

## Dielectric properties of bismuth-containing pyrochlores: A comparative analysis

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The comparative analysis of the dielectric properties of bismuth-containing pyrochlores with different manifestation of atomic order/disorder was carried out. We examined the dielectric properties (including behavior in electric fields) of two pyrochlore compounds: BZN (presumably a composition close to  $\text{Bi}_{1.5}\text{Zn}_{0.5}\text{Nb}_{1.5}\text{O}_{6.5}$ ) ceramics with chemical disorder in both A and B cation sublattices and  $\text{Bi}_2\text{Ti}_2\text{O}_7$  single crystal with fully chemical ordered structure. The fundamental differences between the dielectric properties of the BZN ceramics and  $\text{Bi}_2\text{Ti}_2\text{O}_7$  single crystal were shown. In particular, in the dielectric relaxation behavior (which cannot be described via Arrhenius law in the  $\text{Bi}_2\text{Ti}_2\text{O}_7$ ) or in the influence of the electric fields on the dielectric permittivity (splitting of the field-cooled and zero-field-cooled behaviors was observed for  $\text{Bi}_2\text{Ti}_2\text{O}_7$  below estimated freezing temperature). The results of this study highlights the special role of  $\text{Bi}_2\text{Ti}_2\text{O}_7$  as a candidate material for studying aspects of geometric frustration related with pyrochlore structure in non-magnetic medium and specifies the future directions of research.

**Keywords:** Pyrochlores; relaxor behavior; bismuth titanate; dielectric permittivity; geometric frustration.

### 1. Introduction

The compounds with pyrochlore structure are characterized by developed crystal chemical flexibility,<sup>1–4</sup> structural diversity<sup>5</sup> and, as a consequence, demonstrate a huge variability of physical properties: frustrated magnetism,<sup>6,7</sup> superconductivity,<sup>8,9</sup> ferroelectricity,<sup>10,11</sup> metallic “ferroelectricity”,<sup>12</sup> ferroelasticity,<sup>13</sup> multiferroism,<sup>14</sup> catalytic activity,<sup>15</sup> ionic conduction,<sup>16</sup> radiation resistance<sup>17</sup> and many others. Among the variety of pyrochlore-like materials, one can distinguish the bismuth-containing pyrochlores family that is of great interest due to their dielectric and optical properties as well as photo-catalytic activity. The combination of relatively high dielectric constants ( $\epsilon \sim 100\text{--}1000$ ), low dielectric losses ( $\tan \delta \sim 10^{-4}$ ), low temperature coefficient (both positive and negative) and low sintering temperatures ( $T_{\text{sint}} < 1300$  K) makes them viable as cofired multilayer ceramic capacitors, dynamic random access memory

(DRAM) capacitors and as a blocking layer in metal oxide semiconductor (MOS) transistors.<sup>18–20</sup>

The cubic pyrochlore  $\text{A}_2\text{B}_2\text{X}_6\text{X}'$  structure has  $\text{Fd}\bar{3}m$  space-group and unit cell with  $Z = 8$ . A and B cations occupy the  $16d$  ( $1/2, 1/2, 1/2$ ) and  $16c$  ( $0, 0, 0$ ) Wyckoff positions, respectively. Anions X and X' are located at the  $48f$  ( $x, 1/8, 1/8$ ;  $x$  varies from 0.3125 to 0.375) and  $8b$  Wyckoff positions ( $3/8, 3/8, 3/8$ ), respectively. Another origin choice is possible when atoms A occupy  $16c$  Wyckoff position, B –  $16d$ , X –  $48f$  and X' –  $8a$ .<sup>1</sup> The pyrochlore crystal structure usually described as interpenetrating networks of  $\text{BX}_6$  octahedra and  $\text{A}_2\text{X}'$  chains [Fig. 1(a)].<sup>21</sup> A typical structural feature of the bismuth-containing pyrochlores is a displacive disorder i.e., bismuth ions occupy not  $16c$  Wyckoff position as in idealized cubic pyrochlore but  $96g$  or  $96h$  Wyckoff positions (these positions are shifted by  $30^\circ$  relative each other around central  $16c$  position) which are displaced on  $\sim 0.4$  Å relative to  $16c$

