Conductivity Analysis of Bi₄Ti₃O₁₂ Ferroelectric Ceramic: A Comprehensive Study from the Dynamic Aspects of Hopping Conduction

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Abstract

Objectives: We focus solely on a comprehensive conductivity analysis of $Bi_4Ti_3O_{12}$ ceramic, in a bid to bring seminal ideas for dielectric components, in particular frequency and temperature ranges. Methods/Statistical Analysis: The synthesis of Bi₄Ti₃O₁₂ ceramic is based on a mechanical activation method. The following sintering at 1273 K ascertains the Bi₄Ti₃O₁₂ appears to be of single phase crystallizes in orthorhombic form, whose conductivity is determined from the dielectric function in the context of Kramers-Kronig relation on which of this is measured in the frequency domain at varying temperatures. The evaluation of conductivity data is mainly in terms of activation energy. Findings: We find that the separately discussed dc and ac conductivities in similar manner are best isolated into two distinct temperature regions. Charge transport by hopping to the target localized states is the relevant conduction mechanism in bringing insights into the dynamic responses. Variable range and small polaron hopping models associated with the adiabatic small polaron are the decent choices, each of which explaining the dc conductions in these temperature regions. The former involves distant hops, whereas the latter denotes as nearest-neighbour hopping. The percolation treatments applied in the dc conductivity yield promising results if different percolation expressions are used. The correlation between dc and ac conductions for each temperature is irrefutably made through the Barton-Nakajima-Namikawa fitting. In frequency dependence ac regions, the thermally activated hopping carriers are transported in a correlated to a random manner between preferred sites. Performing a Summerfield ac scaling in these temperature regions leads to different scenarios in view of time-temperature superposition principle. Applications/Improvements: Further experiments are encouraged to support the hopping conduction mechanisms from another aspect in order to prompt the use as energy storage function in the electromagnetic application.

Keywords: Charge Carriers, Conductivity, Bi₄Ti₃O₁₂, Ferroelectric Ceramic, Hopping Conduction

1. Introduction

Conductivity, in general definition, is used to reflect macroscopically the fundamental information on the conductive nature of a parallel plate geometry-system under the presence of periodic electric field (i.e., how well/poor a material conducts electric current). From a physical perspective, the microscopic activities of conductivity are regarded as the electrifying parallel electrodes that trigger the movement and mobility of charge carriers within a sandwiched material in contact. These drifting carriers transpire via extended or/and localized states, depending on the position of Fermi level relative to the mobility edge. The deeper the state for carriers to reside, the conduction lifetime of those energetic moving carriers to a

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shallow state becomes longer, promotes the charge storage capacity in an electric field and eventually leads to a small mobility in the form of occasional hops¹. Leaving a deeper state until recapturing to trap into another state is a slow trapping and releasing process involving distribution of traps. Thus it is sometimes called multi-trap and release process¹.

In abiding to the lead regulation, continuous quests are being circulated to strive for the global industrial demands in the context of toxicity-free, eco-friendly substitutes, as in the case of novel BaTiO₃ ceramic with perovskite structure². These moves also pinpoint bismuth titanate (Bi₄Ti₃O₁₂) as one of the innocuous Bi-Aurivillius compound oxides, which has advantageous high temperature piezoelectric properties even operate under harsh atmospheric conditions³. What makes the Bi₄Ti₃O₁₂ compound differs from other structural families is its notorious structural complexity in layered form, with such crystalline structure is built up from the alternate stacking of layers between fluorite-like bismuth-oxygen (Bi₂O₂)²⁺ and pseudo-perovskite (Bi₂Ti₃O₁₀)²⁻blocks^{4.5}.

There has been vast experimental studies over the last decades being devoted to the behaviour of $Bi_{4}Ti_{3}O_{12}$ in terms of photoluminescence^{6.7}, impedance^{8.9}, dielectric¹⁰⁻¹² to name a few, and still constantly ticking along. In the realm of conductivity, not much emphasis had hitherto been given to the Bi₄Ti₃O₁₂ compound and as of yet in a rudimentary stage. To the authors' best knowledge, there were a few Bi₄Ti₃O₁₂-related cases that revealed the passively-discussed conductivity yet devoid of data interpretation and analysis using universally accepted hopping models^{8.9.13}. The unattended hopping models made the understanding of conductivity behaviour became incomplete. The type of conceptual model followed provides a fundamental tuning framework for the development of scientific and industrial-based devices with optimal performances.

The shallow precedent conductivity analysis of $Bi_4Ti_3O_{12}$ initiates our interest to step forward on a thorough analysis. In the present work, we conduct an exclusive endeavor to gather qualitative conductivity information of $Bi_4Ti_3O_{12}$ ceramic at different temperatures, using frequencies as interactive variables. We feature a clear distinct picture of dc conductivity isolated from the ac conductivity, as the overall conductivity trends are separately discussed although both dc and ac are interconnected to a certain extent. In order to understand the dynamic processes in dc and ac regions, we

employ the existing theoretical hopping models based on the observed conductivity behaviors. Also, an extension with respect to percolation treatment is used to answer how the hopping percolation path functions in the macroscopic dc conduction at critical phenomenon.

2. Experimental Procedure

2.1 Raw Materials and Sample Preparation

A ceramic sample of Bi₄Ti₃O₁₂ was prepared by a standard mechanical activation method. The starting materials used were commercially available bismuth oxide (Bi₂O₂, 99 % purity, 80-200 nm) and titanium dioxide (rutile- TiO_{2} , > 99.9 % purity, 100 nm). Both starting materials were readily accessible from US Research Nanomaterials, Inc. The precursor nanopowder oxides were mixed according to the nominal Bi₄Ti₃O₁₂ stoichiometric proportions (2:3 mole ratios) and Ball-To-Powder weight Ratio (BPR 10:1). High energy dry milling of the starting mixtures was then carried out using a SPEX SamplePrep 8000 D Dual Mixer/Mill for 24 h at a constant mill speed of 1425 rpm at ambient atmosphere. The milled mixtures were then pressed into a pellet-type shape at ~120 MPa. The well-prepared pellet was sintered at 1273 K for 4 h in air with heating and cooling rates of 275 K/min. Both surfaces of the sintered pellet were coated with silver paste prior to attaching between a pair of parallel gold electrodes.

2.2 Measurement

The coated pellet in sandwiched geometry was measured using an Agilent 4294A Precision Impedance Analyser in terms of parallel capacitance C_p and conductance G_p , which are convertible into electrical conductivity σ through the dielectric parameters of ε ' and tan δ in accordance to equation (45). The expressions of ε ' and tan δ associated with C_p (in F)and G_p (in S) are respectively represented by¹⁴:

$$\dot{\varepsilon}(\omega) = \frac{C_p(\omega)t}{\varepsilon_0 A} \tag{1}$$

and

$$\tan \delta = \frac{G_{\rm p}(\omega)t}{\varepsilon_0 \epsilon A \omega}$$
(2)

where ε ' is the dimensionless measured number of dielectric permittivity; ε_0 is the permittivity of free space

with the value of ~8.85 x 10^{-12} F.m⁻¹; ω (in rad.s⁻¹) is the angular frequency equals to 2π with f being the varying frequencies in Hz;t and A are the thickness and area of sample with the average measured values of 1.61 x 10^{-3} m and 1.17 x 10^{-4} m², respectively. The measurement conditions were in the frequency range 40 Hz-1 MHz and temperature range 303–673 K.

3. Results and Discussion

3.1 Conductivity Studies

One of the common charge (ion, electron or hole) dynamic examinations is by analyzing a linear response of dc conductivity σ_{dc} over a range of temperatures via an Arrhenius equation given by:

$$\sigma_{dc} = \sigma_0 e^{-\frac{E_{a(\sigma_{dc})}}{k_B T}}$$
(3)

Where σ_0 (in S.m⁻¹) and $E_{a(\sigma_{dc})}$ (in eV) represent the pre-exponential factor and activation energy associated with σ_{dc} (in S.m⁻¹), respectively; k_B (in eV.K⁻¹.mol⁻¹) is the Boltzmann constant with the value of ~5.19 x 10¹⁹; T (in K) is the absolute temperature. The σ_0 and $E_{a(\sigma_{dc})}$ parameters are graphically inferred from the y-intercepts and slopes of the Arrhenius fits as depicted in Figure 1.



Figure 1. Arrhenius plots of σ_{dc} in the temperature interval 303 < T < 673 K.

Based on the evaluation of adjusted R-square (adj-R²) statistics in conjunction with the residual plots, high adj-R² values for each resulting Arrhenius fit are close to unity, indicating the Arrhenius models satisfactorily fit the σ_{dc} data. For the σ_{dc} -related plots, one should bear in mind that the σ_d values for each measured temperature were elaborated based on the dielectric fitting (see supplementary material- dielectric part for details) and BNN relation and the latter will be covered more detail in subsection 3.4. Here, we will only discuss the BNN-derived σ_{dc} as compared to the dielectric-derived σ_{dc} since both give close values of nearly identical activation energies. Based on the evaluated $\mathrm{E}_{\mathbf{a}(\boldsymbol{\sigma}_{\mathrm{dc}})}$ values and well-described linear curves, hopping transport over energy barrier is likely the only essential movement in the dc conduction process of Bi₄Ti₃O₁₂, with the charge carriers thermally activated, as evident from the exponential increase of σ_{dc} with temperature. It is apparent that changes in the slopes (i.e., change in the $E_{a(\sigma_{1,.})}$ across a range of studied temperatures) of the Arrhenius dependence are seen, indicating a dc conduction process (i.e., where the carriers extend their motion to infinity percolation path at low frequency region). In order to move from one position to another localized state, the hopping carriers need to overcome minimum energy barriers with different heights across a temperature range. Higher $E_{a(\sigma_{1,2})}$ of ~0.54 eV in the temperature interval 523 < T < 673 K is accounted to the increasingly hopping rate of carriers, where higher number of carriers are thermally activated, subsequently enhances the $\sigma_{dc}^{\ \ 15}.$ The $E_{a(\sigma_{dc})}$ values obtained are consistent tent to those $Bi_4Ti_3O_{12}$ -reported literatures^{13,16}.

