Complex dielectric behaviours in BiFeO$_3$/Bi$_2$Fe$_4$O$_9$ ceramics

Gilad Orr$^1$ · Andrey Gorychev$^1$ · Paul Ben Ishai$^1$

Received: 31 July 2022 / Accepted: 9 November 2022 / Published online: 21 November 2022
© The Author(s), under exclusive licence to Springer-Verlag GmbH, DE part of Springer Nature 2022

Abstract
The complex dielectric permittivity of a sintered ceramic tablet consisting of 70.5% BiFeO$_3$, 27.7% Bi$_2$Fe$_4$O$_9$ and 1.8% Bi$_{25}$FeO$_{40}$ was analyzed as a function of temperature from –120 °C to 230 °C in two separate temperature runs. The results reveal a complicated dielectric response with two temperature activated relaxation processes. The first is purely Arrhenius relaxation related to hopping processes between Fe$^{3+}$ and Fe$^{2+}$ traps induced by oxygen vacancies at grain boundaries. The second process is more unusual. Its characteristic relaxation time follows a quasi-Vogel–Tammann–Fulcher temperature behavior and from fitting the critical temperature point is estimated at $T_0 = 766 K$. It is absent in the second temperature run. It can be related to dynamic rearrangements of domain boundaries between different crystallites in the ceramic. The results also reveal a ferroelectric phase transition that decayed with repeated heating cycles of the tablet. The ferroelectric phase transition in pure BiFeO$_3$ is 1098 K, whereas the current results show it at 373 K. The origin of this reduction in the critical temperature of the phase transition is traced to locally induced strains on grain boundaries mainly because of unit cell size mismatch between BiFeO$_3$ and Bi$_2$Fe$_4$O$_9$.

Keywords Dielectric response · BiFeO$_3$ · Bi$_2$Fe$_4$O$_9$ · Multiferroics

1 Introduction
Materials with exceptionally high values of dielectric permittivity are clearly of technological interest because of their wide application in the electronic industry. One class of materials fitting this description are the multi-ferroics, capable of simultaneously hosting both ferromagnetic and ferroelectric properties and first predicted by P. Curie [2]. Bismuth Ferrous oxides are the poster boys for multi-ferroics, Of these Bismuth Ferrite, BiFeO$_3$, first studied seriously by Smolensky in 1958 and later produced as a single phase [3], has taken the podium position as the archetypal multi-ferroic [4, 5]. The unit cell of Bismuth Ferrite is a perovskite type structure at room temperature belonging to the space group R3c [6, 7] with 2 formula units involved in the basic unit cell [1], reproduced in Fig. 1, resulting in a rhombohedral. For clarity, the oxygen atoms are not shown. They occupy the face centers of the Bismuth cubes. As has been noted, this structure results in a room temperature ferroelectric polarization along the [111]$_{\text{cubic}}$ axis as well as a distortion to the oxygen octahedra by rotating it approximately 11–14° around the [111] axis [5]. This leads to an Fe–O–Fe angle of $\theta = 154–156^\circ$ [5], the significance of which is to control both the magnetic ordering and orbital overlap between Fe and O. This is the source of BFO’s magnetic behavior. The ferroelectric transition [5] is at $T = 825^\circ$ C, meaning that the pure BFO is ferroelectric and anti-ferromagnetic (type G) at room temperature [7, 8]. Unlike most inorganic perovskites the polarization axis is along the diagonal [111]$_{\text{perovskite}}$ direction [9], while its magnetic axis is perpendicular to the same axis. Indeed, its intrinsic polarization along this access has been measured at 100 μC/cm$^2$. The Néel temperature for BFO is around 640 K (367 °C) and above this the structure tends towards tetragonal [7]. Beyond the ferroelectric transition, the structure resolves as cubic. Currently, BFO and its derivatives are some of the rare room temperature multi-ferroics and as such have found many applications in nanoelectronic devices [10], spintronic applications [11], photovoltaics and others [12]. However, single crystals are not simple to grow and frequently, it is more feasible to work with thin films or ceramics [8]. Because of the volatility of Bi$^{3+}$ and the aggregation of oxygen vacancies along poly crystalline boundaries, it is not uncommon during sintering for the formation...
of secondary phases, such as the mullite-like structured Bi$_2$Fe$_4$O$_9$ [13] or the selenite-like form, Bi$_{25}$FeO$_{40}$. Bi$_2$Fe$_4$O$_9$ is an intriguing multi-ferroic in its own right, it is paramagnetic at room temperature and its structure is very different, belonging to the orthorhombic Pbam space group [13]. Unlike BFO, Bi$^{2+}$ ions sit in the channels formed by the FeO$_6$ octahedra, parallel to the c-axis. The result is that the stereochemically 6s$^2$ Lone Pair Electrons (LPE), responsible for its rather poor ferroelectric behaviour [14], are similarly aligned [15]. Its Néel temperature is 264 K and at room temperature, it is anti-ferromagnetic. A comparison of unit cell sizes of the two reveals that there is considerable mismatch between them (see Fig. 2).