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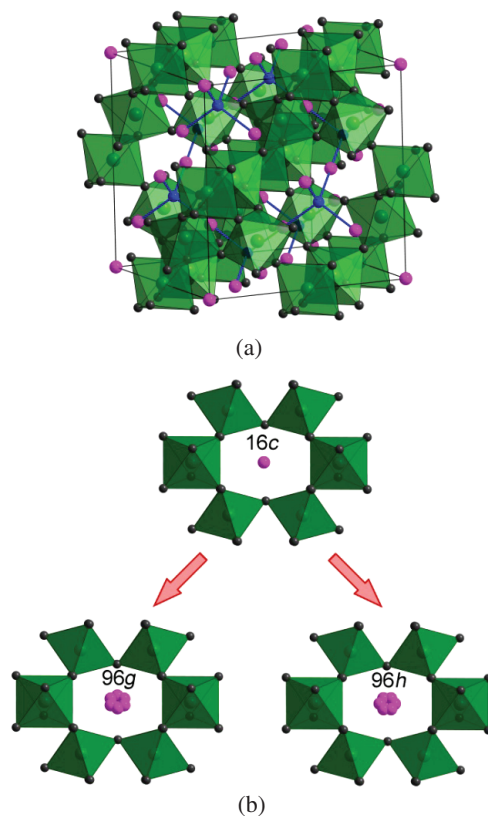


Fig. 1. (Color online) (a) The crystal structure of idealized cubic  $A_2B_2X_6X'$  pyrochlore with space group  $Fd\bar{3}m$ . Atoms designation: A (16c) – purple, B (16d) – green, X (48f) – black, X' (8a) – blue. (b) Local environment for bismuth on the 16c Wyckoff position in idealized pyrochlore and for bismuth on the 96g and 96h Wyckoff positions in the real compounds. Atoms X' on the 8a Wyckoff position not shown.

position [Fig. 1(b)].<sup>22–25</sup> The occupation of such displaced positions is 1/6 that is why there is no average symmetry lowering.

According to some researchers, temperature-activated hopping of A-cations between symmetrically equivalent positions can be the origin of the high dielectric constant and dielectric relaxation in the bismuth-containing pyrochlores.<sup>22,26,27</sup> This model was proposed on the result of the broadband dielectric spectroscopy<sup>26,27</sup> and, in particular based on the observed correlation between resonant frequencies of the infrared O–A–O and O'–A–O' bending phonon modes and the attempt jump frequency ( $f_0 = 1/2\pi\tau_0$  where  $\tau_0$  is the characteristic relaxation time) obtained from the Arrhenius law (1):

$$f = f_0 e^{\frac{-E_a}{kT_m}}, \quad (1)$$

where  $f_0$  is the preexponential jump frequency;  $E_a$  is the barrier-energy for thermally activated process (activation energy);  $T_m$  is the temperature of the maximum in

the imaginary part of the dielectric permittivity;  $k$  is the Boltzmann constant. Such Debye-type dielectric relaxation was found in many bismuth-containing pyrochlores including  $\text{Bi}_{1.5}\text{Zn}_{1.0}\text{Nb}_{1.5}\text{O}_7$  ( $\text{Bi}_{1.5}\text{Zn}_{0.92}\text{Nb}_{1.5}\text{O}_{6.92}$ ) (BZN),  $\text{Bi}_{1.5}\text{Zn}_{1.0}\text{Ta}_{1.5}\text{O}_7$ ,  $\text{Bi}_{1.5}\text{Mg}_{1.0}\text{Nb}_{1.5}\text{O}_7$ ,  $\text{Bi}_{1.56}\text{Fe}_{1.09}\text{Nb}_{1.15}\text{O}_7$  and many others. All of them are characterized by the step-like frequency-dependent anomaly of the dielectric permittivity at temperature about 100–200 K which are not the cause of any ferroelectric phase transition as wrongly mentioned in some pervious works.<sup>28</sup> The problem of the absence of the ferroelectric behavior in bismuth-containing pyrochlores despite of relatively high bismuth displacements (which are comparable to the displacements of ions with lone-pair electrons in the known ferroelectrics, like  $\text{PbTiO}_3$ ) is discussed in the terms of geometrical frustration of the pyrochlore lattice.<sup>29–32</sup> But in the vast majority of the bismuth-containing pyrochlores a random distribution of various ions between different sublattices takes place, for example in BZN A-site occupied by  $\text{Bi}^{3+}$  and  $\text{Zn}^{2+}$  but B-site occupied by  $\text{Zn}^{2+}$  and  $\text{Nb}^{5+}$ . As a result it is impossible to separate the effects of geometrical frustration and chemical disorder in these compounds.

