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Magnetoelectric properties of multiferroic Aurivillius type $Bi_7Fe_3Ti_3O_{21}$ ceramics

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Abstract

Multiferroic $Bi_7Fe_3Ti_3O_{21}$ ceramic materials having six perovskite-like layers were prepared by solid state reaction from simple oxides and sintered at 1263 K. The microstructure and magnetoelectric properties were investigated. Based on dielectric measurements, the value of magnetoelectric coupling coefficient was figured. The magnetization as a function of temperature and magnetic field at selected temperatures was examined. Additionally, the hysteresis loop at 2 K was measured. The molar concentration of magnetic ions Fe^{3+} in the multiferroic $Bi_7Fe_3Ti_3O_{21}$ compound was also determined.

Keywords: *$Bi_7Fe_3Ti_3O_{21}$, magnetic properties, magnetoelectric coupling, multiferroics*

I. Introduction

Nowadays, technological development chases scientists to find advanced materials, whose application will keep up with the civilization's progress. Smart materials, where multiferroics belong, are one of them. The distinct feature of multiferroic materials is that at least two of primary ferroic order parameters exist simultaneously [1]. Due to their properties, they are widely used, among others in spintronic and magnetoelectric devices, such as electrically controllable microwave elements, magnetic-field sensors [2], electrically controlled microwave devices, ferromagnetic resonance devices [3,4] or magnetic tunnel junction (MTJ) device used in magnetic random access memories (MRAM) [5,6]. Very important class of multiferroic materials is characterized by the Aurivillius phase structure [7] with general formula $Bi_{m+1}Fe_{m-3}Ti_3O_{3m+3}$. These compounds have a layered type structure [8,9] where perovskite-like $(A_{m+1}B_mO_{3m+1})^{2-}$ blocks are contained between two fluorite-like layers $(Bi_2O_2)^{2+}$ [10]. The A position is mostly taken by bigger cations with 12-fold coordination like e.g. Ba, Sr, Ca or Bi, while the 6-fold coordination site B is occupied by smaller ions, e.g. Fe, Ti, Ta [11,12]. The m is the number of perovskite-like layers in a structural packet (integer or fraction) [13].

The aim of this work was to obtain and study the six perovskite-like layers multiferroic $Bi_7Fe_3Ti_3O_{21}$ ceramic materials. The microstructure, electric and magnetic properties were investigated and magnetoelectric coupling coefficient was determined on the basis of dielectric measurements.

II. Experimental method

The $Bi_7Fe_3Ti_3O_{21}$ ceramics were prepared by solid-state reaction with conventional mixed oxides method. Stoichiometric amounts of bismuth oxide Bi_2O_3 (Aldrich 99.9%), titanium dioxide TiO_2 (Poch 99.9%) and iron oxide Fe_2O_3 (Sigma-Aldrich 99%) were weighed and preliminary mixed in mortar for 45 min. The initial mixture was ground in the planetary mill (250 r/min) for 24 h (with ethanol and YSZ balls). The next step was to re-mix the mixture after drying in the mortar for 30 min. The synthesis reaction was car-

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ried out in accordance with the following equation:

$$3.5Bi_2O_3 + 1.5Fe_2O_3 + 3\,TiO_2 \longrightarrow Bi_7Fe_3Ti_3O_{21} \quad (1)$$

The synthesis process took place at the temperature T = 1123 K for t = 4 h (5 °C/min) in muffle furnace and the purpose of it was to form the Aurivillius phase. After drying the synthesized powder was ground in a mortar for 30 min and mixed in the planetary mill under the same conditions like previously. After the next remilling in the mortar the powder was pressed (200 MPa) into pellets (∅= 10 mm, H = 1 mm). To obtain a ceramic material with a well-formed microstructure the pellet samples were sintered in closed corundum crucibles at T = 1263 K for t = 4 h (5 °C/min).

X-ray powder-diffraction (XRD) analysis was conducted to study the crystal structure and carried out at room temperature (RT) on a diffractometer Phillips X'Pert Pro using Cu-Kα radiation. The data were collected in the 2θ range from 10° to 80° in steps of 0.02°.

The microstructure was examined by scanning electron microscope JEOL JSM-7100F TTL LV with an energy dispersion spectrometer. The qualitative and quantitative analysis of the chemical composition was carried out by using the X-ray microanalysis method.

For electric measurements the samples were coated by platinum electrodes. To recombine the part of frozen defects formed during sintering process the virgin samples were rejuvenated by thermal treatment at T = 723 K prior to the measurements. The Agilent E4980A impedance analyser was used for dielectric measurements in the frequency range from 0.1 to 1000 kHz at the temperature range from 293 to 723 K.

In addition to the magnetoelectric effect study, the measurements of magnetization dependence as a function of magnetic field and temperature were carried out using the SQUID magnetometer (Quantum Design MPMS XL7). The magnetization was measured at T = 2, 100, 200 and 300 K in the applied magnetic field $\mu_0 \cdot H$ up to 7 T. The hysteresis loop was examined at 2 K at the magnetic field between −7 and +7 T. The magnetization as a function of temperature was determined in field cooling (FC) and zero field cooling (ZFC) modes at the applied magnetic field of $\mu_0 \cdot H = 0.1$ T.