Furthermore, the net dipole moment from the LEP is aligned along the c-axis for the mullite-type structure, rather than along the diagonal as for the perovskite structure of BFO. One must assume that in mixed ceramics the domain boundary between the two phases will be a source of rich dielectric behaviors. The ferroelectric behaviour is strongly influenced by the grain boundary [16]. Competing grain directions and locally induced stresses will give rise to depolarizing fields as well as interfacial dielectric effects. Combined these lead to a suppression of the peak dielectric constant at the ferroelectric phase transition and can shift the phase transition temperature [16, 17]. This effect can be considered by introducing a local strain term to the thermodynamic potential as a function of the local order parameter [17]. Grain boundary effects in BFO have been noted in the past [18, 19] and are more noticeable in the lower frequencies ($f < 1$ MHz). Having said as such, some work has been done to analyze the response above 1 GHz [20].

The dielectric permittivity of polycrystalline [14] BFO/BFO derivatives and ceramics [19, 20] and has been studied in the past with an emphasis on the high dielectric permittivity that can be obtained with such materials. In the case of Markiewicz et al. [19], the secondary phase was Bi$_{25}$FeO$_{40}$ and they noticed a rich dielectric landscape. Most of the behaviour could be related to motion along grain boundaries, along with distinct dielectric processes arising from carrier hopping between Fe$^{2+}$ and Fe$^{3+}$ sites, as was shown by X-ray Photoelectron spectroscopy or the short range hopping of oxygen vacancies. In this study, we concentrate on BFO/Bi$_2$Fe$_4$O$_9$ ceramics and consider the characteristics of the observed behaviours in terms of the frequency and temperature trends, rather than in terms of their dielectric constants, as is traditionally done [14, 21].

### 2 Material preparation

BFO synthesis results in a composition of three stable phases, depending on the ratio between the Fe- and Bi-based molecules in the starting materials, the synthesis temperature, the annealing history and impurities [22]. The three stable phases are BiFeO$_3$, the mullite-like Bi$_2$Fe$_4$O$_9$ and sillenite-like Bi$_{25}$FeO$_{40}$. In this work, we are interested in the BFO and mullite-like phases which are non-symmetric while avoiding the cubic Bi$_{25}$FeO$_{40}$. To compare similar previous work in the field [19], we opted for a low temperature sol–gel-based synthesis [23] that maintains the grain size in the tenths of nanometers.

Bi(NO$_3$)$_3$·5H$_2$O and Fe(NO$_3$)$_3$·9H$_2$O were dissolved in distilled water forming a 0.015 mol solution of each. This was followed by mixing both solutions and adding 0.3 cc of 70% nitric acid (HNO$_3$). The solution was stirred for half an hour after which a 0.05 mol solution of tartaric acid was added followed by another half an hour of stirring. The material was poured into a specially assembled temperature-controlled flask with a stirring mechanism where the temperature was maintained at 100 °C for approximately 7 h. The resulting gel was dried at 100 °C until it became an orange brown powder. Disks with 12.7 mm diameter were

---

Fig. 1 The unit cell of BiFeO$_3$ (reproduced from Ref. [1]) the axis directions are given for both the cubic and hexagonal frames of reference. For clarity, the oxygen ions are not shown.

Fig. 2 A comparison of the unit cell sizes between BFO and mullite-type Bi$_2$Fe$_4$O$_9$ reproduced from [13]
from 600 mg of powder using a pressure of approximately 100 MPa and then annealed at 650 °C for 2 h. This annealing temperature was chosen based on Selbach's work [22, 24] which has demonstrated that by relying on Gibbs energy, BiFeO₃ is a metastable compound with Bi₂Fe₄O₉ and Bi₂₅FeO₄₀ being slightly more stable within the 447 ~ 767 °C temperature range. Hence, the material, slowly transforms into those compounds. Due to the 1:1 ratio between the Bi and Fe the mullite-like structure was expected to prevail.

