

DETERMINATION OF THE MAGNETOELECTRIC COUPLING COEFFICIENT FROM TEMPERATURE DEPENDENCES OF THE DIELECTRIC PERMITTIVITY FOR MULTIFERROIC CERAMICS $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$

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Received January 22, 2013

In the multiferroic materials, the dielectric and magnetic properties are closely correlated through the coupling interaction between the ferroelectric and magnetic order. We attempted to determine the magnetoelectric coupling coefficient from the temperature dependences of the dielectric permittivity for multiferroic $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$. Multiferroic ceramics $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ belong to materials of the Aurivillius-type structure. Multiferroic ceramics $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ was synthesized via sintering the Bi_2O_3 and Fe_2O_3 mixture and TiO_2 oxides. The precursor material was ground in a high-energy attritorial mill for 5 hours. This material was obtained by a solid-state reaction process at $T = 1313$ K. We investigated the temperature dependences of the dielectric permittivity for the different frequencies. From the dielectric measurements, we determined the temperature of phase transition of the ferroelectric-to-paraelectric type at about 1013 K. Based on dielectric measurements and theoretical considerations, the values of the magnetoelectric coupling coefficient were specified.

DOI: 10.7868/S0044451013110114

1. INTRODUCTION

Multiferroics are multifunctional materials, because they possess simultaneously several so-called ferroic orders such as ferromagnetism, ferroelectricity, and/or ferroelasticity.

The origin and understanding of the coupling phenomena between different physical properties within one material is a central subject of solid state science. Much theoretical and experimental attention in this field is currently focused on the magnetoelectric coupling coefficient [1–3].

Multiferroic ceramics $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ belong to materials of the Aurivillius-type structure. This material is characterized by a high phase transition temperature (1023 K) and interesting dielectric properties, and can therefore be used in constructing different new-generation electronic devices. This type of ceramics is promising owing to the possibility of its use as different types of memory elements [4].

Layered perovskite-like structure bismuth oxides (BLPO) are composed of regular bismuth layers $(\text{Bi}_2\text{O}_2)^{2+}$ interlaced with perovskite packs.

Structures of this type were first discovered by Aurivillius in 1949 [5, 6], and in 1969 Subbaro [7] described them with the general formula

$$\text{A}_{m-1}\text{Bi}_2\text{O}_{3m+3}, \quad (1)$$

where big cations A are Ba, Sr, Ca, Bi, and Pb and B cations are small cations of transition metals Ti, Nb, Ta, Mo, W, Fe, and Mn, and m is the number of perovskite layers along the axis from the perovskite pack ($m = 1, 2, 3, 4, 5, 8$). This means that the layers built of regular octahedron oxides of the m thickness interlace with bismuth-oxide layers. BLPO-type structure bismuth exists only in a trivalent Bi^{3+} form. The Fe^{3+} cation can be found in tetrahedral (bismuth-oxide) layers and in position A of the perovskite layers [8]. Compounds of this type can be described by the general formula

$$\text{Bi}_{m-1}\text{Bi}_2\text{B}_m\text{O}_{3m+3}. \quad (2)$$

In BLPO structures, the positions of atoms A and B

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can be filled by the atoms of one, two or more chemical elements, however, in accordance with the dependence

$$\sum X_A V_A + X_B V_B = 6m, \quad (3)$$

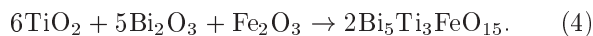
where X is the ion concentration in position A or B and V is the valence of individual ions.

From the technological standpoint, it is important to obtain ceramics of high density and high purity, which should have a direct effect on the physical properties of ceramics, whereas engineering requires ceramics production technology to be relatively simple. In examining and choosing ceramics production methods, the economic aspect must also be taken into account. Therefore, it is very important that the preparation of a good quality ceramics material should be relatively cheap [6, 7].

In this paper, we present the results of measurements of the dielectric permittivity depending on the temperature and theoretical investigations of the magnetoelectric coupling in multiferroic Aurivillius-type ceramics. We apply theoretical considerations to the experimental results that were obtained for the multiferroic ceramics $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$, to determine the magnetoelectric coupling coefficient.