Bismuth titanate  $\text{Bi}_2\text{Ti}_2\text{O}_7$  is unique pyrochlore compound due to its fully chemical ordered structure, i.e., A-site occupied by only  $\text{Bi}^{3+}$  and B-site occupied by only  $\text{Ti}^{4+}$ . In addition, according to first principles calculations the hopping of bismuth ions between equivalent crystallographic positions is possible and is associated with low activation energy which are comparable with others bismuth-containing pyrochlores.<sup>33,34</sup> But, until recently, it was not reported about the growth of large (suitable for dielectric measurements) impurity-free single crystals with a composition close to stoichiometry, and the results of the dielectric properties study of the  $\text{Bi}_2\text{Ti}_2\text{O}_7$  ceramics were contradictory.<sup>35,36</sup> A year ago, we reported on the preparation and study of the structure and dielectric properties of the  $\text{Bi}_2\text{Ti}_2\text{O}_7$  single crystal.<sup>32,37</sup> In particular, it was shown that, unlike other bismuth-containing pyrochlores, attempts to describe the dielectric relaxation of  $\text{Bi}_2\text{Ti}_2\text{O}_7$  single crystals using the Arrhenius equation lead to physically insignificant values of the fitting parameters. However, the relaxation behavior is well described by the empirical Vogel–Fulcher relation, which is typical for many dipole and spin glasses, as well as relaxor ferroelectrics. The discovered relaxor-like behavior of the  $\text{Bi}_2\text{Ti}_2\text{O}_7$  single crystal makes it a candidate-material for studying aspects of geometric frustration related with pyrochlore structure in nonmagnetic medium. But there are still many unclear physical questions: are there signs of nonergodic behavior at low temperatures? and is it possible to induce a ferroelectric phase transition by an electric field? as in the canonical relaxor  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$  (PMN), and is the freezing dynamics manifested in the high-frequency region? This work is aimed at taking a small step towards answering these fundamental questions about the nature of the polar state in the  $\text{Bi}_2\text{Ti}_2\text{O}_7$  single crystal. The main goal of this study was to compare the dielectric properties in electric fields of various

bismuth-containing pyrochlores in particular BZN ceramics with chemical disorder in both A and B cation sublattices and  $\text{Bi}_2\text{Ti}_2\text{O}_7$  single crystal with fully chemical ordered structure.

## 2. Experimental Details

The objects of the experimental study were ceramics and single crystal of the bismuth-containing pyrochlores BZN and  $\text{Bi}_2\text{Ti}_2\text{O}_7$ , respectively. The  $\text{Bi}_2\text{Ti}_2\text{O}_7$  single crystals were grown using slow cooling of the melt of a mixture of  $(1-x)\text{Bi}_2\text{O}_3 \cdot x\text{TiO}_2$  oxides with  $x = 0.6$  from 1473 K to 1173 K at a rate of 7.5 deg/h in yttrium-stabilized zirconium oxide crucibles. The crystal growth details and structure characterization were given in Ref. 32. The sample was in the form of a rectangular plate with the sizes of  $4 \times 4 \times 1 \text{ mm}^3$ .

The  $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$  powder was obtained by two-stage solid-phase synthesis at temperatures  $T_1 = 1073 \text{ K}$  and  $T_2 = 1103 \text{ K}$  with holding for  $\tau_{1,2} = 10 \text{ h}$ .  $\text{Bi}_2\text{O}_3$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{ZnO}$  were used as reagents. The synthesis was carried out according to the following scheme:

- $\text{Bi}_2\text{O}_3 + \text{Nb}_2\text{O}_5 \rightarrow 2\text{BiNbO}_4$  (1123 K,  $\tau = 10 \text{ h}$ )
- $3\text{BiNbO}_4 + 2\text{ZnO} \rightarrow 2\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ .

