Structure and electroconductivity of nanostructured ceramics BiFeO₃

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Abstract. We present results of study of structure and electrical conductivity of the nanostructured ceramics BiFeO₃ measured for direct and alternating currents (from 1 kHz to 10 MHz) in the temperature range 25-500 °C. The power-law nature of the frequency dependence of the conductivity is discussed in the framework of the model of the correlated barrier jumps of charge carriers, presumably between two- and trivalent iron ions Fe²⁺ → Fe³⁺.

1. Introduction
Ceramics based on BiFeO₃ (BFO) were obtained by the method of spark plasma sintering (SPS) of a nanopowder synthesized by burning a precursor on the basis of aqueous solutions of Bi(NO₃)₃ and Fe(NO₃)₃ with the addition of glycine. The SPS method was chosen since BFO nanoparticles do not achieve to 62 nm (size of the antiferromagnetic cycloid) under crystallization in this process because of its short short duration and relatively low temperatures. This size of the antiferromagnetic cycloid is essential for the practical application of BFO multiferroic [1-3]. Relatively high values of electrical conductivity, which reduce the contribution of the ferroelectric phase to the linear magnetoelectric effect [1,2], are disadvantages of this ceramics. Some researchers relate the high conductivity of BFO to presence of extrinsic phases [4,5], other ones - to transport of the oxygen vacancies [6,7] or transformation of the iron ions Fe²⁺ → Fe³⁺ [8].

The structure and morphology of the nanostructured BFO ceramics were studied in a transmission electron microscope Titan 80-300 and the PANalytical Empyrean series 2 X-ray diffractometer. Active conductivity studies (G) were carried out using the LCR-78110G meter from Good Will Instrument Co. A silver paste was used to make electrodes for disk-shaped samples with a thickness of ~1 mm and a diameter of ~ 4 mm.

2. Results and discussion
The nanopowder used for sintering of the ceramics was synthesized by a new technology [9], which differs from the method given in [10], by the amount of glycine and nitric acid. The nanopowder consisted of BFO nanocrystals and amorphous phase. The amount of the former was decreased down to 6% or 4% after heat treatment at 600 °C for 0.5 hours. The X-ray diffraction pattern of the obtained ceramics (Figure 1) and particle sizes (50–60 nm) estimated using the Wolf-Scherer formula did not
differ significantly from the data for the heat-treated powder. The density of the BFO ceramic obtained by the SPS- method (~ 7.6 g/cm³) is close to the theoretical value.

Figure 2 illustrates the crystal structure and the morphology of the cleavage surface of BFO ceramics, which indicates a fairly high packing density of the grains. Note that extrusion of voids between particles onto the grain surface is observed under pressing. Defects in the form of pores are observed at the boundaries between the grains (see Figure 2a). Presence of nanoscale defects in the crystal structure of the BFO grains themselves was established by TEM method. These defects may be formed as a result of the transition from the agglomerate of nanoparticles (in the original powder) to the crystalline grain after pressing and sintering the ceramic. As seen in Figure 2(b), these defects represent the crystal lattice distortions extended from about atomic level to 50 nm and more.

![Figure 1. Diffractogram of nanostructured ceramics BFO.](image)

![Figure 2. The morphology of the chip surface (a) and the crystal structure of grain (b) for BFO ceramics.](image)

Temperature dependences of conductivity of the ceramic (Figure 3) in the temperature range 25-500 °C were investigated for direct $\sigma_{dc}$ and alternating $\sigma_{ac}$ currents in the frequency range 1 kHz–10 MHz. These dependences demonstrate two ranges separated by a temperature of about 350 °C, with different temperature coefficients of the conductivity.
Below 350 °C the $\sigma_{dc}$ and $\sigma_{ac}$ values practically coincide ($\sim 10^{-8} \Omega^{-1} \text{cm}^{-1}$) for frequencies $<100$ kHz. At higher frequencies, the conductivity is described by a power function. On the conductivity isotherms obtained in the range 1 kHz – 10 MHz (Figure 4) a frequency dispersion is observed above $\sim 350$ °C, which is amplified with frequency increase. Beginning from 1 MHz (Figures 3 and 4) the anomaly is noticeably manifested, i.e. maximum of $\sigma$ appears at some temperature $T^*$ exceeding 480 °C. It was assumed [11, 12] that the temperature dependence of the BFO conductivity is affected by an oxygen non-stoichiometry of the bismuth ferrite which The oxidation-reduction reaction leads to increase of number of both the Fe$^{3+}$ ions and lattice defects with temperature increase [12]:

$$\text{O} \leftrightarrow \frac{1}{2}\text{O}_2 + V_{o}^\circ + 2e^-; \quad \text{Fe}^{3+} + e^- \leftrightarrow \text{Fe}^{2+} \quad (1)$$

Formation of the oxygen vacancies causes appearance of free electrons, so the BFO ceramics may be considered as $n$-type semiconductor. Electron hopping occurs between Fe$^{3+} \rightarrow$ Fe$^{2+}$ ions located in the nodes of the octahedra of the BFO crystal lattice.

