FULL PAPER

Characterization of dielectric relaxations in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ via diverse complex planes: Effect of dipole polarization and dc conductivity

Xue-Tong ZHAO^{1,†}, Wen-Yue ZHENG¹, Jie-Xin ZHANG¹, Jie LIANG¹,
Han CHEN¹, Chao XU², Li-Jun YANG¹ and Rui-Jin LIAO¹

¹State Key Laboratory of Power Transmission Equipment & System Security and New Technology, Chongqing University, Shapingba District, Shazheng Street No. 174, Chongqing 400044, China

²State Grid Zhejiang Electric Power Co. Jiaxing Power Supply Company, Jiaxing 314033, China

The physics of the dielectric relaxations induced by dipole polarization and dc conductivity are clarified via conjoint analysis of various complex planes. Taking $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramic as a model sample, a typical dielectric relaxation induced by dipolar polarization is presented in the low-temperature range of 123–163 K. An obvious relaxation peak can be observed in dielectric permittivity and electric modulus planes, however, the relaxation peak gets blurred when characterized in impedance and conductivity planes because it is strongly covered by static permittivity or optical frequency permittivity effect. In the high-temperature range of 433–473 K, no evident relaxation is found in permittivity and conductivity planes, while a new dielectric relaxation process induced by dc conductivity arises in impedance and modulus planes. The activation energies of the low-temperature and high-temperature relaxation peaks are 0.094–0.097 and 0.92–0.93 eV, which corresponds to the bulk defect and grain boundary defect of the $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramic, respectively.

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1. Introduction

Broadband dielectric spectrometer as a quick, precise and nondestructive examination tool was widely used to measure the ac response of dielectrics. Some terms like ‘Impedance Spectroscopy’, ‘Frequency Domain Spectroscopy’, ‘Dielectric Spectroscopy’ or ‘Dielectric Relaxation Spectroscopy’, were adopted to describe the electric polarization and electrical conduction processes.^{1)–4)} The diversity of these terms is historical and appeared because studies were made by scholars from different backgrounds, e.g., in electronic physics, solid-state physics, physical chemistry, and materials science. Several dielectric parameters, e.g., the permittivity ε^* , the electric modulus M^* , the conductivity σ^* , and the impedance Z^* were generally used to analyze the dielectric relaxation induced by the molecular motions of dipolar molecules in insulating materials and the hopping conduction of charged carriers in polar solids and semiconductors.²⁾ It is also notable that these four typical dielectric parameters are closely correlated with each other and can be easily transformed into each other according to the complex plane equations:^{5),6)}

$$\varepsilon^*(\omega) = \frac{1}{M^*(\omega)} = \frac{\sigma^*(\omega)}{j\omega\varepsilon_0} = \frac{1}{j\omega C_0 Z^*(\omega)} \quad (1)$$

[†] Corresponding author: X.-T. Zhao; E-mail: xzt201314@cqu.edu.cn

where ω is the angular frequency, ε_0 is the permittivity of vacuum, $C_0 = S\varepsilon_0/l$ is the capacitance of the empty measuring cell, S is the electrode area, l is the distance between the electrodes.

Different complex planes provide different information of ac responses in dielectrics, leading to various analysis for physical mechanism. The complex permittivity ε^* is often used to analyze the dynamic molecular or ionic polarization based on Debye equation.⁷⁾ The complex conductivity σ^* is mostly employed to describe the charged carriers transport in dielectric materials.^{8),9)} The complex impedance Z^* is commonly used for equivalent circuit analysis to reveal the electrical properties of polycrystalline ceramics with different structures, e.g., grain, intergranular phases, domain/grain boundary.^{10),11)} The complex electric modulus M^* which does not exhibit a clear physical meanings were introduced to describe the ion conductance,¹²⁾ the interfacial polarization effect,¹³⁾ and electrode polarization.¹⁴⁾