III. Results and discussion

XRD analysis of the Aurivillius type ceramics (Fig. 1) confirmed that the $Bi_7Fe_3Ti_3O_{21}$ material shows face-centered orthorhombic structure. All line indexes connected with the Aurivillius structure were assigned. The lattice parameters obtained on the basis of X-ray pattern are: a = 5.4926 ± 0.0030 Å, b = 5.5401 ± 0.0030 Å and c = 57.7243 ± 0.0222 Å.

Scanning electron micrographs of the fracture of the $Bi_7Fe_3Ti_3O_{21}$ ceramics were shown in Fig. 2. The microstructure consists of plate-shaped grains with mostly sharp corners and varying size (inset of Fig. 2). The anisotropy of the plates is characteristic for the Aurivillius phases [14]. A lot of small grains can be noticed. The Archimedes method with distilled water was used to determine the relative density of ceramics in question and found the ceramics density to be equal to 6865 kg/m^3.

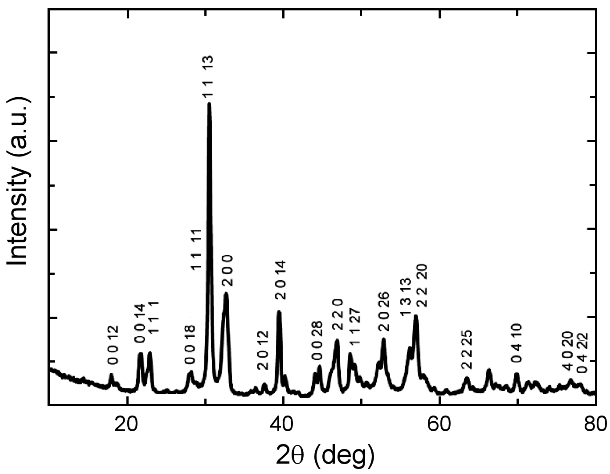

Figure 1. XRD spectrum for $Bi_7Fe_3Ti_3O_{21}$ ceramics

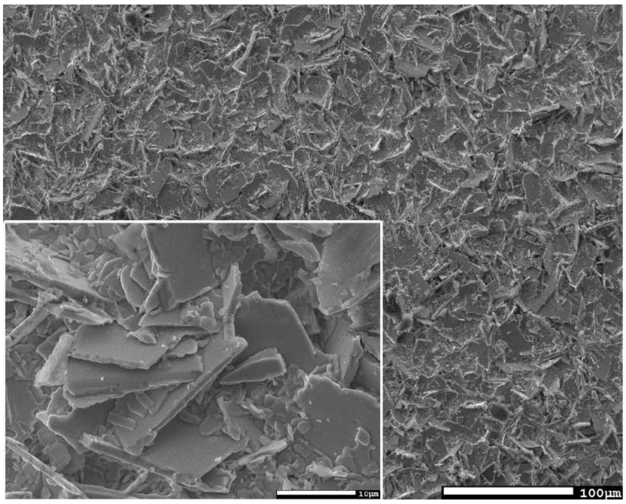

Figure 2. SEM images of $Bi_7Fe_3Ti_3O_{21}$ ceramics (magnification 250 (inset 2500))

Figure 3 presents the qualitative analysis of the chemical composition of the material. The result clearly indicates the chemical homogeneity of the sample and lack of foreign admixtures and impurities. The quantitative chemical analysis (Table 1) was aimed at determining the degree of compliance of the actual content of elements with theoretical stoichiometry. The differences between the theoretical and experimental percentage of constituting cations of $Bi_7Fe_3Ti_3O_{21}$ ceramics are in the range of measurement uncertainty of the X-ray microanalysis method. The results clearly indicate high compliance of the chemical composition of the obtained ceramics with the theoretical stoichiometric composition.

The temperature dependencies of the dielectric constant $\varepsilon'(T)$ are shown in Fig. 4. The value of dielectric constant increases with increasing temperature. The value of the maximum of the dielectric constant ε'

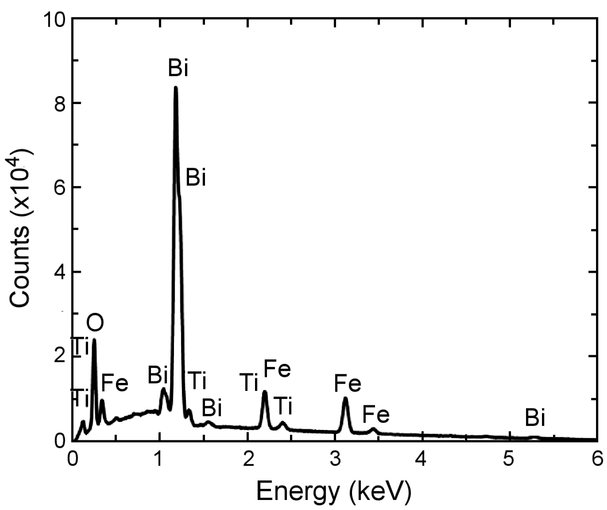

Figure 3. The EDS spectrum of $Bi_7Fe_3Ti_3O_{21}$ ceramics

Table 1. Theoretical and experimental percentage of constituting cations of $Bi_7Fe_3Ti_3O_{21}$ ceramics