From now onwards, to avoid confusion and make picture clearly distinguishable to the readers, the conductivity will be differentiated and classified into temperature regions I and II. Region I corresponds to the lower temperature interval 303 < T< 473 K and region II corresponds to the higher temperature interval 523 < T < 673 K. We reasonably believe that the dc conduction path in these temperature regions to be resulting from different types of hopping transport mechanisms. From the initial rough judgment, it sounds reasonable to extend the temperature region II by including the σ_{dc} data at 423 and 473 K as the linear fits could give very high adj-R²values of ~0.99 (see Figure S3 in the supplementary material). Yet, the corresponding intuitive linear fits will in fact mislead the data interpretations. As an evidence, the following logarithmic plots of $\sigma_{_{ac}}(\omega)$ – $\sigma_{_{dc}}$ ~ w^2 as illustrated in Figure 2(a) and (b) are justified, with each curve at different temperatures is characterized by their respective linearity. In the temperature region II, each plot of $\sigma_{ac}(\omega) - \sigma_{dc}$ falls on a straight fit line which gives very high adj-R² value tending towards unity (Figure 2(b)). Come to the temperature region I, neither of the resulting logarithmic plots follow the linearity as evident from the poor adj-R² values (Figure 2(a)). From the standpoint of relaxation process due to hopping charge movement, once linearity is satisfactorily validated from the plot of $\sigma_{ac}(\omega) - \sigma_{dc}$, the following conductivity relation is expected to hold which correlates with the relaxation time τ (in s) if $\omega^2 t^2 < 1^{17}$:

$$\sigma_{ac}(\omega) - \sigma_{dc} = \frac{\omega^2 \tau^2}{1 - \omega^2 \tau^2}$$
⁽⁴⁾

Where σ_{ac} (in S.m⁻¹) is the ac conductivity. The applicability of equation (4) is examined via the logarithmic plot of τ against ω^2 as shown in the inset of Figure 2(b). Each plot of the temperature region II is well described by their respective marked solid straight lines, accompanied by their very high adj-R² values close to unity.



Figure 2. Log-log plots of $\sigma_{ac}(\omega) - \sigma_{dc}vs. \omega^2$ in the temperature interval (a) 303 < T < 473 K and (b) 523 < T < 673 K. The inset of Figure 2(b)shows the corresponding frequency dependence of τ

3.2 High Elevated Temperature Dc Conductivity Studies

3.2.1 Triberis and Friedman (TF) Approach – Temperature Region II

In what follows, the interpretation of $\sigma_{_{dc}}$ findings is on the basis of percolation approach in conjunction with

Generalized Molecular Crystal Model (GMCM) proposed by Triberis and Friedman (TF)^{18,19}. In the temperature region II, one considers a thermally activated charge carrier hops from a localized state to a nearest-neighbour state is governed by the domination of multi-phonons via absorption or emission. Both involved localized states are in random spatial distribution of energy and space in such a way that hopping between states is only possible under the presence of an external field²⁰. At high temperatures, the intrinsic transition rate $\gamma_{i,j}$ for a charge carrier to undergo thermally activated hop from an initial occupied lattice site ito a subsequent empty lattice site j separated by a percolation distance $R_{i, j}$, takes the following exponential form²¹:

$$\gamma_{i,j} = \gamma_0 e^{(-2\alpha R_{i,j})} e^{-\frac{\epsilon}{k_B T}} x \begin{cases} \frac{\Delta E_{j,i}}{2k_B T} \\ \frac{\Delta E_{i,j}}{k_B T} \end{cases} \text{ valid if} \begin{cases} E_j > E_i \text{ (absorption)} \\ E_j < E_i \text{ (emission)} \end{cases} (5) \end{cases}$$

Wherea (in cm⁻¹) is the spatial extent of localized electronic wave function; $\Delta E_{i,j} = -\Delta E_{j,i}$ (in eV) corresponds to the transition energy between sites i and j; γ_0 (in s⁻¹), the pre-exponential factor for $\gamma_{i,i}$ is expressed as:

$$\gamma_0 = \left(\frac{t^2}{h}\right) \left(\frac{\pi}{2\text{Ei}, j\text{kBT}}\right)^{1/2} \tag{6}$$

Where, t (in eV) is the transfer integral calculated using equation (19) from sub subsection 3.2.2; h(in eV.s) is the Planck constant with the value of ~4.14 x 10⁻¹⁵; $E_{i,}$ (in eV) represents the binding energies at sites i and j, respectively. γ_0 is correlated with Z_0 through the relation:

$$Z_0 = \frac{k_B T}{\gamma_0 q^2}$$
(7)

Where q is an electronic charge with the value of ~1.60 x 10⁻¹⁹ C; Z_0 (in Ω) is the pre-exponential factor for Arrhenius equation of critical percolation impedance Z_c (in Ω):

$$Z_{c} = Z_{0} e^{\left(\frac{T_{0}}{T}\right)^{2/5}}$$
(8)

 $Z_{_c}$ in a manner is analogous to $Z_{_{i,\;j}}$ (in $\Omega)$ in the Arrhenius form of:

$$Z_{i,j} = Z_0 e^{\left(2\alpha R_{i,j} + \frac{E_{i,j}}{k_B T}\right)}$$
(9)

Where the resulting random impedance network $Z_{i,j}$ interconnecting different lattice sites is equivalently based on the study of charge transport between random distributed localized states in a disordered system¹⁹. In view of these facts, $R_{i,j}$ in combination with the energy pairs of

 E_i and E_j become the determinative roles to the magnitude of impedance. Bearing in mind that $R_{i,j}$ is regarded as R_{hop} where the latter is hopping distance calculated from equation (27) in sub subsection 3.2.2. Accordingly, the percolation considerations based on $\gamma_{i,j}$ for the hopping carriers between sites at spatial distance eventually lead to the macroscopic analytical expression for σ_{dc} as^{22.23}:

$$\sigma_{dc} = \left(Z_0\right)^{-1} e^{\left(-\frac{T_0}{T}\right)^{2/5}}$$
(10)
with

$$T_{0} = \frac{8.5(N_{c})^{1/2}(\alpha)^{3/2}}{k_{B}N(E_{F})}$$
(11)

Where T_0 (in K)refers to the characteristic temperature coefficient, which strongly depends on α and N(E_F). By referring to equation (10), the satisfactory Arrhenius plots of ln $\sigma_{dc} \sim T^{2/5}$ shown in Figure 3 are the modified versions to the conventional Arrhenius model, with the additional informative parameters of T_0 and Z_0^{-1} are gleaned from the slopes and intercepts of the $T^{-2/5}$ plots. From the T_0 value, it is possible to estimate numerically the α value in such a way that the parameters of N(E_F) and N_c are deduced by referring equations (21) and (27) since these parameters convey the same physical meanings as in the TF model.



Figure 3. Natural logarithmic plots of σ_{dc} with respect to T^{-2/5} in the temperature region II 523–673 K

In order for percolation to occur, the following criteria have to be fully met which generally consist of²¹:

$$\frac{\mathbf{R}_{i,j}}{\mathbf{R}_{\max}} + \frac{\mathbf{E}_{i,j}}{\mathbf{E}_{\max}} \le 1$$
(12)

with

$$R_{max} = \left(\frac{T_0}{T}\right)^{2/5} (2\alpha)^{-1}$$
and
(13)

$$E_{max} = \left(\frac{4k_{\rm B}T}{3}\right) \left(\frac{T_{\rm o}}{T}\right)^{2.5} \tag{14}$$

$$Z_c \ge Z_{i,j}$$
 (15)

$$\xi_c \ge \xi_{i,j} \tag{16}$$

Where ξ_c is the dimensionless critical percolation exponent; E_{max} (in eV) is the maximum energy separating i and j sites associated with the percolation cluster. The calculated percolation determinative parameters are tabulated in Table 1. The values obtained are consistent with the proposed percolation conditions, confirming the dc conduction takes place via percolation.