Temperature has a great effect on the microscopic physical motion of the dielectrics, inducing much visible changes in the ac response. In the low-temperature range, the dc conductivity is negligibly low in the dielectrics, thus ac response mainly reflected the intrinsic localized motion such as dipolar fluctuations, variable-range-hopping of carriers.¹⁵⁾ For example, two different intrinsic oxygen vacancy defects with activation energies of 0.041 and 0.16 eV can be found in BaTiO_3 ceramic below 100 K.¹⁶⁾ The

intrinsic interstitial Zn_i^{**} with activation energy of 0.24 eV was detectable at about 173 K in ZnO ceramic,¹⁷⁾ and bulk defect of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ with activation energy of 0.054–0.10 eV was found at around 100 K.^{18),19)} In the high-temperature range, the dc conductivity can be enhanced significantly in the dielectrics. The long-range migration of charged carriers is usually impeded by interface barriers from grain/domain boundary, and intergranular phases.²⁰⁾ Dielectric relaxation processes can arise because the moving carriers may be trapped and de-trapped from the interface states. Ac response analysis is a straightforward way to separate these contributing factors through their frequency and/or temperature dependent response characteristics. Unfortunately, dielectric relaxation induced by both the dipole polarization and dc conductivity can appear at nearly the same frequency region. Consequently, the measured current of the materials consists of the displacement current and the conductive current, which cannot be distinguished from each other based on the Maxwell equations. Specifically, this may give rise to theoretical and experimental inconsistency when interpreting the data in some complex planes.²¹⁾ For example, J. R. Macdonald proposed that it can cause inaccuracy when analyzing ac response of a conducting medium using the electric modulus spectra.²²⁾ Therefore, it is of great importance to clarify these effects from the actual physical properties of the investigated material via conjoint analysis of various complex planes.

Dielectric ceramics generally contain complicated microstructures, such as grain, domain, and grain boundary, which can generate thermally activated bulk and interface defects. The typical dielectric relaxations can be observed under an external ac electric field. This work concerns the spectroscopic features of the ac response induced by localized dipole polarization and long-range migration of charged carriers in dielectric ceramics. As an application, the dielectric relaxations of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics are characterized via conjoint analysis of various complex planes and the relaxation mechanisms are discussed in detail.

2. Theoretical analysis

2.1 Dielectric relaxation induced by dipole polarization

For an ideal dielectric material, the conduction current is negligibly low and the dependence of complex permittivity ε^* with frequency follows the Debye equation,⁷⁾

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + j\omega\tau} \quad (2)$$

with the real and imaginary (ε' , ε'') parts of ε^* as follows,

$$\varepsilon'(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2\tau^2}, \quad \varepsilon''(\omega) = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{1 + \omega^2\tau^2} \quad (3)$$

where ε_s and ε_∞ denote the static and optical permittivity, and τ is the dipolar relaxation time.

In addition, the electric conductivity, the impedance, and the electric modulus are closely correlated with the permittivity ε^* , which can be described based on Eqs. (1)–(3).

$$\sigma^*(\omega) = \sigma'(\omega) + j\sigma''(\omega) = \omega\varepsilon_0\varepsilon'' + j\omega\varepsilon_0\varepsilon' \quad (4)$$

$$Z^*(\omega) = Z'(\omega) - jZ''(\omega) = \frac{1}{\omega C_0} \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} - j \frac{1}{\omega C_0} \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} \quad (5)$$

$$M^*(\omega) = M'(\omega) + jM''(\omega) = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} + j \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} \quad (6)$$

Ac conductivity spectra can be obtained due to the displacement current occurs in this system, and complex conductivity equation can be given according to Eqs. (3) and (4),

$$\sigma^* = \sigma_\infty - \frac{\sigma_\infty}{1 + j\omega\tau} + j\omega\varepsilon_0\varepsilon_\infty \quad (7)$$

with

$$\sigma_\infty = \varepsilon_0 \frac{(\varepsilon_s - \varepsilon_\infty)}{\tau} \quad (8)$$

where σ_∞ is a constant achieved from the real part of ac conductivity for $\omega \rightarrow \infty$. The real and imaginary parts of complex conductivity can be given,

$$\sigma'(\omega) = \sigma_\infty - \frac{\sigma_\infty}{1 + \omega^2\tau^2},$$

$$\sigma''(\omega) = \sigma_a''(\omega) + \sigma_b''(\omega) = \omega\varepsilon_0\varepsilon_\infty + \frac{\sigma_\infty\omega\tau}{1 + \omega^2\tau^2} \quad (9)$$