3 Methodology

3.1 XRD

XRD phase structure acquisition of the synthesized material disks prior to sintering and after, was carried out using a PANalytical X’Pert Pro fitted with a Cu Kα source (λ = 1.5406 Å). Phase analysis was based on Rietveld refinement routines (FullProf Suite) [25] with the peaks compared to those generated using the Crystallography Open Database (COD) [26]. Particle size was estimated using parameters obtained by fitting of the peaks in Matlab using the Scherrer equation [27].

3.2 Dielectric measurements

Silver electrodes of 4 mm diameter were deposited by vapour deposition on the ceramic tablet of 0.48 mm thickness. Dielectric measurements were made use a Novocontrol Broadband Dielectric Spectrometer based on an Alpha Impedance Analyser [28] in the frequency range 0.2 Hz to 10⁷ Hz. Temperature control was provided a Quattro PID temperature controller (Novocontrol GmbH, Hamburg, Germany). The initial temperature protocol was 20 °C to –120 °C and then –120 °C to 200 °C. A further measurement was made at 90 °C under a bias voltage 0 V to –40 V, –40 V to 40 V and 40 V to 0 V with a voltage step ΔV = 4V.

The sample was cooled and stored at room temperature for a month, while the initial set of measurements were analyzed. Based on these results, the measurement was repeated in the same frequency range, but temperature range from 0 °C to 230 °C, primarily to concentrate on the noted ferroelectric phase transition (see Fig. 2a).

4 Results and discussion

4.1 XRD

The XRD patterns for the powder and the sintered tablet are presented in Fig. 3. A direct comparison of the patterns in panels (a) and (b) reveals little change, indicating the sintering did not change composition. From Rietveld refinement [27], the composition of the tablet is 70.5% BFO, 27.7% Bi₂Fe₄O₉ and 1.8% Bi₂₅FeO₄₀.

To assess particle size, the dominant features of the two main constituents were fitted using gaussians (shown in panels (c) and (d)).

\[
f(\theta) = \sqrt{\frac{2}{\pi}} \frac{A_i}{\sigma_i} \cdot \exp \left( -2 \frac{(\theta - \theta_i)^2}{\sigma_i^2} \right),
\]

where \( A_i \) is the amplitude, \( \theta_i \) is the position and \( \sigma_i \) is the width of peak \( i \). The results are listed in Table 1. Particle size is derived using the Scherrer equation [29],

\[
d = \frac{K \cdot \lambda}{\sigma_i \cdot \cos(\theta_i)},
\]

where \( K \) is the Scherrer shape factor, usually taken as 0.92 for cubic grains, and \( \lambda \) is the X-ray wavelength (1.54187 Å). The size range calculated by Eq. 2 is shown in Table 1. BFO crystallites are notably larger than the secondary phase Bi₂₅FeO₄₀.

4.2 Dielectric permittivity

The dielectric permittivities and losses for the BFO ceramic tablet are presented in Fig. 4. The upper graphs show the dielectric permittivity (a) for the initial measurement and for the final measurement (b). The dielectric losses are shown in the bottom graphs, respectively. It is apparent that the dielectric landscape is rich, with two relaxations, marked 2 and 3 in the figure, inside the measurement window and dc conductivity is present in the higher temperatures. The dielectric values are broadly in line with those measured by Markiewicz et al. [19] in the same frequency range, but with the selenite-like structure as the secondary phase. One notes a phase transition, marked 1 in the figure, with \( T_c = 100.6 \) °C (373 K). The transition temperature was established by finding the extremum in the temperature derivative of the dielectric permittivity. While the feature is still present in the second measurement, it is greatly diminished, indicating that continued reheating of the tablet has led to a further modification of the phases. The bias measurement around 90 °C, close to the phase transition temperature of 100.6 °C, revealed no hysteresis.

