# Chapter 3: Part B-Fractional Power-Law Spectral Response of CaCu₃Ti₄O₁₂— A Many-Body Effect

## Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-B.1: Non-Linearity and Microscopic Disorder</td>
<td>59</td>
</tr>
<tr>
<td>3-B.2: Fractional Power-law (Dissado-Hill) Dielectric Spectra</td>
<td>59</td>
</tr>
<tr>
<td>3-B.3: Correlations versus Temperature</td>
<td>61</td>
</tr>
<tr>
<td>3-B.4: Thermal Conductivity of Disordered Dielectrics</td>
<td>63</td>
</tr>
<tr>
<td>3-B.4.1: Evidence of Electrical-Disorder in Thermal Conductivity of CaCu₃Ti₄O₁₂</td>
<td>65</td>
</tr>
<tr>
<td>3-B.5: Colossal Dielectric Constant of Ca₀.₉Li₀.₁Cu₃Ti₄O₁₂</td>
<td>66</td>
</tr>
<tr>
<td>3-B.6: References</td>
<td>68</td>
</tr>
</tbody>
</table>
3-B.1: Non-Linearity and Microscopic Disorder

Double-Perovskite-like CaCu$_3$Ti$_4$O$_{12}$ (CCTO) is highly disordered material at the nanoscale [1], due to the site/anti-site admixture of Ca- and Cu-ions, enhancing which improves the dielectric properties [1-2]. This disorder makes CCTO electrically heterogeneous and a highly nonlinear material, having a huge $\alpha = d\log(I)/d\log(V)$ coefficient ever observed [3], with vastly superior applicability. The non-linearity here is intrinsic, as semiconducting and insulating intra-grain locations have been resolved in the tunneling microscopy [4-5]. However, the disorder-borne non-linearity has not yet been recognized in the dielectric spectra of CCTO, crucial for its understanding and the relevant-property-control. Debyean exponential-decay as the generic relaxation mechanism is not applicable here, due to the disorder and cooperative motion of the relaxing entities. To understand the intrinsic heterogeneities, dielectric spectra of CCTO were analyzed with the Dissado-Hill (D-H) formulation [6], featuring fractional power-laws, applicable to the cooperative response in the disordered materials, characterizing their microscopic interactions.

3-B.2: Fractional Power-law Dielectric Spectra (Dissado-Hill Formalism)

The generic Debyean relaxation is inappropriate to the disordered materials with interacting dipoles; rather the non-Debyean behaviour of dielectric permittivity $\varepsilon^* = \varepsilon - i\varepsilon''$ is observed in several disordered dielectrics [7-9]. Here, the dielectric loss $\varepsilon''$ in frequency-domain can be described by the following power-laws:

$$\varepsilon''(\omega) \approx (\omega/\omega_p)^{n-1}, \quad \omega > \omega_p \quad (1)$$

$$\varepsilon''(\omega) \approx (\omega/\omega_p)^m, \quad \omega < \omega_p \quad (2)$$

$\omega_p$ is the frequency corresponding to the maximum dielectric-loss rate $\varepsilon''$. Limiting values of the exponents ($n = 0$, $m = 1$) correspond to the Debyean exponential-relaxation of the non-interacting (single) dipoles, comparatively explaining the relaxation behaviour of weak dipolar solutions or of the gaseous-state dipoles. For the real solid materials having interacting dipoles, the situation quite changes the parameters $n$ and $m$. For most of the materials, these parameters are independent of the temperature in their thermodynamically stable phase. The Dissado-Hill (D-H) many-body model [6] contains the parameters in relations (1) and (2), and explains the non-Debyean behaviour when interactions are present between the relaxing entities of the system.
Dissado-Hill model concerns the high-to-low frequency energy-transfer from the quickly-excitile single-dipoles to their slowly-reverberating collective degrees of freedom [6-12]. Lower-frequency cascading down of the energy, rather spontaneously gained by the individual dipoles from the applied field, is determined by the disorder, via dynamically-cooperative structure-modulations. The incipient energy-transformation (from potential to kinetic form, for times $t < 1/\omega_p$) proceeds with rapid orientation-flips of the dipoles into their excited low-energy/amplitude oscillations [12-13]. Subsequently (for times $t > 1/\omega_p$), each abrupt shock-transition ripples through to the slower many-body resonant flip-flops of the interacting dipole-clusters, dissipating the initial (locally-stored) electrical potential energy to the (macroscopic) heat-bath over longer times. Thus, the full relaxation proceeds in two stages; having relatively short “transition” and much longer “adjustment” time-scales respectively [7, 14].