where the value of the real part σ' increases from 0 to σ_∞ with the frequency increasing from the low frequency limit to high frequency limit. The imaginary part of the conductivity consists of two parts; the first part $\sigma_a'' = \omega\varepsilon_0\varepsilon_\infty$ is mainly dominated by ε_∞ and is proportional to frequency, while the second part $\sigma_b'' = \sigma_\infty\omega\tau/(1 + \omega^2\tau^2)$ is a Debye-type process and its relaxation time τ is the same to that of the dipolar polarization in ε^* plane.

The complex impedance equation can be given as follows after conversion with the use of Eqs. (3) and (5).

$$Z^* = \frac{Z_0}{1 + j\omega\tau_d} + \frac{1}{j\omega\varepsilon_s C_0} \quad (10)$$

The real part and imaginary part can be expressed,

$$Z' = \frac{Z_0}{1 + \omega^2\tau_d^2},$$

$$Z'' = Z_a'' + Z_b'' = \frac{1}{\omega\varepsilon_s C_0} + \frac{Z_0\omega\tau_d}{1 + \omega^2\tau_d^2} \quad (11)$$

with

$$Z_0 = \frac{(\varepsilon_s - \varepsilon_\infty)\tau}{C_0\varepsilon_s^2} (\omega \rightarrow 0) \quad (12)$$

where Z_0 is a constant achieved from the real part of impedance when $\omega \rightarrow 0$, τ_d is the relaxation time of displacement current, and its relationship with the relaxation time, τ , of the dipolar polarization in this system can be given,

$$\tau_d = \frac{\varepsilon_\infty}{\varepsilon_s} \tau \quad (13)$$

Finally, the electrical modulus equation can be further deduced based on Eqs. (3) and (6),

$$M^* = \varepsilon_\infty^{-1} - \frac{\varepsilon_\infty^{-1} - \varepsilon_s^{-1}}{1 + j\omega\tau_d} \quad (14)$$

where the real and imaginary part of the modulus can be given as follows,

$$\begin{aligned} M' &= \varepsilon_\infty^{-1} - \frac{\varepsilon_\infty^{-1} - \varepsilon_s^{-1}}{1 + \omega^2\tau_d^2}, \\ M'' &= \frac{(\varepsilon_\infty^{-1} - \varepsilon_s^{-1})\omega\tau_d}{1 + \omega^2\tau_d^2} \end{aligned} \quad (15)$$

2.2 Dielectric relaxation induced by dc conductivity

Generally, the complex permittivity ε^* consists of two parts including the polarization relaxation and the dc conductivity. The Eq. (2) can be rewritten as,

$$\begin{aligned} \varepsilon^*(\omega) &= \varepsilon'(\omega) - j\varepsilon''(\omega) \\ &= \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2\tau^2} - j \left[\frac{\sigma_0}{\omega\varepsilon_0} + \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{1 + \omega^2\tau^2} \right] \end{aligned} \quad (16)$$

where σ_0 is the dc conductivity.

For the semiconductor materials with high dc conductance or the dielectric materials working at high temperatures, the dc conductivity can be extraordinarily high and dominates the ac response. Especially in the very low frequency range ($\omega\tau \ll 1$), the permittivity (ε' and ε'') can be controlled by the dc conductivity, and the Eq. (16) can be adjusted as

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - j\varepsilon''(\omega) = \varepsilon_s - j \frac{\sigma_0}{\omega\varepsilon_0} \quad (17)$$