Sintering was carried out using conventional ceramic technology at 1273 K for 2 h. X-ray diffraction analysis shown no impurity phases for both BZN ceramics and  $\text{Bi}_2\text{Ti}_2\text{O}_7$  single crystals.<sup>32</sup> The relative density of the BZN samples was about 93% of the theoretical value. The BZN experimental samples were disks with the diameter of 10 mm and thickness of 1 mm. The base surfaces of the both (BZN ceramics and  $\text{Bi}_2\text{Ti}_2\text{O}_7$  single crystal) experimental samples were covered by the electrodes which were obtained by burning Ag-paste at  $\sim 773 \text{ K}$ .

Dielectric measurements were performed using test stands fitted with a Wayne Kerr 6500B impedance analyzer in the temperature interval of 10–325 K and E7-20 LCR meter in the temperature interval of 78–350 K. Determination of the complex dielectric permittivity  $\varepsilon = \varepsilon' - i\varepsilon''$  ( $\varepsilon'$  and  $\varepsilon''$  are the real and imaginary parts of  $\varepsilon$ , respectively) was carried out at the frequency ( $f$ ) of the measurement electric field varied from 0.1 kHz to 1000 kHz. The samples were cooled in the chamber of a CCS-150 helium closed-cycle refrigerator with a cooling rate 3 K/min. Measurements were taken in four regimes: zero field cooling (ZFC), zero field heating (ZFH), field cooling (FC) and field heating (FH) with the values of bias electric field  $E = 0\text{--}450 \text{ V/cm}$  for FC and FH.

## 3. Results and Discussion

Figure 2 shows the temperature dependences of the real (a) and imaginary (b) parts of the complex dielectric permittivity of the BZN ceramics at different frequencies of the measurement electric field. The typical for the BZN and other bismuth-containing pyrochlores the step-like

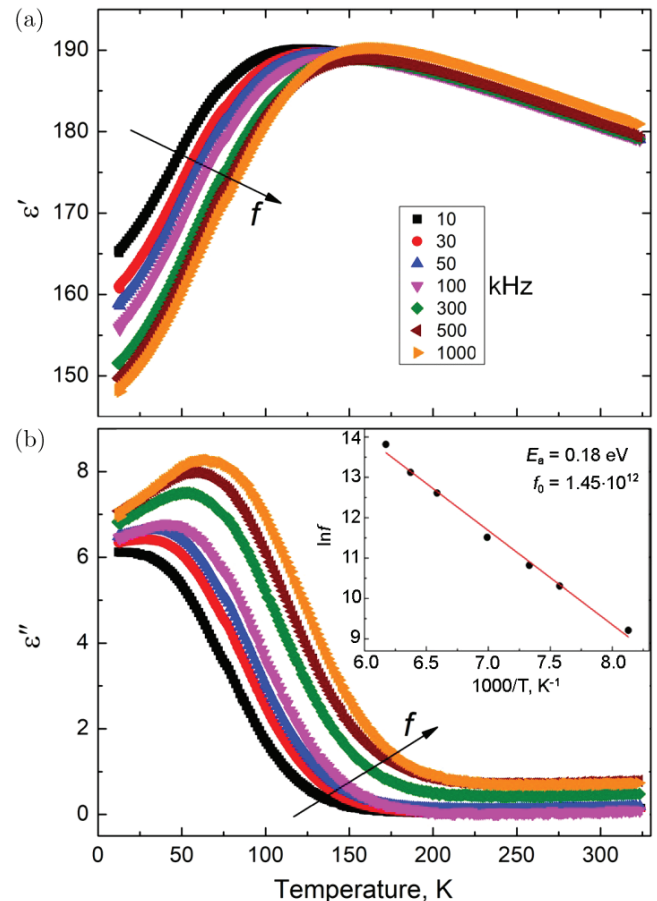


Fig. 2. Temperature dependences of the real (a) and imaginary (b) parts of the complex dielectric permittivity of the BZN ceramics measured at different frequencies (10–1000 kHz) on cooling. Inset shows Arrhenius plot of the studied BZN ceramics.