Following Table 1, localization lengths α^{-1} are of the order of 10⁻⁹ cm, decreasing with increasing temperature due to the reduction in maximum hopping distance R_{max} (in cm) and degree of disorder T_0/T . Degree of disorder take the values of the order of $\sim 10^3$, denoting the considerably low disorder in the hopping-carrier-dominated system of Bi₄Ti₃O₁₂, as supported by the values of σ_{dc} . It is evident from Table 1 that the increase in temperature tends to lessen the carriers' highest hopping distance limit between the randomly distributed localized states due to the decrease in α^{-1} . Indeed, R_{max} is found to comply with the Arrhenius fit according to the T^{-2/5} law. Greater a⁻¹ establishes fewer localized carriers caused by low disorders in the crystal lattices, which in turn yield higher levels of σ_{dc} . On top of that, the mobility hopping carriers in the region of localized states is favour in the sense that the defects of Bi and Ti ions in the pseudo-perovskite layers of Bi₄Ti₃O₁₂ system are gradually experiencing stability upon increasing temperature¹⁶. Therefore, the degree of disorder in the temperature region II is getting small with increasing temperature (Table 1). The continuous improved defect states with temperature variations allow the percolation of hopping carriers between electrodes since the corresponding small fraction of carriers are poorly localized and thus energetically enhance the conductive behaviour²⁴. These conditions are supported in analogy with the marginal uptrend values of the degree of localization R_{hop}/α^{-1} (i.e., appreciably small values with the condition $\alpha R_{hop} < 1$) with increasing temperature as shown in Table 1.

3.2.2 Mott and Austin (MA) Approach – Temperature Region II

Having acquired some practical facts about the temperature dependence of σ_{dc} in the foregoing sections, we

T [K]	$(R_{hop}/R_{max}) + (E_{i,j}/E_{max})$	Z _c ¹ [x10 ⁵ W]	Z _{i,j} ¹ [x10 ⁻³ W]	$\xi_{c}^{1,2}$ [x10 ¹]	$\xi_{i,j}^{1,3}$	α ⁻¹ [x10 ⁻⁹ cm]	R _{max} [x10 ⁻⁷ cm]	E _{max} [eV]	T ₀ / T[x10 ³]	$\frac{R_{hop}}{[x10^{-3}]}$
	¹ [x10 ⁻¹]									
523	3.23	5.32	61.4	2.80	1.20	9.77	1.37	1.68	4.14	8.24
573	3.06	1.95	22.0	2.70	1.10	9.37	1.26	1.77	3.78	8.50
623	2.91	0.80	9.14	2.61	1.01	9.03	1.18	1.87	3.48	8.71
673	2.78	0.36	4.33	2.53	0.94	7.62	0.96	1.96	3.22	8.97

Table 1. Relevant s_{dc}-associated transport parameters deduced from TF analysis in the temperature region II 523–673 K.

 1 Columns list the σ_{dc} -related determinative TF parameters for percolation condition.

 ${}^{2}\xi_{c}$ is equivalent to $(T_{0}/T)^{2/5}$.

 ${}^{3}\xi_{i,j}$ is equivalent to $2\alpha R_{i,j} + (E_{i,j}/k_{B}T)$.

generally argue that small polaron formation facilitates the high temperature conduction mechanism via thermally activated hopping between the localized states. Yet, the understandable σ_{dc} results in the temperature region II are still in the infancy analysis stages. Here, the σ_{dc} analysis will be expanded further by augmenting the high temperature σ_{dc} analysis, referring to the qualitative treatment of Mott-Austin's Small Polaron Hopping (SPH) model^{25,26}. It is widely accepted that the typical feature of SPH is either associated with adiabatic or non-adiabatic mechanism in which a clear insight into the interaction of lattice distortion coupled with small polaron motion is highlighted. The shortlisted SPH mechanisms are customarily discernible through the following σ_{dc} -modified Arrhenius equation:

$$\sigma_{dc}T^{c} = \sigma_{0}e^{-\frac{E_{a(\sigma_{dc})}}{k_{B}T}}$$
(17)

Where the superscript c= 1 is designated for the adiabatic case whereas c= 3/2 for the non-adiabatic case.



Figure 4. Arrhenius plots, involve the BNN-deduced σ_{dc} trials of adiabatic and non-adiabatic SPH mechanisms in the temperature region II 523–673 K.

As depicted in Figure 4, both linear fits are nicely adhered to their respective data plots with the deduced adj-R² are roughly comparable to each other. Owing to the better adj-R², it seems logical to conclude that the small polaron transport is operative via non-adiabatic model. However, the reliability solely on the goodness of fit in this particular situation is somewhat scientifically scepticism since the adj-R² differences between both models are merely ~0.01. Due to this uncertainty, we employ Emin and Holstein's principle which concisely monitors the inequality condition between t and \emptyset^{27} :

where v_{phonon} (in Hz) is the characteristic phonon frequency with the assigned value of ~1.76 x $10^{13}(v_{\text{pho-}})$ is independently estimated from the FT-IR spectra of Bi₄Ti₃O₁₂, which is ascribed to the Ti-O stretching vibration at 588.16 cm⁻¹); W_{hop} (in eV) refers to the small polaron hopping energy obtained using equation (25). In our concern, the transfer integral t is calculated independently using the following relation:

$$t = (0.67hv_{phanan}) \left(\frac{T}{T_{Debye}}\right)^{1/4}$$
(19)

Where T_{Debye} (in K)is the characteristic Debye temperature directly related to the v_{phonon} through:

$$\Gamma_{\text{Debye}} = \frac{h \upsilon_{\text{phonon}}}{k_{\text{p}}}$$
(20)

where the experimental estimated $T_{_{Debye}}{\sim}845$ K and $\upsilon_{_{phonon}}$ are strongly dependent on the $Bi_4Ti_3O_{12}$ characteristic. In view of the obtained values of ø and t listed in

Table 2, the inequality condition $t > \phi$ is totally satisfied, signifying the σ_{dc} in the temperature region II is due to the adiabatic SPH. Once the t is tackled, we can estimate the value of N(E_{e})by:

$$N(E_{\rm F}) \approx \left(\frac{t\epsilon_{\rm P}^{3/2}}{q^3}\right)^2 \tag{21}$$

where $N(E_{\rm F})$ (in eV⁻¹.cm⁻³) is the density of localized state near Fermi level; the effective dielectric permittivity is represented by $\varepsilon_{\rm p}$, defined by the fractional dielectric permittivity terms as:

$$\varepsilon p^{-1} = \varepsilon_{\infty}^{-1} - \varepsilon_{s}^{-1} \tag{22}$$

where ε_{∞} and ε_s are the high frequency and static dielectric permittivity, respectively. The former is approximated from the dielectric fitting of ε , while the latter is based on the $\Delta \varepsilon$ parameter of BNN relation.

Table 2. The σ_{dc} -related determinative parameters used to regard the adiabatic SPH model in the temperature region II 523–673 K

T [K]	ø ¹ [x10 ⁻² eV]	$t^{1}[x10^{-2} eV]$	P 1	$a_{el-phonon}^{2}$	$W_{bind}/6^2[eV]$
523	2.26	4.33	1.34	8.86	1.07
573	2.31	4.43	1.35	8.86	1.07
623	2.36	4.52	1.34	8.86	1.07
673	2.40	4.61	1.35	8.86	1.07

¹Columns list the values compatible to the adiabatic feature.

²Columns list the values that confirmed the formation of small polaron.

The N(E_F) distributions in the temperature region II have been estimated to be of the order of ~10²⁵ eV⁻¹. cm⁻³ such that in a typical way the magnitude becomes greater upon rising temperatures, as listed in Table 3. The ascending order of N(E_F) is one of the key determination to the increase in σ_{dc} . It should be pointed out that the sudden boost in N(E_F) from 623 to 673 K is accounted to the small rate of change $\Delta s_{dc}/\Delta N(E_F)$, in turns, ultimately leads to a slight increase in σ_{dc} accompanied by a sudden drop in α^{-1} . As predicted by Mott and Austin, W_{hop} and W_{dis} may contribute to the E_{a(\sigma_{dc})}, depending on the temperature restrictions as follows:

$$E_{a(\sigma_{dc})} = \begin{cases} W_{hop} + \frac{W_{dis}}{2} , & T > \frac{T_{Debye}}{2} \\ W_{dis'} , & T < \frac{T_{Debye}}{4} \end{cases}$$
(23)

Where the static disorder energy W_{dis} (in eV) is established according to the Miller-Abraham's theorem as²⁸:

$$W_{dis} = \frac{0.3q^2}{\varepsilon_s R_{hop}}$$
(24)

On the other hand, W_{hop} , analogous to half of the small polaron binding energy W_{bind} (in eV), is calculated by relating the decisive factors of R_{hol} and R_{hon} :

$$W_{hop} = \frac{W_{bind}}{2} = \left(\frac{q^2}{4\epsilon_p}\right) \left(\frac{1}{R_{pol}} - \frac{1}{R_{hop}}\right)$$
(25)

Where R_{pol} and R_{hop} (both in cm) are the radius and mean separation path between hopping centres associated with the small polaron, respectively. In the present context, both distance-related parameters are calculated using the following equations:

$$R_{pol} = \frac{q^2}{4\epsilon_p E_{a(\sigma_{dc})}}$$
(26)

$$R_{hop} = N_c^{-1/3} = \left(\frac{\pi}{48R_{pol^3}}\right)^{-1/3}$$
(27)

Where N_c (cm⁻³) is the concentration of Ti⁴⁺ ion. R_{hop} exhibits temperature dependence in such a way that the poorly localized carriers require the same energy to perform a shorter hop with increasing temperature (Table 3). These (R_{hop}, W_{hop}) behaviours in the temperature region II support the presuming idea of the most probable hopping activity executed at nearest neighbour sites. As it turns out, shorter hop to some extent facilitate the intrinsic small polaron transport process in the Bi₄Ti₃O₁₂ apparently from the continuous enhancement in σ_{dc} with temperature.