Substituting Eq. (17) into Eqs. (4)–(6),

$$\sigma^*(\omega) = \sigma'(\omega) + j\sigma''(\omega) = \sigma_0 + j\omega\varepsilon_0\varepsilon_s \quad (18)$$

$$\begin{aligned} Z^*(\omega) &= R_0 \cdot \frac{1}{1 + j\omega\tau_0} \\ &= R_0 \cdot \frac{1}{1 + \omega^2\tau_0^2} - R_0 \cdot \frac{j\omega\tau_0}{1 + \omega^2\tau_0^2} \end{aligned} \quad (19)$$

$$\begin{aligned} M^*(\omega) &= \varepsilon_s^{-1} - \frac{\varepsilon_s^{-1}}{1 + j\omega\tau_0} \\ &= \varepsilon_s^{-1} - \frac{\varepsilon_s^{-1}}{1 + \omega^2\tau_0^2} + j \frac{\varepsilon_s^{-1}\omega\tau_0}{1 + \omega^2\tau_0^2} \end{aligned} \quad (20)$$

where $\tau_0 = \varepsilon_0\varepsilon_s/\sigma_0$ is the equivalent conductivity relaxation time, $R_0 = l/(\sigma_0 S)$ is the dc resistance of the sample obtained at the very low frequency ($\omega\tau \ll 1$).

3. Experimental

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) ceramics are fabricated using conventional solid state sintering process. High-purity of CaCO_3 , CuO , and TiO_2 (purity higher than 99.9%, Alfa Aesar) with 1:3:4 stoichiometry as raw materials were ball milled in ethanol for 12 h. The mixture was dried and calcined at 950 °C for 10 h to synthesize CCTO powder,²⁰⁾ and then pressed into pellets using PVA (Polyvinyl alcohol

3 wt %) as binder. The pressed pellets were heated at 600 °C for 3 h to remove the binder and then sintered at 1100 °C in air for 12 h to promote the growth of grain and grain boundary.²³⁾ The density of the CCTO ceramic was measured using the Archimedes method and its relative density was about 94.5 %. The samples were polished using sandpapers, and the final size is 11.6 mm in diameter and 1.2 mm in thickness. The phase composition and surface morphology are checked by X-ray diffraction (XRD; PANalytical Empyrean) at room temperature and scanning electron microscopy (SEM; Merlin, Carl Zeiss Microscopy LLC), respectively. Before the electrical tests, both sides of the samples were sputtered with gold as electrodes. The dc current–voltage (I – V) behavior was tested with the pA meter and a Delta oven. The ac responses of the samples are recorded via a Novocontrol broadband dielectric spectrometer using 1 V ac small-signal voltage for the low-temperature electric polarization characterization in the range from 10^2 to 10^7 Hz and 123 to 163 K, and for the high-temperature dc conductivity characterization from 10^{-1} to 10^4 Hz and 433 to 473 K.

4. Results and discussion

4.1 Microstructural and morphological characterization

Figure 1 shows the XRD patterns of the CCTO sample versus the 2 theta scale. The peaks can be indexed by a body-centered cubic perovskite-related structure of space group Im-3 according to inorganic crystal structure database 032002. Apparently no secondary phase is detected in the as-prepared CCTO sample, which indicates that the CCTO ceramic is well fabricated by the solid state sintering. The SEM characterization of CCTO ceramics are presented in **Fig. 2**, revealing a clear grain and grain boundary structure. In the CCTO ceramics, the average grain size was estimated to be 14.47 μm using Nano measure software (Nano Measurer 1.2), and no secondary phases can be observed.

4.2 I – V properties

The I – V characteristics was tested to analyze the physical nature of charged carriers transportation over the grain

Fig. 1. XRD patterns of the CCTO ceramic.

Fig. 2. The SEM photographs of the CCTO ceramic sample.

Fig. 3. The current–voltage dependence of the CCTO sample, and the inset shows the Schottky barrier height.

boundaries in the CCTO ceramic. The breakdown field was calculated by $E_{1\text{mA}} = U_{1\text{mA}}/d$ (d is the thickness) and the nonlinear coefficient α was calculated by $I = kU^\alpha$, where I and U is the current and voltage, respectively. As shown in Fig. 3, the CCTO sample exhibits a nonlinear I – V property. The nonlinear I – V behavior is originated from Schottky barriers at the grain boundary, and the thermionic emission current Eq. (21) is often used to describe the low-current region of the CCTO ceramics.

$$J = AT^2 \exp\left(\frac{\beta E^{1/2} - \Phi}{kT}\right) \quad (21)$$

where J is the current density, A is the Richardson constant, T is the absolute temperature, β is a constant, E is the applied electric field, Φ is the Schottky barrier height, and k is the Boltzmann constant. Figure 3 shows the electrical property and Schottky barrier calculation process of the CCTO sample, and the dependence of current density at low-current region on temperature is presented in the inset of Fig. 3. The breakdown field $E_{1\text{mA}}$ is 2162 V/cm, and the non-linear coefficient α and barrier height Φ are at about 4.3 and 0.56 eV, which indicates that the thermionic emission current crossing the Schottky barriers was achieved.