The dielectric permittivity at 0.13309 Hz is presented in Fig. 5(a). The vicinity of the phase transition was modelled using the Curie–Weiss expression, \( \varepsilon'(T) = C_i/(T - T_c) \), where \( i = 1,2 \) for temperatures below and above \( T_c \), respectively [16, 17]. According to Landau’s phenomenological theory for phase transitions [16], the ratio \( C_1/C_2 \), depends on whether the phase transition is first order (\( C_1/C_2 = -8 \)) or second order (\( C_1/C_2 = -2 \)). In our case, it is –1.64, close
to – 2 indicating that this is a second-order structural ferroelectric phase transition, consistent with the lack of hysteresis noted in the bias measurement. MacKenzie et al. [14] also noted an anomaly in the dielectric permittivity of $\text{Bi}_2\text{Fe}_4\text{O}_9$ at 252 °C, which they associated with the reported magnetic transition temperature in pure $\text{Bi}_2\text{Fe}_4\text{O}_9$. However, this is far from the anomaly reported here. Another possibility is that it is related to the BFO phase. While the main ferroelectric phase transition is at 825 °C [5], GHz spectroscopy of nearly pure BFO also found phase transition at 130 °C [30]. Catalan et al. suggested that this was due to the presence of secondary phases [5]. Likewise, the mismatch between BFO/$\text{Bi}_2\text{Fe}_4\text{O}_9$ crystallines can lead to large strains, as has been noted in other crystalline systems [31]. Figure 6 of ref [5] shows that a pressure of 4 GPa would be enough to reduce $T_c$ in BFO to 100 °C and this is easily achievable on the local level of the domain boundary [31]. Therefore, we speculate that this transition is a locally induced strain effect on BFO crystallites in the immediate vicinity of $\text{Bi}_2\text{Fe}_4\text{O}_9$ crystallites.

The complex dielectric permittivity, $\varepsilon^{\ast}(i\omega) = \varepsilon'(i\omega) - i\varepsilon''(i\omega)$, where $\varepsilon'(i\omega)$ is the dielectric permittivity and $\varepsilon''(i\omega)$ is the dielectric losses, was modelled using a sum of 3 Havrilak-Negami (HN) functions along with a dc conductivity term, 

$$\varepsilon^{\ast}(i\omega) = \varepsilon_{\infty} + \sum_{j=1}^{3} \frac{\Delta \varepsilon_{j}}{1 + (i\omega \tau_{j})^{\alpha_{j}}} + \frac{\sigma_{dc}}{i\omega \varepsilon_{0}},$$

where $\varepsilon_{\infty}$ is the higher frequency contribution to the dielectric permittivity, $\Delta \varepsilon_{j}$ is the dielectric strength of the $j$th process, $\tau_{j}$ is the corresponding characteristic relaxation time, $0 < \alpha_{j}, \beta_{j} \leq 1$ are the shape parameters, $\sigma_{dc}$ is the dc conductivity, $\omega$ is the cyclic frequency, $i$ is the root of $−1$ and $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m is the permittivity of free 

---

Table 1 The gaussian fitting parameters of Fig. 3(c) and (d)

|          | $A_1$ | $A_2$ | 201   | 202   | $\sigma_1$ | $\sigma_2$ | Size (nm) |
|----------|-------|-------|-------|-------|------------|------------|-----------|
| BFO      | 179.7 | 180.2 | 31.86 | 32.17 | 0.257      | 0.225      | 31.5–36.9 |
| $\text{Bi}_2\text{Fe}_4\text{O}_9$ | 36.5  | 44.2  | 28.35 | 29.05 | 0.276      | 0.298      | 27–29.7   |

---

Fig. 3 XRD patterns for a BFO tablet. a powder, b sintered tablet. The characteristic peaks for BFO and $\text{Bi}_2\text{Fe}_4\text{O}_9$ are labelled, c a gaussian fit for the $\text{Bi}_2\text{Fe}_4\text{O}_9$ feature and d gaussian fit for the BFO feature.
Complex dielectric behaviours in BiFeO$_3$/Bi$_2$Fe$_4$O$_9$ ceramics

In the first set of measurements, the 3rd process was used to model the tail of relaxations situated at frequencies lower than the bounds of the measurement window but intruding to the data. For the second measurement at high temperatures (above 0 °C), 3 HN processes are found inside the measurement window and so lower frequency processes are modelled using a Left-hand Jonscher function \[ A \cdot (i\omega)^{-n}, \] where \( A \) is the amplitude and \( 0 < n < 1 \).