The viewpoint of $T_{Debye}/2$ signifies that the $E_{a(\sigma_{dc})}$ is governed by the upper expression of equation (23). In other words, the emergent multi-phonon process is viable in the temperature region II in such a way that the small polaron energetically hops upward over the potential barrier to other localized state by the sum of W_{hop} + $W_{dis}/2$. Interestingly, it is noticed that the temperatures of 423 and 473 K are well above the benchmark of $T_{Debye}/2$. However, recalling the preceding subsection 3.1 certifies that neither 423 nor 473 K can do the trick in relating small polaron contribution to that of nearest-neighbour site hops.

Comes to the recalculated $E_{a(\sigma_{dc})}$ using equation (23), a closer inspection on the resulting $W_{hop} + W_{dis}/2$ noticeably reveal an inconsistency to the value of $E_{a(\sigma_{dc})}$

evaluated from the Arrhenius equation (3). Such striking discrepancy in $E_{a(\sigma_{dc})}$ envisages that some hidden parameters are in favour to the small polaron transport. By cross checking the $E_{a(\sigma_{dc})}$ differences derived using equations (3) and (23), we notice that the residual values after subtraction are in great commonality with the tvalues reported in Table 2. Therefore, the "missing values" in the recalculated $E_{a(\sigma_{dc})}$ are likely from the transfer integral t. This perspective is eminently reasonable since in the context of adiabatic hopping, σ_{dc} is rewritten as:

$$\sigma_{dc}T = \sigma_0 e^{-\frac{\epsilon_0 + W_{hep} - t}{k_B T}}$$
(28)

In which ε_0 (in eV) in this particular case represent the energy difference between identical lattice fluctuations with or without the charge carriers²⁸. In consideration of adiabatic, the hopping probability of small polaron becomes high as it gains sufficient responding time to follow the lattice fluctuations even with the successive occurrence of a minute coincidence between neighboring states. In such a coincidence situation, larger t (typically t > ~0.01 eV) is intuitively observed and the probability factor P should be around unity. For high temperatures (T > T_{Debye}/2), P is likewise a checking platform for the nature of adiabatic hopping through the correlation with t:

$$P = \frac{t^2}{\hbar v_{phonon} \sqrt{k_B T W_{hop}}} \approx 1$$
(29)

Where \hbar (in eV.s) is the Dirac constant with the value of ~6.58 x 10⁻¹⁶. As evident from Table 2, t is all the way large enough than 0.01 eV and the calculated P values are all the way in accordance with equation (29). These strong evidences conclude that the hopping transport in the temperature region II is definitely operative via adiabatic way, and larger t is somewhat the reason behind the weak localization feature for the small polarons.

We further characterize the observed SPH in terms of mobility behaviour. Since the small polaron mobility is subjected upon adiabatic hopping conduction, its temperature dependence is well expressed in the following equation³⁰:

$$\mu_{driff} = \left(\frac{\upsilon_{phonon} R_{hop}}{k_{B}T}\right) e^{-\frac{W_{hop}}{k_{B}T}}$$
(30)

where μ_{drift} (in cm².V⁻¹.s⁻¹) is the drift mobility. In a favourable thermally activated SPH condition, the high temperatures induced μ_{drift} can be accounted to

the reduced R_{hop} and strong electron-phonon coupling strength. Importantly, the resulting low values of μ_{drift} are substantially less than the upper limit for SPH mobility ~0.1 cm².V⁻¹.s⁻¹. The underlying μ_{drift} in our case evidently rule out the band transport interpretation as the small polaron becomes localized in a highly constrained manner. Also, the band transport is only relevant for the situation in which the acceptable μ_{drift} values should be larger than ~1 cm².V⁻¹.s⁻¹. Moreover, its μ_{drift} should be delivered in a manner inversely proportional to the temperature, in contradiction to the present temperature dependence of μ_{drift} (Table 3).

Given the fact that the realistic μ_{drift} is an increasing function of temperature, equation (30) can be realized in the following Arrhenius-type exponential form:

$$\mu_{driff}T = \mu_0 e^{-\frac{W_{hop}}{k_B T}}$$
(31)

The Arrhenius representative plot for equation (31) is shown in Figure 5. The evaluated W_{hop} associated with the thermally activated μ_{drift} gives very close value as in the W_{hop} derived from equation (25). Both conclusive indications of W_{hop} values acknowledge us the way the adiabatic hopping pans out in interpreting the σ_{dc} data-temperature region II.



Figure 5. Arrhenius plots of μ_{drift} in the context of adiabatic SPH mechanism in the temperature interval 303 < T < 673 K

It is credible to practice the following small polaron's criterion which makes use of W_{hind} :

$$t \le \frac{W_{bind}}{6}$$
 (32)

As a result of significant low t and large $W_{bind}/6$, the invoked equation (32) is inevitably satisfied at this point, indicating the formation of small polaron in the tem-

perature region II. An alternately supportive approach to equation (32) can be accomplished by estimating the dimensionless small polaron coupling strength $\alpha_{el-phonon}$ through the expression:

$$\alpha_{\text{el-phonon}} = \frac{W_{\text{bind}}}{h\upsilon_{\text{phonon}}}$$
(33)

Other words, $\alpha_{el-phonon}$ is a measuring scale for electronphonon interaction. By employing equation (33), $\alpha_{el-phonon}$ take the value of ~8.86 (i.e., $\alpha_{el-phonon}$ is independent of temperature). It has been widely accepted that $\alpha_{el-phonon} > 4$ reflects the existence of strong electron-phonon interaction in solids^{25,31}. Thus, it appears reasonable to say that a relative strong coupling exists between electrons and lattice distortions in the Bi₄Ti₃O₁₂ ceramic; that is, once again ensure the small polaron is essentially formed in the temperature region II.

3.3 Low Elevated Temperature Dc Conductivity Studies

A manifest truth on the change of $E_{a(\sigma_{dc})}$ makes the dc conduction process in the temperature region I differs from those happening in the temperature region II. This is irrefutably true as seen from the obvious non-Arrhenius characteristic shown in Figure 2(a). In this section, we treat the observed σ_{dc} being pointed towards a variable range hopping conduction (VRH) wherein the nearestneighbour hopping process is no longer acceptable. With further decrease in temperature, the phonon (absorbed or emitted) assists to the VRH of carriers between random spatial distributions of localized states near Fermi level E_{F} becomes significantly scarce²¹. Therefore, the intrinsic transition rate $\gamma_{i,i}$ at low temperatures becomes³²:

$$\gamma_{i,j} = \gamma_0 e^{\left(-2\alpha R_{i,j}\right)} e^{-\frac{\varepsilon}{k_B T}} x \begin{cases} \frac{\Delta E_{j,i}}{k_B T} \text{ valid if} \\ 1 \end{cases} \quad \begin{array}{l} E_j > E_i \text{ (absorption)} \\ E_j < E_i \text{ (emission)} \end{cases} \quad (34)$$

According to the pioneering VRH treatment proposed by Mott (i.e., being limited to $T < T_{Debye}/4)^{33}$, the charge hopping transport occurs in the region of localized states is interpreted by the following novel Arrhenius equation:

$$\sigma_{\rm dc} = \sigma_0 e^{\left(-\frac{T_0}{T}\right)^{1/4}} \tag{35}$$

From what the GMCM and percolation theory claim²² [19], the exponential term of $T^{-1/4}$ can be generalized to:

$$T - \frac{r}{r+d}$$
(36)

Where in our dubbed notation, r is known as the energy's dimension; d is the spatial dimensionality of the hopping transport process in the Bi₄Ti₃O₁₂, which takes 1, 2 or 3. Following this generalized equation, the fabrication of VRH can be achieved by picking r= 1, d= 3. Unlike the VRH, adjusting merely on r to 2 bring to the analytical expression $\ln s_{dc}$ ~T^{2/5} temperature dependence, which is reminiscent of TF approach discussed in sub subsection 3.2.1. With d= 3, we figure out that the thermally activated nature of a hop in the Bi₄Ti₃O₁₂ for the entire investigated temperatures is being treated in three-dimensional (3D) mode. This 3D mode can be anticipated by drawing the attention towards the great strength of electron-phonon coupling ($\alpha_{el-phonon} > 4$).

Having known the value of T beyond $T_{Debye}/4$, it seems literally illogical to employ VRH model in explaining the dc conduction activity in the temperature region I. From the statistical experimental evidences that have been acknowledged, the VRH beyond room temperature up to 900 K turns to reality provided that the great Coulomb gap between the initial and final hopping localized states is approximately compensated^{34,35}. Therefore, complementing the Mott's VRH model with a T^{1/2} in the temperature

Table 3. Some estimated SPH-physical quantities relative to σ_{dc} analysis in the temperature region II 523–673 K.