4.3 Dielectric relaxations characterization

4.3.1 Dielectric relaxation at low temperature

Frequency dependence of real and imaginary parts of ε^* , σ^* , M^* , and Z^* for CCTO sample measured from 123 to 163 K are shown in Figs. 4(a)–4(d), respectively. In Fig. 4(a), the curves of real part ε' are flat at low frequency which are close to the static dielectric permittivity ε_s . An obvious dielectric relaxation process can be observed in the characteristic frequency range of 10^3 – 10^5 Hz, where ε' and ε'' curves intersect each other. Similarly, the relaxation process occurs in the same characteristic frequency range in σ^* plane as shown in Fig. 4(b). However, the relaxation peak of σ'' curves is not so clear as that in ε'' curves because it is strongly covered by $\sigma_a'' = \omega\varepsilon_0\varepsilon_\infty$ according to the Eq. (9). The relaxation process can be observed in electric modulus spectra and impedance plane, but occurs at a little higher frequency range (10^5 – 10^6 Hz). It indicates that the relaxation time τ_d obtained from electric modulus spectra and impedance plane will be smaller than τ obtained in permittivity and conductivity spectra. Similarly to σ'' curves, the relaxation peaks in Z'' curves are covered by $Z_a'' = 1/\omega\varepsilon_s C_0$. The activation energies (E_l) of the relaxation peaks are calculated according to Arrhenius formula in the inset of Figs. 4(a)–4(d). The values calculated from different planes are nearly equal to 0.094–0.097 eV corresponding to the reported bulk defect of CCTO,^{18),(24),(25)} which indicates the relaxation peaks in these four planes follow the same mechanism but present different relaxation characteristics.

At low temperature range, the effect of dc conductivity on the dielectric relaxation process is so slight that can be neglected. As shown in Figs. 5(a)–5(d), the ac response of CCTO measured at 123 K is selected to be fitted based on the Eqs. (3), (9), (11) and (15), respectively, and the fitting parameters are summarized in Table 1. The static and optical permittivity of CCTO are approximately equal to 17000 and 95, respectively, at 123 K. The relaxation time τ calculated from ε^* and σ^* planes is about 2.53×10^{-5} s, and the imaginary part of σ'' can be separated into two parts of σ_a'' and σ_b'' according to the Eq. (9). As expected, the relaxation peaks appear at a higher frequency when characterized in M^* and Z^* planes because the relaxation time τ_d is reduced to 1.42×10^{-7} s. Similarly, the relaxation process in Z'' spectra can be separated into two parts of Z_a'' and Z_b'' . The Cole–Cole semicircles from ε' – ε'' , σ' – σ'' , M' – M'' , and Z' – Z'' plots were given in the inset of Figs. 5(a)–5(d). It is believed that the Debye-type relaxation process can be clear described in ε^* and M^* planes, but it becomes blurring when exhibited in σ^* and Z^* planes due to the effect of optical frequency permittivity ($\sigma_a'' = \omega\varepsilon_0\varepsilon_\infty$) or static permittivity ($Z_a'' = 1/\omega\varepsilon_s C_0$).

4.3.2 Dielectric relaxation at high temperature

In the high temperature range of 433–473 K, the conductive current (or dc conductivity) of CCTO is strengthened significantly. The ac responses induced by the high conductive current are apparent and presented in ε^* , σ^* , M^* , and Z^* planes as shown in Figs. 6(a)–6(d). In

Fig. 4. Frequency dependence of real and imaginary parts of (a) ϵ^* , (b) σ^* , (c) M^* , and (d) Z^* for CCTO sample from 123 to 163 K. The activation energies of the relaxation peaks are calculated according to Arrhenius formula in the inset.