The D-H function looks similar to but not the same as the Havriliak-Negami (H-N) form [15-16]. It is defined as (WinFit©, NovoControl®)

$$\varepsilon^* (\omega) = \varepsilon' - i \varepsilon'' = \varepsilon_\infty + \varepsilon_0 - \varepsilon_\infty \frac{1}{F_{01} \cdot (1+i\omega \tau)} \cdot \sum \left( \frac{1}{1-n,1-m,2-n,1+i\omega \tau} \right)$$

Where $2F_1$ is the Gaussian Hyper-Geometric function defined as

$$2F_1(a,b,c,z) = \sum_{j=0}^{\infty} \frac{(a)}{(b)} \frac{(c)}{j!} \cdot \frac{z^j}{j!},$$

with

$$(a) = a(a+1)(a+2)....(a+j-2)(a+j-1).$$

The function $F_{01}$ is defined as

$$F_{01}(n,m) = \frac{\Gamma(2-n)\Gamma(m)}{\Gamma(1+m-n)},$$

$\Gamma$’s denoting the usual Gamma functions. Here the fitting parameters $\varepsilon_0$, $\varepsilon_\infty$, and $\tau$ have their usual meanings as in the H-N function, with the indices $n$ and $m$ reflecting the power-law behaviors above and below $\omega_p$ (eqs.1, 2) range from 0 to 1.

It is already established that CaCu$_3$Ti$_4$O$_{12}$ is a highly disordered material, where dipoles interact at the mesoscopic scale. To investigate the dipole-correlations in CaCu$_3$Ti$_4$O$_{12}$, the dielectric data of CaCu$_3$Ti$_4$O$_{12}$ is fitted with the D-H function. The measured real permittivity and dielectric losses fitted with the D-H function are shown in fig.1 below.
3-B.3: Correlations versus Temperature

The fit-parameters $n$ and $m$ exhibit non-trivial $T$-dependences (fig.2) and provide a characteristic

temperature for CCTO. The exponent $m$ (slope of the lower-frequency side of the loss-peak in
the log-log $\varepsilon''$ vs. $\omega$ plot, inset fig.2) is much more sensitive to the temperature, compared to the

high-frequency-side slope $n$; showing two distinct behaviors above and below $\sim$100K. At high

$T$’s, $m$ tends to its limiting value 1 and $n$ to 0, indicating the tendency towards the Debyean (symmetric)

single-particle relaxation of the dipoles, devoid of the correlations. By the same

token, the steeper fall of $m$ below $\sim$100K indicates increasing dipolar correlations, also

confirmed by the exponent $n$ increasing towards 1, with successively asymmetric loss-peaks.

This representation clearly marks 100K as the turning point in the dipolar-correlations, where the

total dielectric losses too have been observed as the maximum [17].
Figure (2). Dissado-Hill correlation parameters \((m, n)\) obtained at different temperatures. Parameter \(n\) \((m)\) describes the power-law behaviour over the frequency range \(\omega > \omega_p (\omega < \omega_p)\), as shown in the inset.