T [K]	R _{polaron} [x10 ⁻¹¹ cm]	R _{hop} [x10 ⁻¹⁰	N(E _F) [x10 ²⁵ eV ⁻¹ .cm ⁻³]	N _c [x10 ²⁹	ε _p	$\begin{array}{c} \mu_{\rm drift} \\ [x10^{-8} \end{array}$	W _{hop}	W _{dis}	$E_{a(\sigma_{dc})}$	t ¹ [x10 ⁻² eV]
		cm]		cm ⁻³]		cm ² .V ⁻ ¹ .s ⁻¹]	[x10 ⁻¹ eV]			
523	8.04	2.00	1.67	1.26	829	1.22	3.22	3.47	4.96	4.42
573	7.97	1.98	1.80	1.29	836	2.04	3.22	3.46	4.95	4.48
623	7.86	1.95	1.95	1.35	848	3.08	3.22	3.41	4.93	4.72
673	6.83	1.70	3.10	2.05	946	3.36	3.22	3.37	4.91	4.91

¹t is calculated based on the subtraction between the $E_{a(\sigma_{d_c})}$ values derived from equations (3) and (23)

1

interval $T_{Debye/4} < T < T_{Debye/2}$ is allowed in which the reconstituted VRH expression becomes:

$$\sigma_{\rm dc} T^{1/2} = \sigma_0 e^{\left(-\frac{T_0}{T}\right)^{1/4}}$$
(37)

This is called Greaves's law³⁶. The Greaves approach placed under scrutiny shown in Figure 6 strongly prove the conjecture of the dominating VRH based on the tolerably linearity. The inferred T_0 value from the VRH is two orders of magnitude higher than TF-derived T_0 of the temperature region II.



Figure 6. VRH-associated Arrhenius relation between ln σ_{dc} T^{1/2} vs. T^{-1/4} in the temperature region I 303–423 K

With the VRH-evaluated T_0 already known, α can be computed using the relation:

$$\alpha = \left[\frac{k_{\rm B}T_0 N(E_{\rm F})}{\lambda^4}\right]^{1/3} \tag{38}$$

Where λ is a proportionality constant depends on the hopping space dimension. For the 3D-VRH conduction, λ takes the value of 2. We make use of equation (21) to estimate $N(E_{F})$. Regarding Table 4, the $N(E_{F})$ distributions in the temperature region I have been estimated to be varied from the order of 10²³ to 10²⁵ eV⁻¹.cm⁻³. Again, the corresponding VRH-derived $N(E_{E})$ show monotonically increasing function of temperature. Hence, we come to a common belief that the increase of $N(E_v)$ is the chief factor to the logarithmic increase in σ_{dc} . It is generally agreed that higher $N(E_F)$ leads higher σ_{dc} . However, monitoring the $N(E_F)$ for the temperatures of 423 and 473 K have instead brushed aside the $N(E_{F})$ - σ_{dc} relationship. In other meanings, the $N(E_{\rm p})$ associated with these low elevated temperatures turns out to be the same order of magnitude $\sim 10^{25} \,\mathrm{eV^{-1}.cm^{-3}}$, which are comparatively larger than those higher temperatures of 623 and 673 K. In such favourable localization region (i.e., entire R_{hop}/α^{-1} more than 6 as shown in Table 6), the boost of σ_{dc} at these particular temperatures is intensely intervened as a consequence of the encumbered carrier mobility in the presence of considerable disorder, due to the defect ionization of oxygen vacancies defined by Kroger-Vink notation (i.e., VRH-derived T₀/T is two orders of magnitude higher than TF-derived T₀/T)³⁷. Thus, larger N(E_F) in this case do not contribute significantly to the σ_{dc} .

Once the $N(E_F)$ is deduced, the VRH-hopping parameters R_{hop} and W_{hop} as a function of $N(E_F)$ at the temperature of interest are respectively represented by:

$$R_{hop} = \left(\frac{3}{4}\right) \left[\frac{3}{2\pi N(E_F)\alpha k_B T}\right]^{1/4}$$
(39)

and

$$W_{hop} = \frac{3}{4\pi R_{hop}^3 N(E_F)}$$
(40)

In the VRH model, dc conduction takes place in such a way that the thermally activated charge carriers rather execute distant hops to search a potential localized state of close energy within the range of $[R_{hop}, N(E_F)]$ so that a minimal energy separation between the interactive localized states is reachable. This is the exact situation elucidates the behaviour of the resulting R_{hop} and W_{hop} in our case wherein the hop of charge carriers marginally span the mean free path is accompanied by a reduced W_{hop} subjected to decreasing temperatures (Table 4).

Table 4. Some estimated VRH-physical quantities relative to σ_{dc} analysis in the temperature region I 303–473 K

T [K]	W _{hop} [x10 ⁻¹ eV]	R _{hop} [x10 ⁻⁹ cm]	$N(E_{\rm F})$ [x10 ²⁴ eV ⁻¹ . cm ⁻³]	N _{path} [x10 ²³ cm ⁻³]	N _{site} [x10 ²⁴ cm ⁻³]	ε _p	$\mu_{drift} \\ [x10^{-7} \\ cm^2. \\ V^{-1} s^{-1}]$
303	3.20	16.1	0.18	0.58	0.23	200	8.22
323	3.36	8.86	1.02	3.48	1.39	354	2.84
373	3.74	6.44	2.39	9.09	3.64	459	1.98
423	4.11	2.88	24.4	102	40.8	975	0.50
473	4.47	2.38	39.8	181	72.3	1128	0.42

To secure the aforementioned VRH derivations, the following VRH conditions have to be checked:

$$R_{hop} \alpha \ge 1$$
 (41)
and

$$W_{hop} > 2k_gT$$
 (42)

Both VRH conditions are satisfied, thereby the concerted VRH model for the interpretation of σ_{dc} behav-

iours in the temperature region I remains unmistakable. Correspondingly, the appreciably large values of $W_{bind}/6$ and $\alpha_{el-phonon}$ reveal the electron-polarizable lattice (phonons) interaction is strong enough for the charge carriers to be localized as small polaron (Table 5).

Having validated the applicability of VRH, it is instructive to examine whether adiabatic or non-adiabatic hopping conduction set in. As depicted in Figure 7, a subtle distinction between adj-R² perplexes the effort in differentiating between both hopping. Due to this vague situation, Emin and Holstein's inequality condition is raised and we find that in the temperature region I, the hopping is well described via adiabatic model. For clarity, the calculated P at different temperatures all close to unity keeps the ideas of the adiabatic response. The resulting values of $W_{bind}/6$, $\alpha_{el-phonon}$ ø, t, and P listed in Table 5 follow the explicit procedures from what we have dealt for the temperature region II in sub subsection 3.2.2.

Table 5. The σ_{dc} -related determinative parameters used to regard the adiabatic SPH model in the temperature region I 303–473 K.

T [K]	ø ¹ [x10 ⁻² eV]	t ¹ [x10 ⁻² eV]	P ¹	α _{el-} 2 phonon	$W_{bind}^2/6^2$ [eV]
303	1.97	3.78	1.34	8.80	1.07
323	2.02	3.83	1.31	9.20	1.12
373	2.15	3.97	1.24	10.3	1.25
423	2.28	4.10	1.19	11.3	1.37
473	2.39	4.21	1.13	12.3	1.49

¹Columns list the values compatible to the adiabatic feature.

² Columns list the values that confirmed the formation of small polaron



Figure 7. Arrhenius plots, involve the BNN-deduced σ_{dc} trials of adiabatic and non-adiabatic SPH mechanisms in the temperature region I 303–473 K

Peculiarly, the temperature dependence of mobility in the VRH region is radically incompatible with the ideas of mobility is an increasing function of temperature. Here, μ_{driff} is a decreasing function of temperature, which at the first place thinking the stereotypical band treatment. However, it makes sense somehow that the small polaron transport still originated from the few phonon-assisted hopping as described by the relatively small magnitudes of μ_{drift} of the order of 10^{-7} cm².V⁻¹.s⁻¹ (Table 4). We attribute the descending order of μ_{driff} due to the mobility edge since it does exist in 3D system^{38,39}. In the VRH region with largely populated N(E_{r}) beyond ~10²⁴ eV⁻¹.cm⁻³, strong localized self-trapped carriers induced by the highly intrinsic disorder permits the co-exist of effective delocalization and inherent localized states, leaving a separation between them as mobility gap. So in this strongly localized system, the existence of thermally activated carriers in localized states is near but not exceeding mobility edge (i.e., Fermi energy lies within the mobility gap closer to the mobility edge in the conduction band). In favour by this mobility edge, most probable small polaron motions are engaged in downward direction through phonon emission in such a way that being trapped in the localized states which are energetically deeper. In these deep lying states, the trapped carriers are immobilized. As a consequence, thermal release them which carrying extremely reduced μ_{driff} to another localized state become difficult. The μ_{drift} in this case exhibit the Arrhenius-like dependence represented by:

$$\mu_{\text{drift}}T = \mu_0 e \frac{E_{a(\text{trap})}}{k_B T}$$
(43)

Where the parameter $E_{a(trap)}$ (in eV) is the activation energy associated with the mean trap depth. This is the average energy required to overcome in order for the trapped carriers to escape from the deep state. Based on the Arrhenius-derived $E_{a(trap)}$ shown in Figure 5, successful trapping and release carriers activities seen in the temperature region I are attributed to the effect of applied electric field, which lower down the potential barrier of a localized state in order to ease the trapping process with sufficient hopping energy⁴⁰.