Fig. 5. The fitting results of real and imaginary parts of (a) ϵ^* , (b) σ^* , (c) M^* , and (d) Z^* for CCTO sample at 123 K. A Cole-Cole semicircle is exhibited in the inset.

Table 1. The fitting parameters for samples of CCTO ceramics at 123 and 473 K

CCTO	ε_s	ε_∞	σ_0 (S/m)	τ (s)	τ_d (s)	τ_0 (s)	E_l (eV)	E_h (eV)
123 K	17000	95	—	2.53×10^{-5}	1.42×10^{-7}	—	0.094–0.097	—
473 K	30000	—	5.7×10^{-4}	—	—	6.21×10^{-4}	—	0.92–0.93

Fig. 6. Frequency dependence of real and imaginary parts of (a) ε^* , (b) σ^* , (c) M^* , and (d) Z^* for CCTO sample from 433 to 473 K. The activation energies of dc conductivity and the relaxation peaks are calculated according to Arrhenius formula in the inset.

Fig. 6(a), the curves of real part ε' are flat which are close to the static dielectric permittivity ε_s . ε' and ε'' curves intersect in the characteristic frequency region (35–360 Hz), and ε'' curves show an inversely proportional frequency dependence following the Eq. (17). In Fig. 6(b), we can see that σ' and σ'' curves intersect in the same characteristic frequency region, below which σ' keeps a constant and is close to the dc conductivity σ_0 , while σ'' curves show a directly proportional frequency dependence obeying the Eq. (18). However, in the high frequency region above the characteristic frequency, σ' curves start to rise with increasing frequency. It means that the ac conductivity dispersion occurs when the applied frequency reaches the characteristic frequency. In most dielectric materials, ac conductivity due to localized states can be described using Jonscher's law:²⁶⁾

$$\sigma'(\omega) = \sigma_0 + A\omega^n \quad (22)$$

where σ_0 is the dc conductivity, A is a material dependent parameter, and n is the power law exponent ($0 < n < 1$).

According to Eqs. (19) and (20), as expected, a relaxation process appears at the same characteristic frequency in the M^* and Z^* planes. As presented in Figs. 6(c) and 6(d),

the relaxation process can be observed accompanied with a relaxation peak which shifts to a high frequency region with the increase of the temperature.²⁷⁾ The activation energy of the dc conductivity and the activation energies (E_h) of the relaxation peaks are calculated according to Arrhenius formula in the insets of Figs. 6(b)–6(d). The values calculated from different planes are 0.92–0.93 eV, which were attributed to the defect relaxation of grain boundary,⁹⁾ and are nearly equal to each other, indicating that the relaxation peaks in the M^* and Z^* planes are indeed induced by the dc conductivity.

Ac response of CCTO at 473 K is fitted based on the Eqs. (17)–(20) and the fitting parameters are summarized in Table 1. As shown in Fig. 7(a), the static permittivity of CCTO are about 30000 at 473 K, while the dielectric loss ε'' shows a straight line with a slope of -1 below the characteristic frequency where ε' and ε'' curves intersect. In Fig. 7(b), below the characteristic frequency, the real part σ' exhibits no dispersion and keeps constant ($\sigma_0 = 5.7 \times 10^{-4}$ S/m), and the imaginary part σ'' presents a straight line with a slope of +1. The relaxation processes appearing in the M^* and Z^* planes are fitted according to Eqs. (19) and (20), and the equivalent conductivity relaxa-

Fig. 7. The fitting results of real and imaginary parts of (a) ε^* , (b) σ^* , (c) M^* , and (d) Z^* for CCTO sample at 473 K. A Cole–Cole semicircle is exhibited in the inset of Figs. 7(c) and 7(d).