frequency-dependent anomaly of the dielectric permittivity is observed at  $\sim 100 \text{ K}$  (at  $f = 10 \text{ kHz}$ ). It is clear seen that values of  $\varepsilon'$  at  $T = T_m$  (where  $T_m$  is the temperature of the maximum) is higher for studied ceramics relative to known literature data.<sup>20,26,27</sup> In particular, BZN shows  $\varepsilon'$  values ( $T = T_m$  and  $f = 10 \text{ kHz}$ )  $\sim 160$  while for the samples under study this value reaches  $\sim 190$ . Similarly, the mismatch is observed in the values of  $T_m$  for both  $\varepsilon'$  and  $\varepsilon''$  peaks: in our case the  $T_m$  typical values are  $\sim 50 \text{ K}$  lower than in the case of known data on the BZN ceramics.<sup>20,26,27</sup> This discrepancy can be easily explained taking into account the nonstoichiometry inherent for BZN. As shown by Levin *et al.*,<sup>22</sup> composition  $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$  is a two-phase mixture of cubic pyrochlore and  $\text{ZnO}$ . In other words, due to  $\text{ZnO}$  deficiency, the real composition of single-phase pyrochlore corresponds to  $\text{Bi}_{1.5}\text{Zn}_{0.92}\text{Nb}_{1.5}\text{O}_{6.92}$ .<sup>22</sup> Thayer *et al.*<sup>20</sup> demonstrate by example of thin films that an increase in  $\text{ZnO}$  deficiency (by fabrication of the thin films with composition  $\text{Bi}_{1.5}\text{Zn}_{0.5}\text{Nb}_{1.5}\text{O}_{6.5}$ ) leads to an increase in the  $\varepsilon'$  and a decrease in the  $T_m$ . A comparison of the

dielectric parameters of ceramics and thin films based on BZN<sup>20</sup> indicates a significant deficiency of ZnO in the samples under study. Taking into account the very close values of the dielectric parameters of the BZN ceramics and thin films (with a minimal ZnO deficiency) it can be assumed that the composition of the samples under study is close to  $\text{Bi}_{1.5}\text{Zn}_{0.5}\text{Nb}_{1.5}\text{O}_{6.5}$ .

As the frequency increases, the both  $\epsilon'$  and  $\epsilon''$  maxima shift towards higher temperatures. The relaxation process can be described by Arrhenius law (1) with values of the activation energy  $E_a = 0.18$  eV and preexponential jump frequency  $f_0 = 1.45 \cdot 10^{12}$  Hz which is in good agreement with the results of studies of other bismuth-containing pyrochlores (in particular BZN).<sup>27</sup> Note that as in the case of thin films, in the case of ceramics the dielectric relaxation parameters ( $E_a$  and  $f_0$ ) of  $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$  ( $\text{Bi}_{1.5}\text{Zn}_{0.92}\text{Nb}_{1.5}\text{O}_{6.92}$ ) and  $\text{Bi}_{1.5}\text{Zn}_{0.5}\text{Nb}_{1.5}\text{O}_{6.5}$  (assuming this composition for the samples under study) are practically the same (for BZN  $E_a = 0.202$  eV and  $f_0 = 6.133 \cdot 10^{12}$  Hz).<sup>27</sup> This result is intriguing because it emphasizes the role of bismuth atoms hopping: ZnO deficiency leads to a decrease in the occupancy in the A and X' sublattices<sup>22</sup> and thus for  $\text{Bi}_{1.5}\text{Zn}_{0.5}\text{Nb}_{1.5}\text{O}_{6.5}$  the A-position is occupied only by bismuth atoms and cation vacancies.

