



Dielectric investigations of BiFeO₃ ceramics

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Abstract

In this paper we present the results from the investigation of the dielectric permittivity of BiFeO₃ ceramics, prepared by mechanochemical synthesis method in a broad frequency and temperature range. The dielectric permittivity is mainly caused by high conductivity, which is suppressed in the frequencies above 1 MHz. The investigated ceramics showed conductivity activation energy $E/k = 11280 \pm 12$ K, and $\sigma_0 = 54161 \pm 800$ S. The plots of M^ revealed conductivity mechanism with $\tau_0 = 1.12 \cdot 10^{-13}$ s, and $E/k = 9245$ K.*

Keywords: dielectric spectroscopy, multiferroics, activation energy

I. Introduction

The magnetoelectric multiferroic materials have drawn a significant amount of interest during past few years, as the coexistence of ferroelectric and magnetic ordering opens the way to a field of totally new applications, such as multistate memories. Bismuth ferrite [1] (BiFeO₃, or BFO) is currently the most intensively investigated multiferroic material due to its huge advantages: simple chemical formula, high Curie temperature (1083 K) [2] and high Neel temperature (625 K) [3,4].

Reviews of the general study of magnetoelectricity appeared by Schmid in 1994 [5] and more recently by Fiebig [6] and by Eerenstein et al. [7]. Current interest in bismuth ferrite was stimulated primarily by paper from Ramesh's group in 2003 [8], which showed that it had unexpectedly large remnant polarization P_r , fifteen times larger than in single crystals, together with very large ferromagnetism of 1.0 Bohr magneton per unit cell. Ironically, both of these claims proved premature. Thus, better single crystals grown in France in 2006-7 had the same polarization as the films, suggesting that the large polarization is intrinsic and not due to epitaxial strain enhancement [9–13]; and the intrinsic magneti-

zation of thin films is now known to be near zero [8,14], ca. 0.02 magnetons/cell, rather than 1.0.

However, there are not many published papers concerning the dielectric spectroscopy of this material. Due to its high conductivity, the real part of the dielectric permittivity can be accurately measured only at high frequencies. The aim of this paper is to measure the dielectric permittivity of BFO and extract the real conductivity of the ceramics.

II. Experimental

The BiFeO₃ nanopowders were prepared by mechanically triggered room temperature synthesis from commercially available oxides Bi₂O₃ and Fe₂O₃ (99% purity from Aldrich) in a SPEX 8000 Mixer Mill. After 120 h of high energy milling of the oxide powders in stoichiometric ratio only the bismuth ferrite powder has been obtained, which was confirmed by X-ray diffraction. This powder was hot-pressed in order to obtain dense ceramics. The more detailed information about preparation of BiFeO₃ ceramics may be found in paper by Szafraniak [15]. The complex dielectric permittivity $\epsilon^* = \epsilon' - i\epsilon''$ was measured by a capacitance bridge HP4284A in the frequency range 20 Hz – 1 MHz and temperature range 300–900 K (Fig. 1). Typical dimensions of samples were ≈ 50 mm² area and ≈ 1 mm thickness.