The conductive behaviour of the $Bi_4Ti_3O_{12}$ system in the temperature region I is also characterized by means of percolation theory. The percolation theoretic treatment is by the same token as outlined in TF approach (sub subsection 3.2.1), but not limited to R_{max} and E_{max} as

T [K]	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	Z _c ¹ [x10 ⁴ W]	Z _{i,j} ¹ [x10 ⁰ W]	ξ _c ^{1,2} [x10 ¹]	ξ _{i, j} ^{1,3}	α ⁻¹ [x10 ⁻¹⁰ cm]	R _{max} [x10 ⁻⁸ cm]	E _{max} [eV]	T ₀ /T [x10 ⁵]	$\frac{R_{hop}^{}/\alpha^{-1}}{[x10^0]}$
303	8.85	11.2	26.2	2.49	2.20	20.7	2.58	0.65	3.85	7.76
323	8.73	7.57	13.7	2.45	2.14	11.6	1.42	0.68	3.61	7.64
373	8.47	3.18	3.52	2.36	2.00	8.73	1.03	0.76	3.13	7.37
423	8.27	1.53	1.19	2.29	1.89	4.03	0.46	0.84	2.76	7.14
473	8.11	0.81	0.49	2.23	1.81	3.42	0.38	0.91	2.47	6.95

Table 6. Relevant σ_{dc} -associated transport parameters deduced from VRH analysis in the temperature region I 303-473 K

¹Columns list the σ_{dc} -related determinative VRH parameters for percolation condition.

 ${}^{2}\xi_{c}$ is equivalent to $(T_{0}/T)^{1/4}$.

$${}^{3}\xi_{i,j}$$
 is equivalent to $2\alpha R_{i,j} + (E_{i,j}/k_{B}T)$.

both derivations are based on the VRH model, which are expressed as:

$$R_{max} = \left(\frac{T_{o}}{T}\right)^{1/4} \left(\frac{1}{2\alpha}\right)$$
 (44)

$$E_{max} = (k_{g}T) \left(\frac{T_{0}}{T}\right)^{1/4}$$
(45)

The three prerequisite percolation circumstances in equations (12), (15), and (16) are again needed to be fulfilled; altogether those listed in Table 6 confirm the functional role of percolation.

Casting the hopping transport into the percolation way is possible in our case by transforming the current hopping system into an equivalent random resistor network characterized by low impedances $Z_{c} > Z_{i} \xrightarrow{32.40}_{i}$. In such percolation scenario, the interconnected random network resembles a short circuit in which the system is being referred as percolation threshold. Therefore, the so called "percolation network", at some stages the entire infinite cluster of networks spanning the entire physical dimensions of the sample, is the effective continuous conduction path for the carriers carrying dc current to percolate from one edge of the sample to another edge^{1,33}. As soon as the formation of continuous conduction path across the sample is completed, this path is at its critical impedance form Z_c , governing the σ_{dc} of the sample. Simultaneously, the dimensionless fraction of 3D-resistor network θ at the percolation threshold holds the following relation⁴⁰:

$$\theta = \frac{N_{\text{path}}}{N_{\text{site}}} = \frac{(R_{\text{max}})^{-3}}{2E_{\text{max}}N(E_{\text{F}})}$$
(46)

In this equivalent conduction path, $\mathrm{N}_{_{\text{path}}}$ and $\mathrm{N}_{_{\text{site}}}$ (both in cm⁻³) represent the densities of conducting paths and sites, respectively. From the temperature independent of obtained θ value of ~0.25 (Table 4), these disclosed values reassure the practical VRH in use with the governing Arrhenius equation expressed in exponential term of T^{-1/4}.

3.4 Ac Conductivity Studies

In this section, we embark with the derivation of alternating current conductivity s_a by relating the measured tan δ in the frequency domain. The duo is interchangeable according to the relation⁴¹:

$$\sigma_{ac}(\omega) = \varepsilon_0 \varepsilon' \omega \tan \delta \tag{47}$$

The entire dynamic response does contain the contribution of s_{dc} that obliterate the true ac conductivity σ'_{ac} . Therefore, the contributions of σ_{dc} and σ'_{ac} have to be individually separated. Regarding to a range of frequencies being explored, the physical interpretation of $\sigma_{d_{r}}$ is peripheral to the matter of steady state transport in sufficiently low frequency domain. Above the steady state σ_{dc} contribution marks its ceased operation, where σ'_{ac} set in to be the sole driven trend and is related to the dielectric relaxation phenomena⁴². In most of the cases, σ_{dc} and σ'_{x} are easily distinguished by referring to the renowned Jonscher's universal conductivity expression⁴³:

$$\sigma_{ac}(\omega) = \sigma_{dc} + A\omega^{n} = \sigma_{dc} + \sigma'_{ac}(\omega)$$
(48)

It is intuitive that σ'_{ac} follows the approximate power law $A\omega^n$ with the dimensionless frequency exponent n lies between the acceptable values 0 and 1. The pre-exponential constant A is dependent to the temperature which equals to $\sigma_{dc}/(\omega_{hop})^n$. Thus, equation (48) becomes:

$$\sigma_{ac}(\omega) = \sigma_{dc} \left[1 + \left(\frac{\omega}{\omega_{hop}} \right)^n \right]$$
(49)

The entire dynamic response as a function of applied frequency (i.e., transition from dc to ac conduction region) becomes tractable if the hopping frequency ω_{hop} (in rad.s⁻¹) is rationally known, which the onset of ω_{hop} is on the cusp of the dominating σ'_{ac} . Figure 8 shows the logarithmic representatives of σ_{ac} at selected operational temperatures, being fitted using equation (49) to see how the fitting is capable to describe the experimental features. Unfortunately, the corresponding fittings yield worthy deviant evidences. As a matter of fact, the experimental curves of σ_{ac} exhibit non-universality characteristics with decreasing temperature, violating the power law especially at the intermediate and high frequency regions.



Figure 8. Representative plots of σ_{ac} at various win log-log functions on the basis of Jonscher's power law

Due to the power law deviation, BNN approach, the abbreviation in honour of Barton, Nakajima, and Namikawa, is put forward⁴⁴. This empirical relation reformulates equation (48) which at first adjustment, the parameter ρ is a coefficient correlates the lower frequency dielectric relaxation with σ_{dr} :

$$\sigma_{dc} = \rho \epsilon_0 \Delta \epsilon \omega_{max} \tag{50}$$

The second adjustment comes to the effect of mobile charge carriers being ubiquitous in $\sigma'_{ac}(\omega)$. These effects, though, tends to cause a polarization mechanism in $\epsilon^{"}$ formalism around the ω_{hop} . By specifying the input of ω_{max} and $\Delta\epsilon$, $\sigma'_{ac}(\omega)$ becomes:

$$\sigma'_{ac}(\omega) = \varepsilon_0 \omega \left[\epsilon''_{HN}(\omega) + \epsilon''_{CC}(\omega) \right]$$
(51)

where $\varepsilon_{HN}^{"}(\omega)$ and $\varepsilon_{CC}^{"}(\omega)$ are the Havriliak-Negami (HN) and additional symmetric Cole-Cole (CC)dielectric relaxation functions, respectively. Here, both dielectric relaxation functions read accordingly as:

$$\varepsilon_{\text{HN}}^{"}(\omega) = \frac{\Delta \varepsilon \sin(\beta_{\text{HN}} \varphi_{\text{HN}})}{\left[1 + 2(\omega \tau_{\text{HN}})^{\alpha_{\text{HN}}} \cos\left(\frac{\alpha_{\text{HN}} \pi}{2}\right) + (\omega \tau_{\text{HN}})^{2\alpha_{\text{HN}}}\right]^{\beta_{\text{HN}}/2}}$$
(52)

where

$$\varphi_{_{_{HN}}} = \arctan\left[\frac{\left(\omega\tau_{_{_{HN}}}\right)^{\alpha_{_{_{HN}}}}\sin\left(\frac{\alpha_{_{_{HN}}}\pi}{2}\right)}{1 + \left(\omega\tau_{_{_{HN}}}\right)^{\alpha_{_{_{HN}}}}\cos\left(\frac{\alpha_{_{_{HN}}}\pi}{2}\right)}\right] (53)$$

And $\omega_{_{HN}}$ is related to $\omega_{_{max}}$ through

$$\omega_{\text{max}} = \omega_{\text{HN}} \left[\frac{\sin\left(\frac{\alpha_{\text{HN}}\pi}{2\beta_{\text{HN}}+2}\right)}{\sin\left(\frac{\alpha_{\text{HN}}\beta_{\text{HN}}\pi}{2\beta_{\text{HN}}+2}\right)} \right]^{1/\alpha}$$
(54)

while

$$\varepsilon''_{cc}(\omega) = \left[\frac{\Delta\varepsilon \left[\left(\omega\tau_{cc}\right)^{1-\alpha_{cc}}\cos\left(\frac{\alpha_{cc}\pi}{2}\right)\right]}{1+2(\omega\tau_{cc})^{1-\alpha_{cc}}\sin\left(\frac{\alpha_{cc}\pi}{2}\right) + (\omega\tau_{cc})^{2(1-\alpha_{cc})}}\right] \quad (55)$$

From the successful BNN fitting, the following governing parameters are collectively extracted: ω_{max} , n= 1 – $\alpha\beta$, ω_{hop} , ρ , and σ_{dc} . The shape parameter α and β , relaxation times τ_{HN} and τ_{CC} as well as dispersive amplitude $\Delta\varepsilon$ are extracted from the dielectric fitting results. As evident from Figure 9, our BNN fitting results are capable of reproducing the experimental data herein the reliability of BNN is unequivocal.