2. THE DIELECTRIC STUDY OF MULTIFERROIC $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$

Simple oxide powders TiO_2 , Bi_2O_3 , and Fe_2O_3 were used in the preparation of mixtures for the synthesis and sintering. Multiferroic ceramics $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ were obtained as a result of the synthesis reaction of the above-mentioned oxide, in accordance with the reaction



The course of the synthesis of complex oxides using a mixture of simple oxides as precursor materials depends mainly on the dispersion degree of the charge, its homogeneity, temperature, and time of sintering. For the purpose of the $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ synthesis, the process of high-energy ball-milling in the vibrating mill SPEX 8000 CertiPrep Mixer/Mill was used. The milling time in the argon protective atmosphere was 5 hours. The synthesis reaction was conducted at $T = 1072$ K for 5 hours by the method of free sintering. The synthesized powder was subjected to pressing giving discs. The second stage of the technology was the free sintering process conducted twice for 5 hours at $T = 1313$ K to obtain the desired material.

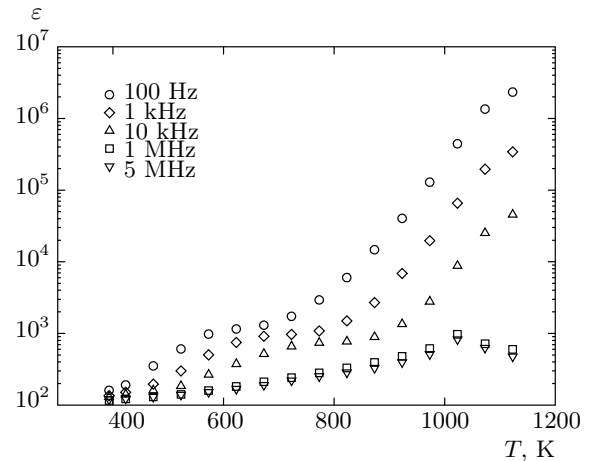


Fig. 1. The electric permittivity as a function of temperature (for different frequencies)

After that, in order to obtain parallelepiped samples, the material was ground off and polished. The pellets with a diameter of 10 mm and a thickness of 1 mm prepared in this way underwent 15 min stress relief annealing in order to remove the stresses that had appeared during grinding. Finally, electrodes were deposited on the prepared samples.

The temperature-dependent dielectric response of multiferroic $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ was measured from $T = 390$ K to $T = 1120$ K in the frequency range from 100 Hz to 5 MHz.

Figure 1 presents the dependence of the dielectric permittivity ϵ as a function of temperature for multiferroic ceramics $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$.

For the lower frequencies (0.1, 1, 10 kHz), the dielectric constant values are very high and increase with increasing the temperature. For the higher frequencies (1, 5 MHz), the dielectric constant values are lower and increase with increasing the temperature to the certain value (which is usually referred to as the transition temperature), and thereafter ϵ decreases with increasing the temperature. The maximum of the dielectric constant is observed at about $T = 1013$ K (Fig. 1). This dielectric anomaly suggests that there is a probability of phase transition of the ferroelectric-to-paraelectric type at $T = 1013$ K.

We observed that the values of dielectric constant decrease as the frequency increases. This indicates the presence of all types of polarizations (ionic, dipole, atomic, electronic, etc.) in the material at lower frequencies. The mechanism of dielectric polarization is probably similar to that of conduction. We supposed that the electron exchange interaction results in a local

displacement of the electrons in the direction of an electric field that determines the polarization. The variation of the dielectric constant with frequency was experimentally affirmed in this ceramics [9].

3. THE THEORETICAL MODEL AND ITS ANALYSIS

The complication of the ferroelectric ferromagnetic system lies in the coupling interaction between the electric and magnetic properties.

For the theoretical description of the temperature dependence of the dielectric constant, the multiferroic system was split into two separated subsystems, the magnetic subsystem and the ferroelectric subsystem.

The two order parameters are imposed on each subsystem, S_i and u_i , with S_i representing the Heisenberg spin for magnetic interaction and u_i is electrical displacement for an electrical polar. The displacement u_i is proportional to the local spontaneous polarization p perpendicular to the electronic spin S_i . In addition, we also take the coupling between the ferroelectric and magnetic subsystems into account.

Following Refs. [10] and [11], the Hamiltonian can be written in three parts as

$$H = H^m + H^e + H^{me}, \quad (5)$$

where H^m is the Hamiltonian of the magnetic subsystem, H^e is the Hamiltonian of the ferroelectric subsystem, and H^{me} is the coupling interaction between the two subsystems.