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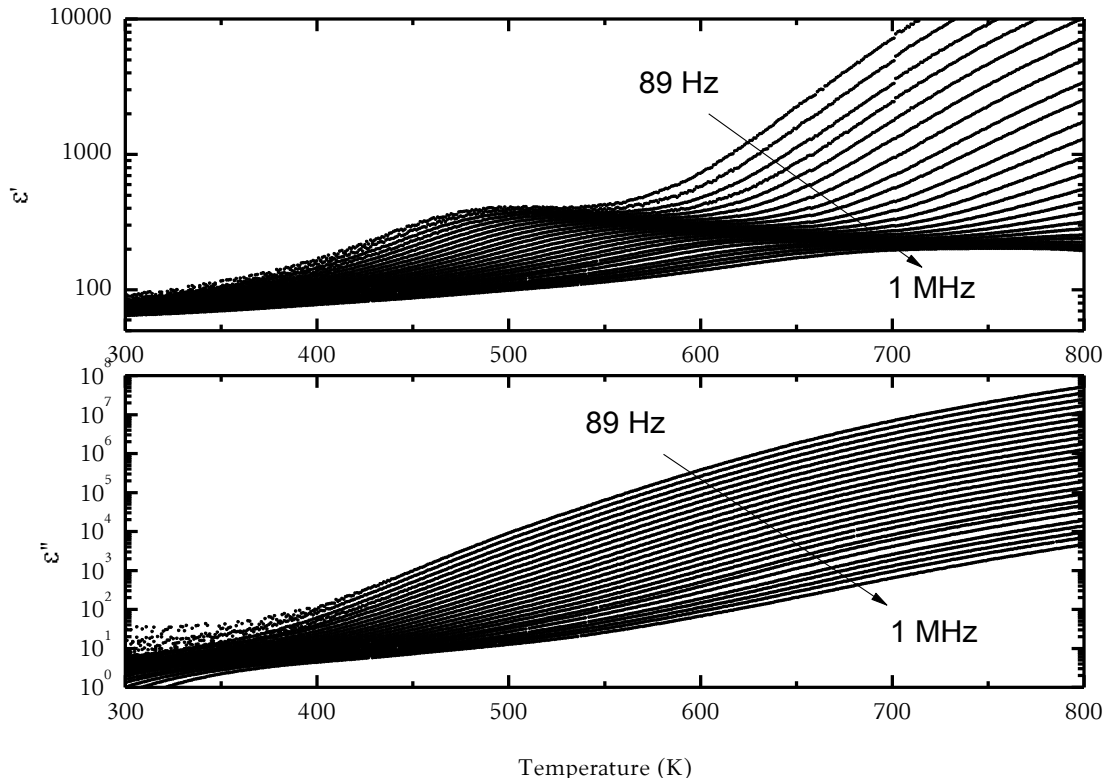


Figure 1. Spectra of real and imaginary parts of dielectric constant of BFO

III. Results and discussion

As bismuth ferrite is susceptible to have parasitic phases, one can expect the anomalies to be related to parasitic phases and defects agglomerated at the grain boundary. Mechanochemical synthesis usually produces oxygen vacancies in material, which lead to valence fluctuation of Fe ions from 3+ to 2+ states, resulting in high conductivity in samples.

Conductivity can be described as a sum of the frequency-independent part σ_{DC} and frequency-dependent part $A \cdot \omega^S$:

$$\sigma = \sigma_{DC} + A\omega^S,$$

where A and S are parameters. σ_{DC} , in turn, depend exponentially over temperature:

$$\sigma_{DC} = \sigma_0 e^{-\frac{E}{kT}}.$$

where E is the activation energy of the conductance mechanism and σ_0 is conductivity at infinitely high temperature. Having conductivity plotted over inverse temperature, one can easily calculate σ_{DC} dependency from temperature and find σ_0 and E (Fig. 2). The investigated ceramics showed activation energy $E/k = 11280 \pm 12$ K, and $\sigma_0 = 54161 \pm 800$ S.

Another formalism, such as electric modulus [16], have been employed to study the ion dynamics in solids

$$M^*(\omega) = \frac{1}{\varepsilon^*(\omega)} = \frac{\varepsilon' - j\varepsilon''}{|\varepsilon|^2} = M' + jM'' = M_\infty \left(1 - \int_0^\infty e^{-j\omega t} \left(-\frac{d\varphi}{dt} \right) dt \right).$$