The data were modelled using an in house fitting routine, Datama [33], based on Matlab [34]. The software is capable of fitting in the complex plain and exploits a logarithmic measure for the merit function \[ \chi^2(\epsilon^*(i\omega_n), \epsilon'(i\omega_n, \{x_j\})) = \sum_{n,j} \left[ \log(\epsilon^*(i\omega_n)) - \log(\epsilon'(i\omega_n, \{x_j\})) \right]^2, \] where \( \epsilon^*(i\omega_n) \) is the measurement data at the frequency point \( \omega_n, \{x_j\} \) is the parameter set defined in Eq. 3 and \( \epsilon'(i\omega_n, \{x_j\}) \) is the model function value for the parameter set and respective frequency point. The advantage is that for data with values varying by orders of magnitude over the frequency range, equal weight is given in the merit function for all frequency points, leading to a more accurate fit. An example of the quality of the fit is presented in Fig. 6.

The dc conductivity for both measurement runs is presented in Fig. 7. In both cases, the conductivity is an
activated process and obeys the Arrhenius expression for conductivity,

$$\sigma_{dc}(T) = \sigma_0 \exp \left( \frac{-\Delta E}{k_B T} \right),$$

where $\sigma_0$ is the high temperature limit of conductivity, $T$ is the temperature in Kelvin, $k_B$ is Boltzmann’s coefficient and $\Delta E$ is the energy of activation for the process. The parameters are listed in Table 2. At $T = 393$ K, the sample undergoes a compositional change, stabilizing at $T = 423$ K and resulting in a doubling of the energy of activation. The dc conductivity during the second measurement run matches these new parameters. Usually, dc conductivity in perovskite systems like BFO, are assigned to the migration of oxygen vacancies [19, 21]. In mullite-like $\text{Bi}_2\text{Fe}_4\text{O}_9$, it has been assigned to intrinsic holes, centered around Oxygen. Reducing $\text{Bi}_2\text{Fe}_4\text{O}_9$ by oxygen loss led to an extrinsic n-type semiconductor via $\text{O}_2^- \rightarrow \frac{1}{2}\text{O}_2 + 2e^- [21]$. However, in the case of BFO, the energies of activation are usually around 0.9 eV to 1.1 eV (87 kJ/mol to 106 kJ/mol), considerably higher than those measured here, although for spark plasma sintering (SPS) of BFO a value of $0.67 \pm 0.07$ eV (64.6 $\pm$ 6.8 kJ/mol) was found [35]. In the selenite-like phase, $\text{Bi}_{25}\text{FeO}_{40}$ dc conductivity has been measured with an activation energy of $0.52 \pm 0.02$ eV (50.2 $\pm$ 1.9 kJ/mol) [21]. Given the very low percentage of this phase in the sample (1.8%), it is unlikely that this is the source of conductivity we see. The value of conductivity at 80 °C is $1.8 \times 10^{-7}$ S/m for the first run and $5.8 \times 10^{-10}$ S/m for the second run. For both runs, dc conductivity was $4.4 \times 10^{-7}$ S/m at 200 °C. This can be compared to the reported values of $2.77 \times 10^{-7}$ S/m for pure $\text{Bi}_{25}\text{FeO}_{40}$ ceramic [21] at 350 °C and more than $2 \times 10^{-6}$ S/m for BFO ceramic [35]. The origin of the low activation energy in SPS BFO was attributed to the reduction, caused by the sintering process itself, along grain boundaries. The removal of oxygen from the sample led to an excess of electrons, which in turn led to a reduction of conducting holes by recombination. One can assume that in our sample a similar process had occurred at the grain boundaries between the two dominant compositions. This is further enhanced as a hypothesis by the dramatic change in conductivity starting a 393 K in the first run. The Novocontrol system maintains the sample temperature by a temperature-controlled Nitrogen flow, possibly leading to further oxygen loss in the sample and activation energies close to those reported to SPS BFO.
The fitting reveals two distinct dielectric relaxations in the first measurement and three distinct relaxations in the second, higher temperature measurement. As stated above this indicates that the first temperature run induced further sintering in the sample. The relaxation times for the processes are presented in Fig. 8.