The Dissado-Hill form as the most appropriate spectral function representing the CCTO dielectric data is verified by comparison with the (force-fitted) Havriliak-Negami [15-16] function; both these computations for \(\varepsilon''(\omega)/100K\) are displayed in fig.3. Evidently, the D-H function fits well over a broader range of spectrum with physically admissible fitting parameters, contrary to the H-N function where its (asymmetry) index optimizes at unrealistic value \((\beta > 1)\). The D-H fitting is also justified from the nature of the relaxation-kinetics (inset, fig.3). Although the character of the relaxation time \((\tau)\) versus \(10^3/T\) Arrhenius-plot over its entire bandwidth is the same for both H-N and D-H cases. However, force-fitting \(\tau_{HN}(T)\) by the Vogel-Fulcher function (as the corresponding \(T\)-domain manifestation of a non-Debyeian H-N spectrum, \(\beta \neq 1\) produces negative/unrealistic \(T_{VF} \approx -58K < 0K\). Rather, a combined exponential-linear fit made on \(\tau_{D-H}(T)\) has been found [17] as more appropriate, to describe the observed sub-linear behavior.
Figure (3). Comparison of the Dissado-Hill (D-H, solid line) and Havriliak-Negami (H-N, dashed line) fits to the loss-peak at 100K. Lower inset—consistent with the unphysical asymmetry parameter $\beta>1$ from the H-N force-fit, the correspondingly force-fitted Vogel-Fulcher kinetics $[\ln \tau_{\text{HN}} \sim B/(T-T_{VF})]$ provides (ve, unacceptable) $T_{VF} \approx -58K$.

Upper inset—Exponential-linear fit to the relaxation time $\ln \tau_{\text{DH}} \sim [\alpha T^{-1} \cdot \mu \exp(-\gamma T^{-1})]$, $\tau_{\text{DH}}$ from the D-H fit.

Thus, from both the spectral and kinetic viewpoints, the allied H-N/V-F formulations are confirmed as unphysical/incorrect descriptions of CCTO’s particulate dielectric behaviour. On the other hand, the D-H/exp-lin combined framework is amenable to a realistic interpretation.

3-B.4: Thermal Conductivity of Disordered-Dielectrics

It is interesting to explore the manifestations of the well-established nano-scale electrical-disorder in CCTO on its thermal properties. The thermal conductivity is a very sensitive and powerful tool to investigate the electrical state of the system [18]. Thermal conductivity of most insulators follows a typical behavior dominated by the phonons as responsible for their thermal transport. Thermal conductivity of insulators is governed by the expression
Here $\kappa$ is thermal conductivity and $C$ is the heat capacity contributed by the lattice, $v$ is the velocity of sound in the crystal (independent of temperature) and the $\ell$ is the mean free path of the phonons. Mean free path is dependent on the rate of energy exchange between different phonon modes and the scattering of phonons from defects and sample-boundary. At the normal and high-temperatures, the mean free path is inversely proportional to the temperature. On lowering the temperature, mean free path increases rapidly in $\sim 1/T$ fashion. More precisely, the mean free path follows the expression ($T^*$ is closely related to the Debye temperature $\Theta_D$)

$$\ell \propto \exp(T^*/T)$$

In the low-temperature range, mean free path becomes constant and depends mainly on the size/geometry of the sample. Second important parameter is the heat capacity, which governs the behavior of thermal conductivity. The thermal conductivity follows $\propto 1/T$ at high-temperatures, because of the near-saturation of $C$ and continuous decreases of the mean free path $\ell \propto 1/T$. Maximum appears in thermal conductivity on lowering the temperature because the means free path sharply increased and finally saturates at low temperature and specific heat continuously decrease on lowering the temperature and eventually varying as $T^3$ same variation reflect in thermal conductivity i.e $T^3$ temperature dependency at low temperature. Most of the Perovskite dielectrics ($\text{BaTiO}_3$, $\text{PbTiO}_3$, $\text{KTaO}_3$, $\text{KNbO}_3$ etc.) follow the conventional thermal conductivity behaviour [18], as shown in figure (4).
Chapter 3: Part B-Fractional Power-Law Spectral Response of CaCu3Ti4O12—A Many-Body Effect