Description of the relaxation process according to Eq. (1) in principle means the absence of correlation effects (or weak correlation) between the dipoles or the hopping motions. But a fundamentally different picture is observed in the case of  $\text{Bi}_2\text{Ti}_2\text{O}_7$  single crystals, whose temperature-frequency dependences are outwardly like BZN (with a significantly lower temperature change in  $\epsilon'$ ), but their dielectric relaxation cannot be described using Eq. (1) with physically significant fitting parameters.<sup>32,37</sup> However, as we showed earlier<sup>32</sup> the frequency dependence of the  $T_m$  is well described by the empirical Vogel–Fulcher relation (2):

$$f = f_0 e^{\frac{-E_a}{k(T-T_{VF})}}, \quad (2)$$

where  $T_{VF}$  is the Vogel–Fulcher temperature. Such temperature behavior is typical for many glassy systems, in particular in relaxor ferroelectrics. In the canonical relaxor PMN, the fitting parameters have a clear physical meaning, for example at  $T = T_{VF}$  the freezing of the dipole reorientation dynamics takes place.<sup>38</sup> However, in many others relaxor ferroelectrics the fulfillment of relation (2) (instead of very similar relation which describes temperature dependences of relaxation time but not frequency dependences of  $T_m$ ) does not always mean glassy freezing and the transition to nonergodic relaxor state.<sup>39</sup>

However, using (2) to describe the frequency dependences of  $T_m$  and comparison of the corresponding fitting parameters make it possible to qualitatively characterize the relaxor material, as well as to demonstrate a significant deviation from the model of uncorrelated (or weak correlated) dipoles described by (1). For example, in the case of BZN ceramics and films

using relation (2) instead (1) lead to insignificant values of  $T_{VF}$  confirming the correctness of the Arrhenius law fitting.<sup>27</sup>

Note that, according to Bush *et al.*<sup>32</sup> and this work, for  $\text{Bi}_2\text{Ti}_2\text{O}_7$  the  $f_0$  values  $\sim 10^{12}$  Hz, which is comparable with the results of the BZN study (for both  $\text{Bi}_{1.5}\text{Zn}_{0.5}\text{Nb}_{1.5}\text{O}_{6.5}$  and  $\text{Bi}_{1.5}\text{Zn}_{0.92}\text{Nb}_{1.5}\text{O}_{6.92}$ ).<sup>20,27</sup> But, by the values of  $E_a$  ( $\sim 0.11$  eV) for  $\text{Bi}_2\text{Ti}_2\text{O}_7$  single crystals exceed values for canonical relaxor PMN ( $E_a = 0.071$  eV)<sup>40</sup> and relaxor ferroelectrics with spontaneous transition to the ferroelectric state:  $(1-x)\text{PMN}-x\text{PbTiO}_3$  and related solid solutions with high  $x$  ( $E_a < 0.050$  eV),<sup>39,41–43</sup>  $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$  ( $E_a \approx 0.023$  eV)<sup>40</sup> and  $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$  ( $E_a \approx 0.014$  eV).<sup>40</sup> On the other hand, in this parameter  $\text{Bi}_2\text{Ti}_2\text{O}_7$  single crystals are inferior to BZN ceramics ( $E_a \approx 0.2$  eV)<sup>27</sup> and to so-called weakly coupled relaxor  $(1-x)\text{BaTiO}_3 - x\text{BiScO}_3$  with  $x = 0.2-0.4$  ( $E_a \approx 0.25$  eV).<sup>44</sup> The  $E_a$  values very similar to those of  $\text{Bi}_2\text{Ti}_2\text{O}_7$  single crystals were reported, e.g., for disordered  $\text{PbIn}_{1/2}\text{Nb}_{1/2}\text{O}_3$  single crystal ( $E_a \approx 0.12-0.13$  eV),<sup>45</sup> and for some compositions of  $(1-x)\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3 - x\text{BaFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$  ( $E_a \approx 0.16$  eV at  $x = 0.25$ )<sup>46</sup> and  $(1-x)\text{BaTiO}_3 - x\text{BaZrO}_3$  ( $E_a \approx 0.16-0.21$  eV at  $x = 0.4-0.7$ ).<sup>47</sup> This comparison underlines significance of the correlation effects between dipoles (or hopping motion) in dielectric relaxor-like behavior of  $\text{Bi}_2\text{Ti}_2\text{O}_7$  single crystals.