Figure 9. Log-log plots of σ_{ac} as a function of ω in the temperature interval 303 < T < 673 K. Note that the blue coloured symbols indicate the effect of σ_{dc}

In view of the whole conductivity spectrum obtained experimentally, these logarithmic plots reveal dispersive σ_{ac} behaviour throughout the entire examined frequency range. Separately described, the region of σ'_{ac} in analogy to the limited path for the hopping motion of charge carriers in a correlated forward-backward way, is both frequency and temperature dependent, where the pronounced temperature dependent is seen in the intermediate frequency region, notably in the temperature range 323 to 473 K. On the other hand, σ_{dc} resides at low frequencies where the charge carriers perform uncorrelated drift over a large distance is less frequency governing⁴⁵, exhibiting nearly constant values with increasing temperature due to the shifting of thermally-activated ω_{hop} towards higher frequencies. Accordingly, the Arrhenius plots of ω_{hop} are analyzed:

$$\omega_{\rm hop} = \omega_0 e^{-\frac{E_{\rm a}(\omega_{\rm hop})}{k_{\rm B}T}}$$
(56)

As illustrated in Figure 10, the resulting activation energy associated with hopping frequency $E_{a(whop)}$, if compared with $E_{a(\sigma_{1,})}$, reveal two physical situations: 1) $E_{a(\omega_{hop})} \approx E_{a(\sigma_{d,c})}$ for the temperature region II; 2) $E_{a(\omega_{hop})} <$ $E_{a(\sigma_{4c})}$ for the temperature region I. Situation 1 is widely observed in various materials, which imply that in order for hopping transition to occur, the activated charge carriers would have required to surmount the approximate energy barriers whilst conducting as well as relaxing¹⁵ [12]. The underlying microscopic behaviour in situation 2 shows the other way round that fraction of $E_{a(\sigma_{1,2})}$ is directed to the charge carrier creation as a consequence of further immobilizing a tiny part of charge carriers from hopping^{15,46}. Overall, $\sigma(\omega)$ is an increasing function of frequency, recapitulate the exemplified hopping conduction involves localized states as the origin governing the present conductivity behavior.



Figure 10. The corresponding activation plots of ω_{hop} in the temperature interval 303 < T < 673 K

The Arrhenius approach of σ'_{ac} is also employed at selected measured frequencies. As expected, the most satisfying Arrhenius plots are yielded when two distinct temperature regions are considered as shown in Figure 11(a) and (b). It is undoubted that σ'_{ac} at any one frequency is a thermally activated process, where the hopping of charge carriers encounter different transport mechanisms, depending on the temperature regions. Important to note, neither measured frequencies in the temperature region II yield $E_{a(\sigma'_{ac})}$ higher than $E_{a(\sigma_{dc})}$ due to the long range charge migration in σ_{dc} region that have to surmount larger energy barrier, which is definitely a hopping conduction process. Conversely, the prominent frequency dispersions (i.e., ~1 kHz to ~100 kHz) observed in the temperature region I give the values of $E_{a(\sigma'_{ac})}$ much higher than $E_{a(\sigma_{dc})}$. On this occasion, forwardbackward hops are being successfully triggered between the adjacent lattice sites owing to the dipolar conduction process, which govern the relaxation phenomena of the surrounding lattice site^{47,48}.



Figure 11. Arrhenius plots of σ'_{ac} at selected measured frequencies in the temperature interval (a) 303 < T < 473 K and (b) 523 < T < 673 K

We test the applicability of Random Barrier Model (RBM) proposed by Dyre to the temperature region II hereof⁴⁹. As the name tells, random varying energy barriers are what the non-interacting charge carriers have to cope with, based on the simplified concept of ac conduction is lower than dc conduction in terms of activation energy, neglecting the Coulomb interaction. The hopping to nearest-neighbour localized state described here is symmetric, happens occasionally depends on the probability of acquiring sufficient energy from its environment^{49,50}. By taking into account the effect of σ_{dc} and τ , the expression of RBM-derived σ_{ac} with the presence of independent variable ω reads empirically as⁴⁵:

$$\sigma_{ac}(\omega) = \frac{\sigma_{dc}\omega\tau \arctan(\omega\tau)}{\frac{1}{4}\ln^2(1+\omega^2\tau^2) + (\arctan\omega\tau)^2}$$
(57)

Using the RBM-derived equation, the predictive σ_{ac} behaviours at best, reconcile with the dispersive experimental trends (Figure 12). The estimated RBM- σ_{dc} and τ fall within the experimental error as their Arrhenius natures shown in Figure 13 yield the activation energies of nearly equal values like the already known $E_{a(\sigma_{dc})}^{-}$ evaluated from equation (3). The practical limitation of RBM in our case is that once the relaxation peaks occur at frequency $\omega > \omega_{HN}$, the RBM-predictive σ_{ac} are not being associated with the experimental trends beyond the vicinity of the relaxation peaks. The deviations from the experimental data mentioned here could be due to the non-power law universality.



Figure 12. Log-log plots of σ_{ac} as a function of ω at the temperature region II of (a) 523 K, (b) 573 K, (c) 623 K, and (d) 673 K

For the temperature region I, since the exponentn strongly reveals a decreasing temperature function (i.e.,

n approach unity with decreasing temperature), the ac conduction mechanism would be clear by considering a pair approximation of random distribution charge defect states wherein between the states involved an electron transfer over a Coulombic potential barrier via single polaron hopping. Such hopping activity is called correlated barrier hopping (CBH) model unveiled by Elliott⁵¹. The validity of CBH used in the present case is diagnosed. A satisfactory linear function of temperature as seen in Figure 14 clarifies the carriers are transported via the CBH way.



Figure 13. Arrhenius plots of τ and σ_{dc} in the temperature region II 523–673 K. The data of τ and σ_{dc} is approximated from the best resemble experimental σ_{ac} curves of RBH (Figure 12)



Figure 14. The behaviours of 1-n and T/(1-n) with respect to the temperature interval 303 < T < 673 K

Following this model, the energy and distance-related parameters relative to a pair of defect states are priori-

tized. The inferred n values leads to the calculation of the maximum barrier height W_{max} (in eV):

$$W_{max} = \frac{6k_{\rm B}T}{1-n}$$
(58)

While the minimum hopping distance R_{min} (in cm) can be approximated by the relation:

$$R_{\min} = \frac{mq^2}{\pi \varepsilon' \varepsilon_0 W_{\max}}$$
(59)

Where m here is the number of charge carriers involved in a hop, takes 1 for mono-hop whilst for bi-hop is 2. The functional involved hopping distance R_{hop} (in cm) is derived as:

$$R_{hop} = \left(\frac{mq^2}{\pi\epsilon'\epsilon_0}\right) \left[W_{max} + k_B T \ln(\omega\tau_{phonon})\right]^{-1}$$
(60)

We disregard the contribution from bi-hopping process with the evidence that $R_{min} < R_{hop}$ does not hold for m= 2. In the dominating mono-hopping process, W_{max} is now referred as binding energy. Between the two neighbouring sites at inter site separation, the interacting charge carriers experience a close proximity situation where superimposition of Coulomb-like potential wells occurs, ultimately leads to a barrier reduction in W_{eff} inferior to W_{max} . Taking into account the combined influential factors of W_{max} and R_{hop} , W_{eff} reads as:

$$W_{\text{eff}} = W_{\text{max}} - \left(\frac{q^2}{\pi \epsilon' \epsilon_0 R_{\text{hop}}}\right)$$
(61)

We only present the results at constant frequencies of 100 kHz and 1 MHz, being ensured that the rest give about the same behaviours with respect to the temperature. Regarding to the scenario between W_{max} and R_{min} , Figure 15(a) offers an insight that increase in temperature ease the removal activity of individual charge carrier. Less energy is required to remove completely the residing charge carrier at instantaneous defect state to another attributed to the shorter R_{min} . However, lowering to W_{eff} simultaneously makes the hopping process deems harder with the evidence that larger R_{hop} gives higher W_{eff} in the increasing temperature condition (Figure 15(b)).

3.5 Ac Conductivity Scaling

Since several temperatures are compiled in the frequency variable conductivity spectra, it is best to introduce a scaling approach which normalizes the conductivity and frequency axes. The role of scaling is crucial to check



Figure 15. Temperature dependence of (a) W_{max} , R_{min} and (b) W_{eff} , and R_{hop} in the temperature region I 303–473 K

the scaled conductivity spectra taken at different temperatures whether being prone to Time-Temperature Superposition Principle (TTSP) that ensued from the merging of the corresponding curves into a single curve. This merging behaviour is normally regarded as master curve. One of the many ways to do this merging is through the realization of Summerfield scaling⁵².+ Such ac scaling expression takes the amended form of $\sigma_{ac}(\omega, T)$, following the insertion of a scaling factor σ_{dc} into both responsible functions:

$$\frac{\sigma_{ac}(\omega)}{\sigma_{dc}} = F\left(\frac{\omega}{\sigma_{dc}T}\right)$$
(62)

where F denotes a temperature-independent scaling function. From Figure 16(a) of the temperature region II, a likely-looking single master curve is yielded in the entire measured frequency range, proving the TTSP as in the relaxation mechanism is independent of temperature⁵³. The scaling behaviour in the temperature region I become entirely different as the scaling output is against the TTSP in the entire measured frequency/temperature range, as evident from the failure of each curve to superimpose on a single master curve. The possible reason for this failure is due to the trapping of ionized oxygen vacancies at grain boundary sites, which consequently limit the charge carrier movement pathways^{16,54}.