The first temperature run, Fig. 8(a), is dominated by two processes (aptly marked Process 1 and Process 2 in the figure). Process 1 is Arrhenius with an energy of activation of \( \Delta E = 5.04 \pm 0.02 \text{kJmol}^{-1} \). This range of activation energy is typical of Maxwell–Wagner processes over domain boundaries [36] and we can readily assign it to mismatched grain boundaries in the ceramic. The second process is more puzzling. At first glance, it can be modeled by a quasi-Vogel Fulcher Tamman (VFT) formula of the form

\[
\ln \sigma_0 = \frac{\Delta E}{RT} + \ln \sigma_0
\]

where \( \sigma_0 \) is the pre-exponential factor, \( R \) is the gas constant, and \( T \) is the temperature.

| Measurement 1 (T < 393 K) | Measurement 1 & 2 (T > 423 K) |
|---------------------------|-----------------------------|
| \( \sigma_0 \) [S/m]      | 0.0695±0.0006               | 123±45                      |
| \( \Delta E \) [kJ/mol]  | 44.59±0.19                  | 76.7±1.4                    |

Fig. 7 An Arrhenius plot of the dc conductivity for the first (black circles) and second (blue squares) measurement runs. The fitting lines are according to the Arrhenius expression. The sample undergoes a compositional change during the first run between \( T = 393 \text{ K} \) and \( T = 423 \text{ K} \).
\[ \tau(T) = \tau_0 \exp \left( \frac{E_0}{k(T_0 - T)} \right) \]  

(4)

With the fitting parameters \( \tau_0 = 10^{14} \text{sec} \), \( E_0 = 199 \text{kJmol}^{-1} \) and \( T_0 = 766 \text{K} \). This is a departure of the usual VFT formula whereby \( T > T_0 \). The VFT formula is usually associated with a glass transition in dielectric science [37]. However, in this case, it can be linked to the dynamic rearrangement of domain boundaries between different crystallites in the ceramic. Thermodynamically the relaxation time is proportional to the probability of a transition between two energy states to the system,

\[ \tau^{-1}(T) \propto P \propto \exp \left( \frac{-\Delta F}{k_B T} \right), \]  

(5)

where \( \Delta F \) is the Helmholtz free energy and \( k_B \) is Boltzmann’s constant. Formally the Helmholtz energy is given by

\[ F = \frac{1}{2} V \sum \sigma_{i,j} e_{i,j} - ST + \sum \mu_i N_i, \]  

(6)

where \( V \) is the volume, \( S \) is the entropy, \( \sigma_{i,j} \) and \( e_{i,j} \) are the stresses and strains between crystallites \( I \) and \( j \), respectively, \( \mu_i \) is the chemical potential of the \( i \) species and the \( N_i \) is the number density. If the transitions between crystallites of BFO and \( \text{Bi}_2\text{Fe}_4\text{O}_9 \) are negligible, then the source of the free energy is the mechanic energy caused by the unit cell size mismatch at the grain boundaries (see Fig. 2). Thermal energy in this case leads to rearrangements to reduce \( F \) to its minimum,

\[ \Delta F = \Delta F = \frac{1}{2} \left( \sum \sigma_{i,j} e_{i,j} + V \sum \sigma_{i,j} e_{i,j} - T \Delta S + \sum \Delta (\mu_i N_i). \right) \]  

(7)

If the boundary strains are proportional to the unit cell sizes and these do not vary, then the variation in free energy depends solely on the changes in volume as the crystallites coalesce (the assumption that there are negligible transition means that the last term in Eq. 7 can be ignored). The volume \( \Delta V \) is understood to refer to any mesoscopic region where the relaxation takes place. The probability of a transition then becomes

\[ \tau^{-1}(T) \propto P \propto \exp \left( \frac{-dV \sum \sigma_{i,j} e_{i,j} - TdS}{k_B T} \right) = \exp \frac{dS}{k_B} \cdot \exp - \frac{dV}{k_B T}. \]  

(8)

One can assume that as the temperature is increased more internal states are accessible, leading to an accelerated rate of change in the respective internal crystalline volumes. An assumption of the form \( \Delta V \propto T / (T_0 - T) \), leads to the modified VFT expression of Eq. (4). The interpretation here is that as the temperature \( T_0 \) is approached the mesoscopic volume tends towards infinity, meaning that constriction effects imposed by the boundary no longer play a significant role in the relaxation. Clearly, as \( T_0 \) is a singularity in the expression the behaviour is not valid in the immediate vicinity of \( T_0 \). \( E_0 \) is the energy of the interface per unit surface area.