**Figure 3.** Temperature dependences of conductivity $\sigma_{dc}$ (inset) and $\sigma_{ac}$.

**Figure 4.** Frequency dependence of the conductivity $\sigma_{ac}$ of the BFO ceramic.
Both concentration and mobility of the oxygen vacancies increase when temperature increases above 350 °C. Closeness of this temperature to the Neel temperature (370 °C,) can be explained by increase of the oxygen vacancies concentration due to increase of volume under transition from an antiferromagnetic (ordered) to a paramagnetic (disordered) state. Frequency dependence of the conductivity of our ceramics, as well as in [13], is described by the double power law:

\[ \sigma(\omega) = \sigma(0) + A\omega^{s1} + B\omega^{s2}, \]

where \( \sigma(0) \) is the frequency-independent conductivity which can be taken as \( \sigma_{dc} \), \( \omega = 2\pi\nu \) is the circular frequency, \( A, B, s1 \) and \( s2 \) are the coefficients depending on temperature and frequency, and the \( B\omega^{s2} \) component appears at frequencies above 1 MHz. The power-law dependence \( \sigma(\omega) \) indicates the hopping nature of the conductivity in BFO [14]. According to our data, frequency indices \( s1 \) and \( s2 \) decrease with increasing temperature. Moreover, the \( s2 \) sign undergoes an inversion above 480 °C. Such a behavior of the \( s1 \) and \( s2 \) indices corresponds to the correlated barrier hopping in the model for ac conductivity [14]. Estimate of the conductivity activation energy \( E_A \) revealed that in the temperature range below 150 °C \( E_A \) decreases from 0.46 eV to 0.042 eV with frequency increase from 1 kHz to 10 MHz (Figure 5). Probably, raising the applied field frequency promotes increase of attempt frequency of charge carriers hopping between localized states.

This means that a charge transfer over short distances at higher frequencies costs a less energy than the transfer over long distances at low frequencies. Following [15], the complex dependence \( \ln\sigma = f(1/T) \) can be separated into three ranges (Figure 5). Above 350 °C (range III), the frequency dependence is weak, and \( E_A \) is relatively high. For example, \( E_A \) is of the order of 0.8 eV for frequencies above 1 MHz in the range 350-480 °C. \( E_A \) decreases from ~0.7 eV to ~0.11 eV in the interval below 350 °C (range II). The activation energy decrease should rise number of carriers overcoming the barrier and, as a sequence, should lead to increase of \( \sigma_{ac} \) with frequency. At a fixed frequency, the activation energy is higher for a higher temperature. Calculations according to [16] showed that the minimum hop length increases with frequency at low temperatures while with increasing temperature it tends to zero. Such a behavior agrees with data in [16].

![Figure 5. Temperature dependence of the conductivity in the coordinates lnσ = f(10^3/T)](image)

We conclude that several competing mechanisms, depending on applied field frequency, contribute into conductivity of the BFO nanoceramics when temperature raises. In the range of medium and high frequencies (> 100 kHz), the hopping mechanism with a short jump length is dominant. Both successful (forward) and unsuccessful (backward) jumps affect hopping conductivity with short-range
hopping in the range of intermediate frequencies from 100 kHz to 1 MHz (the $A\omega^{\alpha}$ component). Increase of the successful jumps number strengthens the conductivity dispersion in this frequency range. Difference in conductivity of grains and boundaries should be taken into account in this case. With frequency increase, the contribution from in-grain conductivity becomes dominant due to the charge transfer between Fe$^{2+}$ and Fe$^{3+}$ ions [17]. The contribution from conductivity along the grain boundaries, where oxygen vacancies are located, is essential at relatively low frequencies.

The anomalous behavior of the high-frequency conductivity in the temperature range above $T^*$ can be explained if we take into account the relation between the hopping frequency $\omega_h$ and the applied alternating field frequency $\omega$. The $\sigma_{ac}$ value (Figure 4) increases with both temperature and $\omega$ passing through a maximum at frequencies higher than 1-2 MHz. As follows from Figure 4, $\omega_h$ is shifted towards low temperatures with $\omega$ increase, while this behavior contradicts to published data [18]. At high frequencies $\omega > \omega_h$, delay of the charge carriers hoppings relatively to the electric field change leads to the appearance of dielectric losses $\tan \delta$, which occurs at the onset of the conductivity decrease. As seen in inset of Figure 6, the $\sigma_{ac}$ relaxation is observed at $\omega > 100$ kHz and at frequencies higher than 1 MHz it is sharply enhanced. In the frequency range 1–10 MHz, the temperature corresponding to $\sigma_{ac}$ maximum is shifted on about $25^\circ C$. This effect is more pronounced for the $ac$ losses, shift of the $\tan \delta$ maximum with frequency reaches $45^\circ C$.

![Figure 6](image-url)  

**Figure 6.** Temperature dependence of the dielectric loss $\tan \delta$ at different frequencies. Inset: frequency dependence of the temperature at which the maxima of $\sigma_{ac}$ (open symbols) and $\tan \delta$ (closed symbols) are observed.

The above results indicate that the short relaxation time of charge carriers is the main factor which determines frequency dependence of the conductivity ($B\omega^{\alpha}$). The gradual “shutdown” of the hopping mechanism of the charge redistribution between Fe$^{2+}$ ions to Fe$^{3+}$, along with the transport of oxygen vacancies, lead to a decrease in the electrical conductivity of BFO ceramics with frequency observed in the studied frequency range.

3. Conclusion

At low frequencies and temperatures, the conductivity of the BiFeO$_3$ ceramics is almost frequency independent. Above $\sim 350^\circ C$ it rises with frequency following to a power function, and the conductivity frequency dispersion strengthens with $\omega$. For $\omega > 1$ MHz, $\sigma_{ac}(\omega)$ passes a maximum at a some temperature $T^*$. At a fixed temperature the conductivity activation energy decreases with frequency. Such a behavior of $\sigma$ results from competition of various conduction mechanisms. Above
100 kHz, the conductivity behavior corresponds to the model of correlated barrier jumps of charge carriers between Fe$^{2+}$ and Fe$^{3+}$ ions.

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