ (0≤x≤0.7): a novel NTC ceramic with high stability. J Eur Ceram Soc. 2020;40(15):5597–5601.

[30] Liu Y, Leng SL, Li SH, et al. Electrical properties and temperature sensitivity of Mo-modified CuFe$_2$O$_4$ ceramics. Mater Res Express. 2018;5(3):036307.

[31] Jumpatam J, Putasaeng B, Chanlek N, et al. Significantly improving the giant dielectric properties of CaCu$_3$Ti$_{1-x}$O$_{12}$ ceramics by co-doping with Sr$^{2+}$ and F$^-$ ions. Mater Res Bull. 2021;133:111043.

[32] Clavel HJL, Avan IT, Lozano G, et al. Understanding the electronic properties of BaTiO$_3$ and Er$^{3+}$ doped BaTiO$_3$ films through confocal scanning microscopy and XPS: the role of oxygen vacancies. Phys Chem Chem Phys. 2020;22(26):15022–15034.

[33] Andoulsi-Fezei R, Sdiri N, Horchani-Naifer K, et al. Dielectric properties of calcium-substituted lanthanum ferrite. J Asian Ceram Soc. 2020;8(1):94–105.

[34] Singh AP, Pandey OP, Sharma P. Impedance spectroscopy and magneto-dielectric analysis of La$^{3+}$ substituted Co$_3$Z hexaferrite. Ceram Int. 2021;47 (16):22550–22557.

[35] Cortés JA, Moreno H, Orrego S, et al. Dielectric and non-ohmic analysis of Sr$^{2+}$ influences on CaCu$_3$Ti$_{12}$O$_{12}$-based ceramic composites. Mater Res Bull. 2021;134:111071.

[36] Xu Q, Lanagan MT, Luo W, et al. Electrical properties and relaxation behavior of Bi$_2$Sn$_2$TiO$_7$-BaTiO$_3$ ceramics modified with NaNBO$_3$. J Eur Ceram Soc. 2016;36 (10):2469–2477.

[37] Wang J, Zhang H, Xue D, et al. Electrical properties of hexagonal BaTi$_6$Co$_{12}$O$_{37}$ ceramic with NTC effect. J Phys D Appl Phys. 2009;42(23):235103.

[38] Yanchevski OZ, Vyvunov OI, Belous AG, et al. Dielectric properties of CaCu$_3$Ti$_{12}$O$_{12}$ ceramics doped with aluminum and fluorsine. J Alloy Compd. 2021;874:159861.

[39] Shahraki MM, Golmohammad M, Cheraghmehr MD, et al. Stable high dielectric properties in (Cr, Nb) co-doped SnO$_2$ ceramics. Mater Chem Phys. 2020;246:122843.

[40] Shanker J, Buchi Suresh M, Saravanan P, et al. Effects of Fe substitution on structural, electrical and magnetic properties of erium ortho-chromite nano polycrystalline material. J Magn Magn Mater. 2019;477:167–181.

[41] Castro-Couceiro A, Yáñez-Vilar S, Sánchez-Andújar M, et al. Maxwell-Wagner relaxation in the CaMn$_{0.8}$Al$_{0.2}$ perovskite. Prog Solid State Ch. 2007;35(2–4):379–386.

[42] Purohit V, Choudhary RNP. Structural, dielectric and impedance properties of lead-free Bi(Sr$_{0.5}$Ba$_{0.5}$)$_3$O$_7$ ceramic. Mater Sci Eng B-Adv. 2019;243:30–37.

[43] Rout A, Agrawal S. Investigation of electrical conduction in Ca$_{6-x}$Na$_x$Y$_2$(SiO$_4$)$_3$F$_2$·xEu$^{3+}$ ceramic by complex impedance and electric modulus spectroscopy. Ceram Int. 2021;47(S):7032–7044.

[44] Cotrima G, Cortés JA, Moreno H, et al. Tunable capacitor-varistor response of CaCu$_3$Ti$_{12}$O$_{12}$/CaTiO$_3$ ceramic composites with SnO$_2$ addition. Mater Charact. 2020;170:110699.

[45] Raymond O, Font R, Suárez-Almodovar N, et al. Frequency-temperature response of ferroelectromagnetic Pb(F$_{1-x}$Nb$_{1/2}$)$_3$O$_7$ ceramics obtained by different precursors. Part II. Impedance spectroscopy characterization. J Appl Phys. 2005;97(8):084108.

[46] Kim CH, Jang YH, Seo SJ, et al. Effect of Mn doping on the temperature-dependent anomalous giant dielectric behavior of CaCu$_3$Ti$_{12}$O$_{12}$. Phys Rev B. 2012;85(24):245210.

[47] Li Z, Zhao P, Wang Z, et al. Dielectric behavior associated with the synergetic microstructure and oxygen vacancies in CaCu$_3$Ti$_{12}$O$_{12}$ ceramics. J Mater Sci-Mater El. 2016;27(7):7327–7334.