This model is further reinforced by the relaxation times of the second run, Fig. 8(b), where the VFT like process 2 is missing. The second measurement run was only made from 0 °C to 230 °C. The 1st process is still evident with approximately the same time scales as the 1st measurement run. It is largely stationary until the phase transition noted at approximately 100 °C, where it becomes Arrhenius. A further change is noted again at 170 °C (440 K) indicating a change in charge mobility along the grain boundaries. A summary of the fitting parameters is presented in Table 3. In addition, two more Arrhenius processes are apparent in the fitting. The second process is replaced a regular Arrhenius relaxation, and an additional relaxation appears in the lower frequencies (noted as process 3 in Fig. 8(b)). The energies of activation are in the range reported by Markiewicz et al. [19] for hopping processes between \( \text{Fe}^{3+} \) and \( \text{Fe}^{2+} \) traps induced by oxygen vacancies at grain boundaries and it is most likely the same in our case.

### 5 Conclusions

BFO and its derivatives hold great promise for applications. However, they are not simple materials to produce because of the reactivity of Bismuth. Understanding the dielectric picture can help decipher an otherwise complicated mosaic. In this paper, we have attempted to do just that using dielectric spectroscopy and the language of dielectric relaxation for a BFO ceramic tablet consisting of 70.5% BFO, 27.7% \( \text{Bi}_2\text{Fe}_4\text{O}_9 \) and 1.8% \( \text{Bi}_{12}\text{FeO}_{40} \). The results reveal an unstable sample where the sintering process is still active. Grain boundary strains result if a partial onset of the Ferromagnetic phase transition at temperatures far lower than...
expected. A kinetic rearrangement of the sample is also revealed by the modification of the dc conductivity of the sample starting from 370 K. Furthermore, the non-Arrhenius relaxation in the first temperature run is explained by way of a thermodynamic model related to the coalition of differing sized crystalline particles. We feel that detailed dielectric studies of these ceramics and their derivatives can lead to more robust sintering regimes.

Data availability All data is available on request from the Corresponding Author.