Table 2. The comparison of dielectric parameters of CCTO ceramics to the reported references

Samples	Conditions	ε'_{l^*}	$\sigma_{h^{**}}$ (S/m)	Grain size (μm)	E_l (eV)	E_h (eV)
Sun et al. ²⁹⁾	1050 °C-20 h	$\sim 4.0 \times 10^4$	—	9 ± 3	0.083	0.70
Li et al. ⁹⁾	1100 °C-20 h	1.0×10^4	3.0×10^{-5}	—	0.09	1.12
Liu et al. ³⁰⁾	1060 °C-48 h	4.2×10^4	—	100	0.089	0.606
Fang et al. ²⁰⁾	1065 °C-20 h	1.8×10^4	—	~ 20.0	0.09	0.63
Zhao et al. ³¹⁾	1100 °C-24 h	0.72×10^4	1.25×10^{-4}	25.8	0.11	1.14
Tang et al. ³²⁾	1000 °C-5 h	$10^3\text{--}10^4$	—	2.4–2.8	0.14	0.65–0.88
This work	1100 °C-12 h	1.7×10^4	5.7×10^{-4}	14.47	0.094–0.097	0.92–0.93

l^* represents the dielectric parameters tested at low temperature, and h^{**} represents the dielectric parameters tested at high temperature.

tion time τ_0 calculated from the two planes is about 2.53×10^{-5} s. The Cole–Cole semicircles from $M'-M''$, and $Z'-Z''$ plots were given in the inset of Figs. 7(c) and 7(d), which means that the relaxation process induced by dc conductivity is a Debye-like relaxation.

However, in the high frequency range above the characteristic frequency (≥ 360 Hz), ε' and σ' do not keep constant any more, and ε'' and σ'' curves start to deviate the inversely and directly proportional frequency dependence of ω^{-1} and ω^{+1} . Consequently, there is an obvious deviation between the theory curves and the experimental data in M^* and Z^* planes in the high frequency range. The discrepancy can be attributed to the ac conductivity dispersion, which means that the long-range motion of charged carriers that mainly contributes to dc conductivity is impeded by the potential barrier of grain boundary because of the high frequency of ac applied field. Meanwhile, ac conductivity grows because the capacitor admittance

becomes stronger than the resistor admittance in the high frequency range.

The model sample of CCTO ceramic used in this work does not show any significant difference in the microstructure and dielectric behavior to other CCTO samples fabricated via a different preparation process as shown in Table 2. It indicates that the conjoint various complex planes can be used to other CCTO ceramics including modified ones. Actually, this method was widely applied to many other dielectric materials such as ZnO varistor ceramics, vitreous ionic conductors, and liquid dielectrics (cyclobutanone) to clarify their electric relaxations, impedance, and charged carriers conduction processes.^{10),12),28)}

5. Conclusions

In this work, characterization of electric relaxation processes is discussed based on the analysis of ε^* , σ^* , Z^* , and M^* planes using CCTO ceramics as an example. It is

suggested that the relaxation peaks with activation energy of 0.093–0.097 eV are induced by the dipole polarization of bulk defect, which can be clearly described in ε^* and M^* planes. However, the relaxation peaks are covered by static permittivity or optical frequency permittivity effect when characterized in Z^* and M^* planes. For the electric relaxation induced by dc conductivity, no evident relaxation process can be found in ε^* and σ^* planes, while a new dielectric relaxation peak with activation energy of 0.92–0.93 eV arises in Z^* and M^* planes. Meanwhile, ac conductivity dispersion caused by grain boundary barrier can be found in the high frequency range (≥ 360 Hz) for CCTO ceramic at 473 K, which cause some discrepancy between theory values and experimental data. Therefore, conjoint analysis of various complex planes is very helpful to understand the physics of an electric relaxation process.