The Hamiltonian of the magnetic subsystem H^m comprises four origins, namely the coupling of the nearest neighbors and the next-to-nearest neighbors, the magnetic static energy, and the single-ion anisotropy energy [12]. This Hamiltonian is given by

$$H^m = - \sum_{\langle i,j \rangle} J_1 S_i S_j - \sum_{[i,k]} J_2 S_i S_k - \sum_i h S_i - D \sum_i S_i^2, \quad (6)$$

where J_1 and J_2 are the nearest and next-to-nearest exchange integrals, h is the external magnetic field along the spin-ordered direction, D is the uniaxial single-ion anisotropy constant, and S_i, S_j, S_k are the Ising spins at sites i, j, k .

The Hamiltonian of the ferroelectric subsystem H^e is composed of three parts. The first part is the kinetic and potential energy of the particle, the second is the nearest-neighbor electric interaction, and the third is

the electric static energy [13]. This Hamiltonian has the form

$$H^e = \sum_i \left(\frac{p_i^2}{2m} - \frac{a}{2} u_i^2 + \frac{b}{4} u_i^4 \right) - \sum_{\langle i,j \rangle} U u_i u_j - \sum_i E u_i, \quad (7)$$

where m is the mass, p_i is the particle momentum, u_i is the electric displacement at site i , a and b represent the double-well potential parameters, U is the polarization interaction coupling parameter, and E is the external electric field, which is parallel to the polarization direction.

The phase transition in ferroelectromagnetics was investigated in Refs. [14, 15]. The authors proposed a possible coupling form to describe the intrinsic magnetoelectric coupling and gave a detailed analysis of the magnetoelectric effect. Therefore, for the coupling interaction between these two subsystems, we introduce the coupling mechanism proposed in Refs. [14, 15] and apply it to the ferroelectric ferromagnets by making simple change of the form

$$H^{me} = \sum_{k \langle i,j \rangle} g u_k^2 S_i S_j, \quad (8)$$

where g is the magnetoelectric coupling coefficient indicating the intensity of the magnetoelectric coupling, u_k is the electric displacement at site k , and S_i, S_j is the spin-pair correlation that directly affects the electric displacement u_k .

To investigate the dielectric properties of multiferroic materials, the Hamiltonian should be expressed in the mean-field approximation, in the form

$$H = H^E + A_1, \quad H^E = H^e + H^{me}, \quad (9)$$

$$H^E = \sum_i \left(\frac{p_i^2}{2m} - \frac{\tilde{a}}{2} u_i^2 + \frac{b}{4} u_i^4 \right) - \tilde{E} \sum_i u_i, \quad (10)$$

$$\tilde{E} = E + U z_1 p, \quad \tilde{a} = a - 2 z_2 g \langle S_i S_j \rangle, \quad (11)$$

where A_1 is a constant that represents the contribution of the magnetic part H^m , \tilde{E} is the effective mean field acting on the ferroelectric subsystem, \tilde{a} is the amended potential-well parameter, u_i is proportional to the local spontaneous polarization p , i. e., $p = \langle u_i \rangle$, $\langle S_i S_j \rangle$ is the average value of the spin-spin correlation, z_1 is the nearest-neighbor number of ferroelectric particles for a given ferroelectric particle, and z_2 is the number of the spin-pair correlations that directly influence a given ferroelectric particle.

Equations for the polarization and the dielectric constant can be obtained from the soft-mode theory, and they are expressed in the forms

$$(-\tilde{a} + 3b\sigma + bp^2)p = z_1Up + E, \quad (12)$$

$$\sigma(-\tilde{a} + 3b(\sigma + p^2)) = k_B T, \quad (13)$$

$$\varepsilon(h, T) = \frac{\partial p}{\partial E} = \frac{1}{-\tilde{a} + 3b(\sigma + p^2) - z_1U}, \quad (14)$$

where σ is the fluctuation of the electric displacement, and we can write $\langle u_i^2 \rangle = \langle u_i \rangle^2 + \sigma$.

Due to the presence of the magnetoelectric coupling, both the polarization p and the dielectric constant ε are functions of the spin-pair correlation $\langle S_i S_j \rangle$. If we consider only the linear term of $\langle S_i S_j \rangle$, then Eq. (14) can be written in the form

$$\varepsilon(h, T) = \varepsilon_0 (1 + \alpha \langle S_i S_j \rangle), \quad (15)$$

where $\varepsilon_0 = (-a + 3b(\sigma_0 + p_0^2) - z_1U)^{-1}$ is the dielectric constant in the absence of the magnetoelectric coupling and $\alpha = 2z_2g\varepsilon_0$ is taken as the normalized magnetoelectric coupling factor.