References

1. A.M. Kadomtseva, Yu.F. Popov, A.P. Pyatakov, G.P. Vorobei, A.K. Zvezdin, D. Viehland, Phase Transit. 79, 1019 (2006)
2. P. Curie, J. Phys. Theor. Appl. 3, 393 (1894)
3. G.D. Achenbach, W.J. James, R. Gerson, J. Am. Ceram. Soc. 50, 437 (1967)
4. I. Velasco-Davalos, F. Ambriz-Vargas, G. Kolhatkar, R. Thomas, A. Ruediger, AIP Adv. 6, 065117 (2016)
5. G. Catalan, J.F. Scott, Adv. Mater. 21, 2463 (2009)
6. C. Michel, J.-M. Moreau, G.D. Achenbach, R. Gerson, W.J. James, Solid State Commun. 7, 701 (1969)
7. D.V. Karpinsky, E.A. Eliseev, F. Xue, M.V. Silibin, A. Franz, M.D. Glinchuk, I.O. Troyanchuk, S.A. Gavrilov, V. Gopalan, L.-Q. Chen, A.N. Morozovska, Npj Comput Mater 3, 1 (2017)
8. N. Wang, X. Luo, L. Han, Z. Zhang, R. Zhang, H. Olin, Y. Yang, Nano-Micro Lett. 12, 81 (2020)
9. V.V. Shvartsmans, W. Kleemann, R. Haumont, J. Kreisel, Appl. Phys. Lett. 90, 172115 (2007)
10. A. Crassous, R. Bernard, S. Fusil, K. Bouzehouane, D. Le Bourdais, S. Enouz-Vedrenne, J. Briatico, M. Bises, A. Barthélémy, J.E. Villegas, Phys. Rev. Lett. 107, 247002 (2011)
11. J. Allibe, S. Fusil, K. Bouzehouane, C. Daumont, D. Sando, E. Jacquet, C. Deranlot, M. Bises, A. Barthélémy, Nano Lett. 12, 1141 (2012)
12. P. Hemme, P. Djemia, P. Rovillain, Y. Gallais, A. Sacuto, A. Forget, D. Colson, E. Charron, B. Perrin, L. Belliard, M. Carayous, Appl. Phys. Lett. 118, 062902 (2021)
13. A. Kirsch, M.M. Murshed, F.J. Litterst, T.M. Gesing, J. Phys. Chem. C 123, 3161 (2019)
14. K.J.D. MacKenzie, T. Dougherty, J. Barrel, J. Eur. Ceram. Soc. 28, 499 (2008)
15. M. Curti, T.M. Gesing, M.M. Murshed, T. Bredow, C.B. Mendive, Z. Für Kristalllographie Cryst. Mater. 228, 629 (2013)
16. M. E. Lines and A. M. Glass, Principles and Applications of Ferroelectrics and Related Materials (Oxford University Press, n.d.).
17. B.A. Strukov, A.P. Levanyuk, Ferroelectric Phenomena in Crystals: Physical Foundations (Springer-Verlag, Berlin Heidelberg, 1998)
18. S. Kumari, N. Ortega, A. Kumar, S.P. Pavunyn, J.W. Hubbard, C. Rinaldi, G. Srinivasan, J.F. Scott, R.S. Katiyar, J. Appl. Phys. 117, 114102 (2015)
19. E. Markiewicz, B. Hilczer, M. Błażyk, A. Pietraszko, E. Talik, J Electroceram 27, 154 (2011)
20. Q. Li, S. Bao, Y. Sun, J. Li, Z. Yu, Y. Li, S. Zhang, Y. Liu, Z. Cheng, J. Alloy. Compd. 735, 2081 (2018)
21. A. Perejón, E. Gil-González, P.E. Sánchez-Jiménez, A.R. West, L.A. Pérez-Maqueda, J. Eur. Ceram. Soc. 39, 330 (2019)
22. G. Orr, A. Goryachev, G. Golan, Bulg. Chem. 52, 40 (2020)
23. S. Chakroborty, M. Pal, New J. Chem. 42, 7188 (2018)
24. S.M. Selbach, M.-A. Einarsrud, T. Grande, Chem. Mater. 21, 169 (2009)
25. J. Rodríguez-Carvajal, in Abstracts of the Satellite Meeting on Powder Diffraction of the XV Congress of the IUCr (International Union of Crystallography, Toulouse, France, 1990), p. 127.
26. S. Gražulis, D. Chateigné, G. Olin, Y. Yang, A. Dufresne, E. Gallais, A. Manakova, J. Butkus, P. Mocek, A. Le Bail, J Appl Crystallogr 42, 726 (2009)
27. T. A. Para and S. K. Sarkar, Challenges in Rietveld Refinement and Structure Visualization in Ceramics (IntechOpen, 2021).
28. User’s Manual “Alpha High Resolution Dielectric Analyser”, (Novocontrol GmbH, 2000)
29. A.L. Patterson, Phys. Rev. 56, 978 (1939)
30. N.N. Krainik, N.P. Khuchua, V.V. Zhdanova, V.A. Evseev, Sov. Phys. Solid State 8, 654 (1966)
31. M.A. Carpenter, E.K.H. Salje, A. Graeme-Barber, Eur. J. Mineral. 10(4), 621 (1998)
32. A. K. Jonscher, Universal Relaxation Law (Chelsea Dielectrics P. London, 1995)
33. N. Axelrod, E. Axelrod, A. Gutina, A. Puzenko, P. Ben Ishai, Y. Feldman, Measure. Sci. Technol. 15, 755 (2004)
34. Matlab, Mathworks (n.d.)
35. A. Perejón, N. Masó, A.R. West, R. Poyato, E. Gil-González, A. Chávez, A. Seoane, P. Lázaro, J. Butkus, P. Mocek, A. Le Bail, J Appl Crystallogr 42, 726 (2009)
36. F. Kremer, A. Schönhals, Broadband Dielectric Spectroscopy, in Theory of Dielectric Relaxation, ed. by F. Kremer, A. Schönhals (Springer, Berlin, 2003), pp.1–33
37. F. Kremer, A. Schönhals, in Broadband Dielectric Spectroscopy, in The Scaling of the Dynamics of Glasses and Supercooled Liquids, ed. by F. Kremer, A. Schönhals (Springer, Heidelberg, 2003), pp.99–129

Publisher’s Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Springer Nature or its licensor (e.g. a society or other partner) holds exclusive rights to this article under a publishing agreement with the author(s) or other rightsholder(s); author self-archiving of the accepted manuscript version of this article is solely governed by the terms of such publishing agreement and applicable law.