Since  $\text{Bi}_2\text{Ti}_2\text{O}_7$ ,<sup>24</sup> like the canonical relaxor PMN<sup>48</sup> does not undergo a macroscopic structural phase transition to the ferroelectric state without external electric field, the question of possible signs of nonergodic behavior at low temperatures is relevant. Figure 3 shows the  $\epsilon'$  temperature dependences of the BZN ceramics (a) and  $\text{Bi}_2\text{Ti}_2\text{O}_7$  single crystal (b) measured at  $f = 5$  kHz and  $f = 1$  kHz, respectively, on cooling with (FC) and without (ZFC) bias electric field. It is clear seen that application of electric field does not change the temperature behavior of the dielectric permittivity of the BZN ceramics [Fig. 3(a)] confirming the linear dielectric properties (dielectric permittivity does not change with electric field) and the ergodic state (the physical properties do not depend on the history) in the considered temperature and electric field ranges. Note that modest values of the dielectric tunability (25–45%) of the BZN (for both  $\text{Bi}_{1.5}\text{Zn}_{0.5}\text{Nb}_{1.5}\text{O}_{6.5}$  and  $\text{Bi}_{1.5}\text{Zn}_{0.92}\text{Nb}_{1.5}\text{O}_{6.92}$ ) thin films were observed only at ultra-high electric fields  $\sim \text{MV/cm}$ .<sup>20</sup>

In the case of  $\text{Bi}_2\text{Ti}_2\text{O}_7$  single crystal, on the contrary, even relatively low electric fields ( $E = 0.38$  kV/cm) affect the  $\epsilon'$  ( $T$ ) curve [Fig. 3(b)]: a slight increase in the dielectric permittivity was found in the FC regime at all frequencies at  $T > T_{VF}$  estimated in Ref. 32. The discovered nonlinearity of the dielectric permittivity may not contradict the results of the Esquivel-Elizondo *et al.*<sup>36</sup> who noted that  $\text{Bi}_2\text{Ti}_2\text{O}_7$  is a linear dielectric at room temperature. The point is that the change in  $\epsilon'$  at  $E = 0.38$  kV/cm is very small ( $< 1\%$ ), which may not be reflected in the  $P(E)$  dependence even at large  $E$ . But at the same time, the detected nonlinearity is reproducible both during heating and cooling and fundamentally distinguishes  $\text{Bi}_2\text{Ti}_2\text{O}_7$  from BZN and other bismuth-containing pyrochlores.