4. RESULTS AND DISCUSSION

The dielectric properties of the material are characterized with the dielectric constants ε . The measurements of ε were made for several different frequencies. In the low-frequency region, the dielectric constant values are very high and increase with increasing the temperature. In the high-frequency region, the maximum can be observed in the temperature dependence of the dielectric constant for 1013 K (Fig. 1). This maximum is related to the ferroelectric–paraelectric phase transition.

Figure 1 indicates that the dielectric constant values decrease with increasing the frequency. This may be attributed to the dipoles resulting from changes in valence states of cations and space charge polarization. At higher frequencies, the dielectric constant remains independent of the frequency because the electric dipoles cannot follow the fast variation of the alternating applied electric field and the friction between them increases accordingly.

Using Eq. (15) and the experimental results, we attempted to determine the magnetoelectric coupling coefficient g .

The measurement results shown in Fig. 1 were approximated by the above dependence. The calculation results are shown in the Fig. 2a and 2b. Solid lines show the results of the approximation.

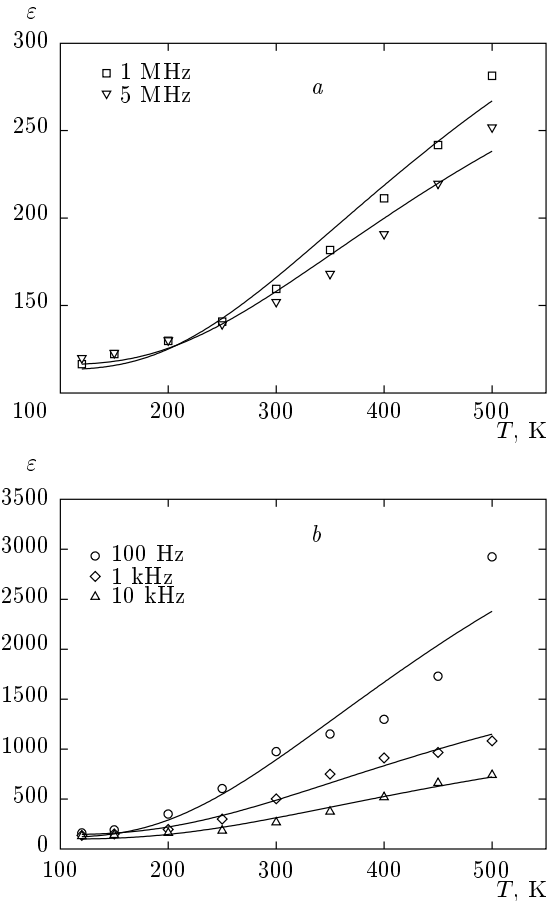


Fig. 2. The electric permittivity as a function of temperature: solid lines are fitting lines: *a* — high frequency, *b* — low frequency

The results of calculations of the magnetoelectric coupling coefficient are shown in Table.

The calculations show that the value of the magnetoelectric coupling coefficient increases with increasing the frequency, from $g = 0.021$ for $f = 100$ Hz to $g = 0.194$ for $f = 5$ MHz. The magnetoelectric coupling coefficient shows the dispersion, which results from dispersion of the dielectric permittivity [9]. This is due to the presence of ionic, dipole, atomic, and electronic polarizations, which are frequency-dependent.

5. CONCLUSION

In this paper, we have investigated the dielectric permittivity and the magnetoelectric coupling in multiferroic ceramics.

We attempted to determine the magnetoelectric coupling coefficient from the temperature dependences

Table. Values of the magnetoelectric coupling coefficient

Frequency f	100 Hz	1 kHz	10 kHz	1 MHz	5 MHz
Magnetoelectric coupling coefficient g	0.021	0.044	0.070	0.179	0.194

of the dielectric permittivity for multiferroic ceramics $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$.

Based on dielectric permittivity measurements and theoretical considerations, the values of the magnetoelectric coupling coefficient were specified.

This work was realized in the framework of research project No. N R15 0005 04 financed by the Polish Ministry of Science and Higher Education.

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