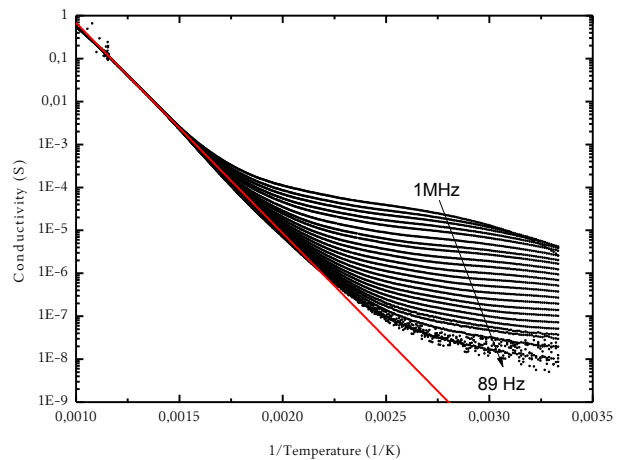


Figure 2. Conductivity of BFO over inverse temperature (line – fit of σ_{DC})

under ac electric field. However, there is a debate on which of these formalisms provides better insights into the phenomena of ion dynamics [17]. Both formalisms are compared in this paper. The complex electric modulus spectra represent a measure of distribution of ion energies or configurations in the disordered structure and also describe the electrical relaxation of ionic solids as a microscopic property of these materials. Electric modulus M^* can easily be calculated from complex dielectric permittivity:

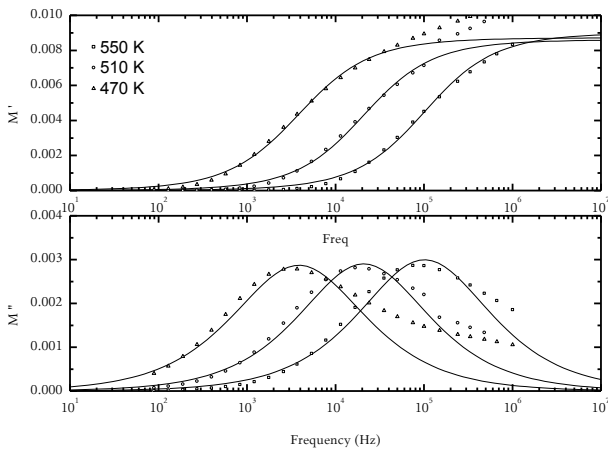


Figure 3. Electrical modulus of BFO at different temperatures

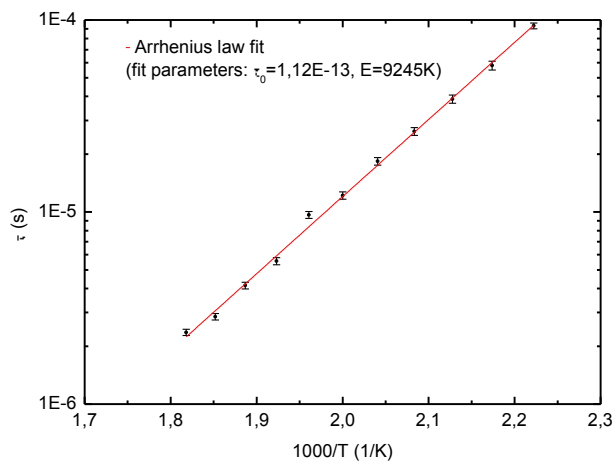


Figure 4. The mean relaxation time of the electrical modulus temperature dependence

The function $\varphi(t)$ gives the time evolution of the electric field within the materials. Obtained frequency dependent $M^*(\nu)$ are presented in Fig. 3. The real modulus M' shows dispersion as the frequency increase and tends to saturate at M_∞ at higher frequencies. The imaginary modulus M'' exhibits a maximum M''_{max} centered at dispersion region of M' . The maxima of the electrical modulus separate the regions where the charge carrier moves in a single well potential with charge transport between different wells. In this case we are getting the different activation energy and attempt relaxation time: $E/k = 9245$ K and $\tau_0 = 1.12 \cdot 10^{-13}$ s (Fig. 4).

IV. Conclusions

Our dielectric investigations showed high conductivity of BFO. Knowing the properties of this material, it is possible to develop a MERAM (Magnetoelectric Random Access Memory) based on BiFeO_3 . A scheme of such a device has been proposed by Bibes and Barthélémy [18], but it is vitally important to decrease the conductivity of BFO.

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