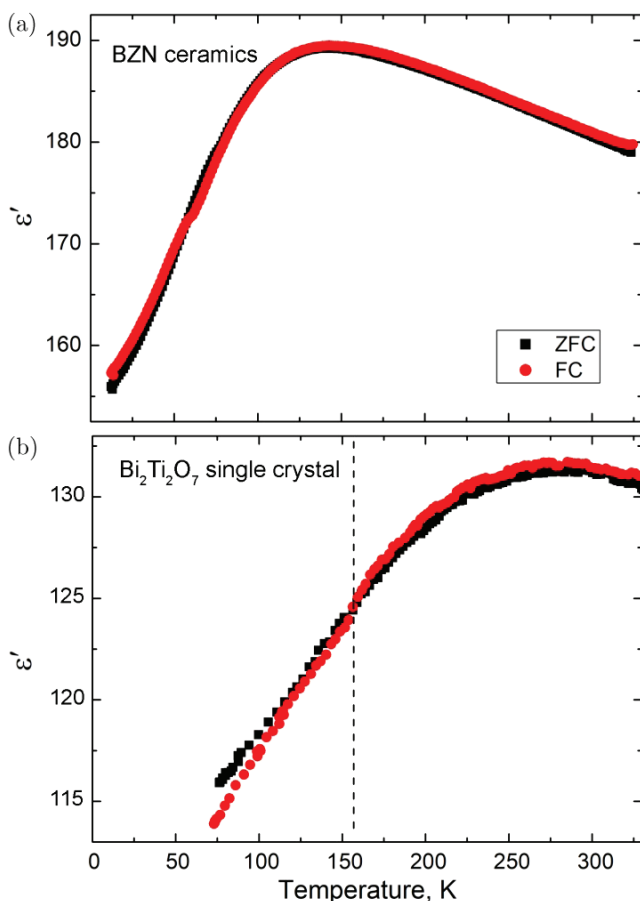


Fig. 3. The  $\varepsilon'$  temperature dependences of the BZN ceramics (presumably a composition close to  $\text{Bi}_{1.5}\text{Zn}_{0.5}\text{Nb}_{1.5}\text{O}_{6.5}$ ) (a) and  $\text{Bi}_2\text{Ti}_2\text{O}_7$  single crystal (b) measured at  $f = 5$  kHz and 1 kHz, respectively, on cooling with (FC) and without (ZFC) bias electric field ( $E = 0.35$  kV/cm and 0.38 kV/cm for BZN and  $\text{Bi}_2\text{Ti}_2\text{O}_7$ , respectively). Dashed line marks  $T_{\text{VF}}$  estimated in Ref. 32.

The observed  $\varepsilon'$  enhancement at  $T > T_{\text{VF}}$  is typical for many relaxor-like compounds in low electric fields. For example, (110)-oriented PMN crystals (see  $E = 3$  kV/cm and 5 kV/cm on Fig. 3(b) from Ref. 49) or  $(1-x)\text{PMN}-x\text{PbTiO}_3$ .<sup>50,51</sup> However, at  $T < T_{\text{VF}}$ , the FC and ZFC splitting is clearly seen which indicates nonergodic dielectric behavior typical for many glassy systems.<sup>52</sup>

These data, even in relatively weak electric fields, clearly demonstrate deviations of the  $\varepsilon'(T)$  curves of the  $\text{Bi}_2\text{Ti}_2\text{O}_7$  from the ergodic behavior characteristic of BZN and other bismuth-containing pyrochlores. However, further studies in higher electric fields, as well as in the IR and THz frequency ranges, are necessary to establish the nature of the low-temperature state in  $\text{Bi}_2\text{Ti}_2\text{O}_7$  single crystal.

#### 4. Conclusions

In this work, we carried out a comparative study of the dielectric properties in electric fields of BZN ceramics with

chemically disorder in both A and B cation sublattices and  $\text{Bi}_2\text{Ti}_2\text{O}_7$  single crystal with fully chemical ordered structure. Analysis of the BZN dielectric spectroscopy results shown significant deviation of the  $\varepsilon'$  and  $T_m$  from the literature data. Taking into account the nonstoichiometry inherent for BZN we assume that the composition of the samples under study is close to  $\text{Bi}_{1.5}\text{Zn}_{0.5}\text{Nb}_{1.5}\text{O}_{6.5}$  which is in agreement with previous study of the BZN thin films with different compositions.<sup>20</sup> We found that dielectric relaxation parameters ( $E_a$  and  $f_0$ ) of the studied BZN ceramics are practically the same as for the  $\text{Bi}_{1.5}\text{Zn}_{0.92}\text{Nb}_{1.5}\text{O}_{6.92}$  though ZnO deficiency leads to a decrease in the occupancy in the A and X' sublattices. Studies of dielectric properties in electric fields have shown fundamental differences between the BZN ceramics and  $\text{Bi}_2\text{Ti}_2\text{O}_7$  single crystal. In the case of the BZN ceramics, the electric field did not lead to change the temperature behavior of the dielectric permittivity confirming the linear dielectric properties and the ergodic state. But for  $\text{Bi}_2\text{Ti}_2\text{O}_7$  obtained FC and ZFC splitting, even in relatively weak electric fields, clearly demonstrate deviations of the  $\varepsilon'(T)$  curves from the ergodic behavior. Note also that the possible correlations between the bismuth atoms displacements at low temperatures were discussed earlier in the course of the crystal structure studies<sup>53,54</sup> and first-principle calculations.<sup>34,55</sup> In addition, our study in electric fields also showed qualitative analogy with some data on PMN crystals,<sup>49</sup> which relaxor behavior are believed to be largely associated with compositional (chemical) disorder and random quenched electric fields.<sup>56–59</sup> This study confirms the previously selected trend<sup>30,32</sup> for the separation of  $\text{Bi}_2\text{Ti}_2\text{O}_7$  from other bismuth-containing pyrochlores, as a candidate material for studying aspects of geometric frustration related with pyrochlore structure in nonmagnetic medium.

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