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References

- 1) S. Lanfredi and A. C. M. Rodrigues, *J. Appl. Phys.*, **86**, 2215–2219 (1999).
- 2) L. J. Yang, T. T. Zou, B. F. Deng, H. B. Zhang, Y. Mo and P. Peng, *IEEE Access*, **7**, 45670–45678 (2019).
- 3) L. Guan, X. L. Feng, G. Xiong and J. A. Xie, *Sensor. Actuat. A-Phys.*, **168**, 22–29 (2011).
- 4) H. Smaoui, M. Arous, H. Guermazi, S. Agnel and A. Tourelle, *J. Alloy. Compd.*, **489**, 429–436 (2010).
- 5) M. A. Alim, *Act. passive Electron. Compon.*, **19**, 139–169 (1996).
- 6) Y. W. Huang, K. N. Wu, Z. L. Xing, C. Zhang, X. N. Hu, P. H. Guo, J. Zhang and J. Y. Li, *J. Appl. Phys.*, **125**, 084103 (2019).
- 7) P. Debye, “Polar Molecules”, Chemical Catalogue Company, New York (1929).
- 8) W. Li and R. W. Schwartz, *Appl. Phys. Lett.*, **89**, 242906 (2006).
- 9) J. Y. Li, X. T. Zhao, F. Gu and S. T. Li, *Appl. Phys. Lett.*, **100**, 202905 (2012).
- 10) X. T. Zhao, R. J. Liao, N. C. Liang, L. J. Yang, J. Li and J. Y. Li, *J. Appl. Phys.*, **116**, 014103 (2014).
- 11) T. T. Fang and C. P. Liu, *Chem. Mater.*, **17**, 5167–5171 (2005).
- 12) P. B. Macedo, C. T. Moynihan and R. Bose, *Phys. Chem. Glasses*, **13**, 171–179 (1972).
- 13) G. M. Tsangaris, G. C. Psarras and N. Kouloumbi, *J. Mater. Sci.*, **33**, 2027–2037 (1998).
- 14) F. Q. Tian and Y. Ohki, *IEEE Trans. Dielectr. Electr. Insul.*, **21**, 929–931 (2014).
- 15) C. C. Wang and L. W. Zhang, *Appl. Phys. Lett.*, **90**, 142905 (2007).
- 16) L. Fang, W. Dong, F. G. Zheng and M. R. Shen, *J. Appl. Phys.*, **112**, 034114 (2012).
- 17) P. Cheng, S. Li, L. Zhang and J. Li, *Appl. Phys. Lett.*, **93**, 012902 (2008).
- 18) J. Y. Li, X. T. Zhao, S. T. Li and M. A. Alim, *J. Appl. Phys.*, **108**, 104104 (2010).
- 19) I. P. Raevski, S. M. Maksimov, A. V. Fisenko, S. A. Prosandeyev, I. A. Osipenko and P. F. Tarasenko, *J. Phys. Condens. Matter*, **10**, 8015–8032 (1998).
- 20) T. T. Fang and H. K. Shiau, *J. Am. Ceram. Soc.*, **87**, 2072–2079 (2004).
- 21) J. R. Macdonald, *J. Phys. Chem. Solids*, **70**, 546–554 (2009).
- 22) J. R. Macdonald, *J. Non-Cryst. Solids*, **197**, 83–110 (1996).
- 23) L. Fang, M. Shen, F. Zheng, Z. Li and J. Yang, *J. Appl. Phys.*, **104**, 064110 (2008).
- 24) C. C. Homes, T. Vogt, S. M. Shapiro, S. Wakimoto and A. P. Ramirez, *Science*, **293**, 673–676 (2001).
- 25) G. Chiodeli, V. Massarotti, D. Capsoni, M. Bini, C. B. Azzoni, M. C. Mozzati and P. Lupotto, *Solid State Commun.*, **132**, 241–246 (2004).
- 26) A. K. Jonscher, “Universal relaxation law”, Chelsea Dielectrics Press, London, (1996).
- 27) E. Barsoukov and J. R. Macdonald, “Impedance spectroscopy theory, experiment, and applications”, 2nd ed., Wiley, New York (2005).
- 28) J. Swiergiel and J. Jadzyn, *Ind. Eng. Chem. Res.*, **50**, 11935–11941 (2011).
- 29) D. L. Sun, A. Y. Wu and S. T. Yin, *J. Am. Ceram. Soc.*, **91**, 169–173 (2008).
- 30) L. Liu, H. Fan, P. Fang and L. Jin, *Solid State Commun.*, **142**, 573–576 (2007).
- 31) X. Zhao, L. Ren, R. Liao, J. Li, L. Yang and F. Wang, *J. Electron. Mater.*, **45**, 3079–3086 (2016).
- 32) Z. Tang, Y. Huang, K. Wu and J. Li, *J. Eur. Ceram. Soc.*, **38**, 1569–1575 (2018).