Thermal conductivity of disordered amorphous solids however shows a different character. In disordered/amorphous solids, thermal conductivity continuously decreases with decreasing temperature, because of the limitation of mean free path by the relevant microstructural dimension, as shown in the figure (4) for amorphous SiO2, PMN, and NaNbO3. κ(T) of PMN shows characteristics of amorphous materials, due to the presence of polar nano-regions (PNR). The glass-like thermal conductivity behaviour of NaNbO3 comes from the co-existence of ferroelectric and antiferroelectric phases. The thermal conductivity of BaTiO3 too becomes glass-like in its nanoparticle form [19].

3-B.4.1: Evidence of Electrical-Disorder in Thermal Conductivity of CCTO

CaCu3Ti4O12 has a cubic crystalline structure but its thermal conductivity data is much different from the usual crystalline insulators, and rather similar to amorphous-like (glass, silica) behavior [20]. The magnitude of CCTO thermal conductivity is quite low compared to other Perovskite dielectrics. Temperature dependent thermal conductivity of a polycrystalline sample of CaCu3Ti4O12 shown in figure (5) exhibiting glass-like behaviour is quite surprising, since it is a stoichiometric compound with no compositional disorder. Anomalous thermal conductivity of this pure crystalline material owes to its electrical inhomogeneity. The low value of κ(T) in CCTO is mainly due to the large scattering of phonons off the nanoscale electrical-disorder.

![Graph showing thermal conductivity of CaCu3Ti4O12](image)

Figure (5). Thermal conductivity of CaCu3Ti4O12. Warming and cooling across the step-anomaly near 100K (inset).
Monotonic increase of thermal conductivity with temperature, observed in CCTO is similar to the well-known universal feature in disordered materials. Consistently, $\kappa(T)$ here exhibits a plateau over 40 to 100K and a steeper drop below $\Theta_D/10 \approx 40K$; the Debye temperature $\Theta_D$ being 408K [21]. Moreover, an additional feature in the form of a clear step “transition” is detected around 100K. This ‘transition’ in $\kappa(T)$ coincides with the manifestation of dipolar-interactions onset below $\approx$100K, as observed in its permittivity behaviour. At high-temperatures, there are almost no dipolar correlations and below $\approx$100K the dipolar-cooperativity ensues. This ‘transition’ is hysteretic in nature and shows $\approx 8K$ hysteresis between warming & cooling cycles.

3-B.5: Colossal Dielectric Constant of $\text{Ca}_{0.9}\text{Li}_{0.1}\text{Cu}_3\text{Ti}_4\text{O}_{12}$

![Figure (6). Low-temperature complex permittivity of $\text{Ca}_{0.9}\text{Li}_{0.1}\text{Cu}_3\text{Ti}_4\text{O}_{12}$.](image)
CCTO is established as highly electrically-disordered, confirmed by the dielectric-spectral-analysis and thermal conductivity behaviour. The dielectric properties of CCTO can be altered by tuning of the disorder. The Li-doped sample \(\text{Ca}_{0.9}\text{Li}_{0.1}\text{Cu}_3\text{Ti}_4\text{O}_{12}\) has been prepared to control the disorder. Dielectric spectra of \(\text{Ca}_{0.9}\text{Li}_{0.1}\text{Cu}_3\text{Ti}_4\text{O}_{12}\) have been found to undergo considerable modification vis-à-vis CCTO; the activation-energy/temperature-scale upshifts from \(\sim 100\) K to nearly the room-temperature. The low-frequency permittivity is higher at high-\(T^*\)s compared to CCTO, and maintains the CDC-feature (fig.6), along with clear associated relaxation peaks at the \(\varepsilon'\)-steps. On cooling, the permittivity reduces to almost the intrinsic value \(\sim 100\), calculated theoretically for CCTO [22].
3-B.6: References