To what extent the deviation from Summerfield scaling, an adjustable scaling parameter ψ is introduced, which is a power of the base temperature that revamp the numerator in equation (62) to become:

$$\frac{\sigma_{ac}(\omega)}{\sigma_{dc}} = F\left(\frac{\omega T^{\Psi}}{\sigma_{dc}T}\right)$$
(63)

By using this improved equation with appropriate ψ values for each temperature, Figure 16(b) shows a near perfect single master curve for temperature region II, whereas in the temperature region I, the overlapping of different temperatures spectra are only relevant in both low and high frequency ends. The incapable merging using equation (63) is seen from the shifting of onset frequencies in the prominent conductivity dispersive regions. This unmerging case denotes the deviation of the proportionality between $\sigma_{dc}T$ and ω_{hop} .

Besides serving as a check for the extent of scaling deviation, ψ value is capable to unfold some useful information regarding to the interaction of charge carriers. The small yvalues in the temperature region II confirm the marginal deviation from the conventional Summerfield scaling, along with the negative signs which signify that the non-interacting charge carriers are responsible for the RBM conduction mechanism. In the temperature region I, the positive ψ values denote the taking part of Coulomb exchange between the interacting charge carriers in the dynamic process^{50,54}.

4. Conclusions

In summary, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramic prepared via mechanical activation at sintering temperature of 1273 K was the subject being concerned through the intensive conductivity analysis at varying temperatures and frequencies. The separable dc and ac conductions have been discussed in the hopping context using the phenomenological conductivity models. In dc regions, Arrhenius plots have been initially made to distinguish the prevalent thermalized charge carriers in the two distinct temperature regions 303-473 K and 523-673 K. Due to the highly subjective Arrhenius results, Emin and Holstein's inequality condition and other small polaron supportive approaches were employed, confirmed the taking part of small polar-



Figure 16. Summerfield scaling plots of the conductivity spectra in the (a) conventional and (b) modified versions in the temperature interval 303 < T < 673 K

ons in performing adiabatic 3D hopping dc conduction throughout the measured temperatures. However, the small polarons were transported in different hopping ways, from the worthy-evidences of dc activation energy values of ~0.16 (303-473 K) and ~0.54 eV (523-673 K). In the 303–473 K region, the variable range hopping was few phonons assisted, involved energetically deeper localized states in the vicinity of mobility edge where the drift mobility was further restricted with increasing temperature. In the 523-673 K region, the efficient small polaron hopping would be engaged to the nearest-neighbour localized states induced by multi-phonon process, where the drift mobility is enhanced with increasing temperatures in the low disorder condition. The interactive role of density of localized state at Fermi level (DOS) became influential to the values of dc conductivity in the 523-673 K region. The presence of highly disorder states made a difference in the 303-473 K region, which weaken the influential role of DOS. The activated nature of dc conduction in the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and percolation condition were able to reach an accord, followed T^{-1/4} Mott's analytical expression for the 303–473 K region, while T^{-2/5}Triberis and Friedman's analytical expression for the 523–673 K region.

In our case of prominent frequency dispersive response, BNN was taking advantage by incorporating the Havriliak-Negami and Cole-Cole dielectric relaxation functions, explained the deviation from a universal conductivity curve. In ac regions, two distinct temperature regions similar to dc regions were distinguished. The best way of figuring out the ac conduction in the 523-673 K region was being directly to the random barrier model, pointed the way of ac transport being dominated by the non-interacting charge carriers, which thermally activated hops over randomly varying energy barriers to reach the nearest-neighbour localized site. In the 303-473 K region, the onus was on the correlated barrier hopping model, accounting the pair approximation ac conduction based on the underlying fact that frequency exponent is a decreasing function of temperature. The Summerfield scaling behaviour in the 523-673 K region followed the time-temperature superposition principle (TTSP), but not the case in the 303-473 K region since overlapping of each temperature curve was completely failed. The negative sign of scaling function confirmed the contribution of non-interacting charge carriers to the ac transport in the 523-673 K region. The positive sign in the 303-473 K region marked the Coulomb exchange between the interacting charge carriers.

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Supplementary Material

Dielectric Data of $Bi_4Ti_3O_{12}$ at Sintering Temperature of 1273 K– Fitting Results

The frequency-domain representation of dielectric relaxation spectra (ϵ ' and ϵ ") at different temperatures were fitted using an executable program "DielParamFit. exe", which is based on the following complete empirical functional form of complex permittivity $\epsilon^*(\omega)^{S1}$:

 $\epsilon^*(\omega) = \epsilon' - i\epsilon''$

$$= -i\frac{\sigma_{dc}}{\varepsilon_0\omega} + \varepsilon_{\infty} + \frac{A_{Debye}}{1 + i\omega\tau_{Debye}} + \frac{A_{CC}}{1 + (i\omega\tau_{CC})^{1 - \alpha_{cc}}}$$

$$+ \frac{A_{CD}}{1 + i\omega\tau_{Debye}} + \frac{A_{HN}}{1 + i\omega\tau_{CC}}$$
(s1)

+
$$\frac{1}{1 + (i\omega\tau_{CD})^{1-\beta_{CD}}}$$
 + $\frac{1}{[1 + (i\omega\tau_{HN})^{\alpha_{HN}}]^{\beta_{HN}}}$

where the s_{dc} and ε^{00} terms represent the low frequency dc conductivity and the limiting high frequency permittivity, both of which being influential to the imagi-

nary ε " and real ε ' parts of the complex permittivity at the variables of angular frequency ω , respectively; the last three dispersion terms are recognised as Cole-Cole (CC), Cole-Davidson (CD), and Havriliak-Negami (HN) functions, each of which has its own relaxation time τ and dispersion amplitude A with the shape parameters α and β that characterizing the departures from the ideal Debye characteristic. It is worth noting here that each of the aforementioned addend can be included or omitted, depending on behaviour of the material.

The fitting results of ε ' and ε " for each measured temperature are separately depicted in Figure S1(a)–(i), each of which is featured by any combination of the given dispersion terms in equation (S1), depending on the measured temperature ranges. Throughout the entire investigated frequency range, the fittings are capable of describing the material's multi-relaxation processes in a manner that:

1. Resembling the CC process at intermediate frequencies, and is of the CD-type (based on the HN formula with α = 1) at sufficiently high frequencies, in addition to the sole contribution of s_{dc} in the imaginary part at low frequencies that at the same time obscures the Debye response (303-423 K).

2. Best represented by two CC processes, with the first occurring CC process being masked by the strong low frequency dispersion as a consequence of the dominant $s_{dc'}$ followed by the second CC process (based on the HN formula with β = 1) covering up to 1 MHz (473-673 K).

S1. Constantino, G. A program for the fitting of Debye, Cole-Cole, Cole-Davidson, and Havriliak-Negami dispersions to dielectric data. Journal of Colloid and Interface Science, 2014, 419, 102–106.





Figure S1(a)-(i). The frequency dependence of ε ' and ε " measured at various temperatures, with their respective fitting patterns according to equation (S1), conditionally.

Evidence on Phase Formation of $\rm Bi_4Ti_3O_{12}$ Identified using PAN alytical X'Pert HighScore



Figure S2. (a) The room temperature X-ray reflection lines of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ sample sintered at 1273 K that matches well with (b) the Inorganic Crystal Structure Database (ICSD) of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ reference pattern (reference code: 98-000-8636). Further matching details about the corresponding peak-related parameters are listed in Table S1.

Table S1. The complete list of the XRD peak from the data presented in Figure S2(a) with reference to the given ICSD of the orthorhombic-type $Bi_4Ti_3O_{12}$.

Peak Position, 2θ (degree)	Miller Indices	Relative Intensity	Peak Intensity (Counts)
21.683	-8	7	2285
23.362 ¹	-111	20.92	6826
24.601	-113	1.73	564
26.94	-115	3.54	1155
30.123 ¹	-117	100	32631
32.905 ¹	-20	19.32	6305
33.154	-200	16.55	5402
34.731	-24	1.31	428
36.887	-26	2.49	814
37.11	-206	2.67	871
38.424 ¹	-14	8.18	2671
39.713 ¹	-28	8.23	2686
39.906 ¹	-208	9.74	3177
42.872	-1113	2.31	753
44.127	-16	1.13	369
47.350 ¹	-220	14.89	4860
47.842	-1115	5.79	1888
48.79	-224	0.44	145
49.895	-18	1.03	337
50.37	-226	2.18	712
51.413 ¹	-214	8.01	2615
51.585 ¹	-2014	11.44	3732

52.627	-228	2.84	925
53.264	-1117	2.86	933
53.591	-311	2.26	737
55.426	-315	0.58	188
56.960 ¹	-137	9.96	3251
57.270 ¹	-317	12.41	4050
58.672	-2212	1.55	507
61.287	-2018	0.45	141
62.523	-3111	6.01	1961
64.348	-1121	3.85	1256
65.827	-3113	0.56	184
66.681	-2216	0.97	315
68.95	-40	1.03	336
69.437	-400	3.16	1030
69.686	-3115	2.87	936
72.22	-2022	0.97	315
73.186	-48	0.5	164
74.184	-331	0.53	171
77.235	-337	2.58	843
78.579	-224	1.79	583
78.967	-2024	1.57	513

¹Primary peaks that confirm the phase formation of $Bi_4Ti_3O_{12}$.

Additional Information Related the Arrhenius Plot of $\sigma_{_{dc}}$ Presented in Section 2.1



Figure S3. An attempt to include the data of 423 and 473 K in the Arrhenius plot of σ_{dc} , which capable of yielding very high-adjacent R² values that approaching to unity. However this situation was found impracticable, as evident from the experimental evidence shown in Figure 2(a).