Element	Theoretical [%]	Experimental [%]
Bi	69.33	69.98
Fe	7.94	9.95
Ti	6.81	6.57
O	15.92	13.50

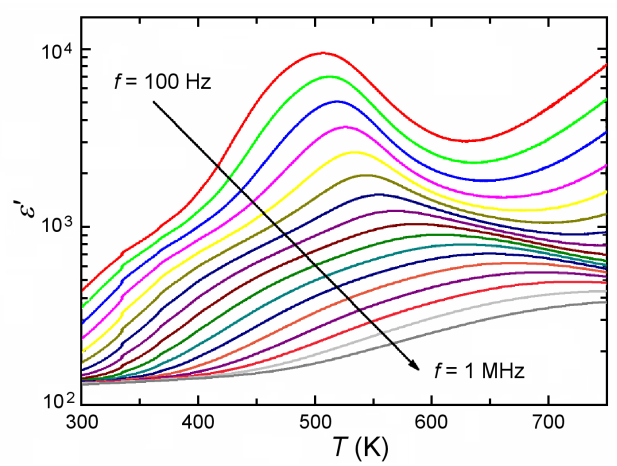

Figure 4. The part of dielectric constant as a function of temperature for the different frequencies of measuring field (100 Hz–1 MHz)

decreases with increasing of the frequency while the temperature of this maximum shifts to higher values. The strong dependence of the maximum of the dielectric constant ε' on the measurement field's frequency testifies to the relaxation processes taking place in the sample.

$Bi_7Fe_3Ti_3O_{21}$ ceramic material belongs to a group of multiferroic materials that are characterized by the occurrence of the magnetoelectric effect. The magnetoelectric effect was examined based on the dielectric measurements [15]. The magnetoelectric coupling coefficient was determined to check the relation between electrical and magnetic properties. Taking into consideration the Alcantara, Gehring and Janssen theory, the multiferroic materials can be treated like a system which contains two subsystems – electric and magnetic. These subsystems are coupled with each other [16,17]. The Hamiltonian is a quantum-mechanical operator connected with system energy and describes magnetic subsystem, electric subsystem and coupling between them:

$$H = H^m + H^\varepsilon + H^{m\varepsilon} \tag{2}$$

where H^m is the Hamiltonian of the magnetic subsystem, H^ε is the electric subsystem and $H^{m\varepsilon}$ is the coupling interaction between two subsystems [18]. Based on Eq. 2 and using the mean field approximation, the dielectric constant can be determined by following expression:

$$\varepsilon(T) = \varepsilon_0(1 + \alpha\langle S_i S_j\rangle) \tag{3}$$

where ε_0 is the dielectric constant of vacuum, $\alpha = 2z_2 \cdot \gamma \cdot \varepsilon_0$ is the normalized magnetoelectric coupling coefficient (z_2 is the number of the spin-pair correlations; γ is the magnetoelectric coupling coefficient indicating the intensity of the magnetoelectric coupling) and $\langle S_i S_j\rangle$ is the spin-pair correlation [19]. Calculations of the magnetoelectric coupling coefficient consisted in approximation of experimental data (Fig. 5a) with the theoretical relation Eq. 3.

The results of approximation of dielectric constant measured in the range from RT (room temperature) to 400 K for several frequencies are presented in Fig. 5b. The values of the magnetoelectric coupling coefficient γ are presented in Table 2. Results of calculations show that the strongest magnetoelectric effect occurs in the sample for the frequency of measuring field f = 100 kHz and equals to γ = 0.0869 while the weakest one is γ = 0.0226 for f = 1 kHz.

Table 2. The values of the magnetoelectric coupling coefficient γ [CGS] for multiferroic $Bi_7Fe_3Ti_3O_{21}$ ceramics

$Bi_7Fe_3Ti_3O_{21}$	Frequency			
	1 kHz	10 kHz	100 kHz	1 MHz
γ	0.0226	0.0432	0.0869	0.0722

In addition to the magnetoelectric effect study, the measurements of magnetization dependence as a function of magnetic field (Fig. 6) and temperature (Fig. 7) were carried out. Figure 6 shows the magnetic field dependences of magnetization for the Aurivillius type $Bi_7Fe_3Ti_3O_{21}$ ceramics and the hysteresis loop at 2 K. The investigated material shows very weak magnetic properties. The maximum magnetization value M at 2 K reaches the 0.8 emu/g in the magnetic field of 7 T. The $M(H)$ dependencies at 100, 200 and 300 K are straight lines. The small hysteresis loop is observed at 2 K with the value of coercivity less than 0.1 T.

The curves in Fig. 7 show magnetization as a function of temperature measured in FC and ZFC modes at the applied magnetic field of $\mu_0 \cdot H$ = 0.1 T. It can be seen that the FC and ZFC curves diverge below 220 K displaying the behaviour of a spin glass. Moreover, in the

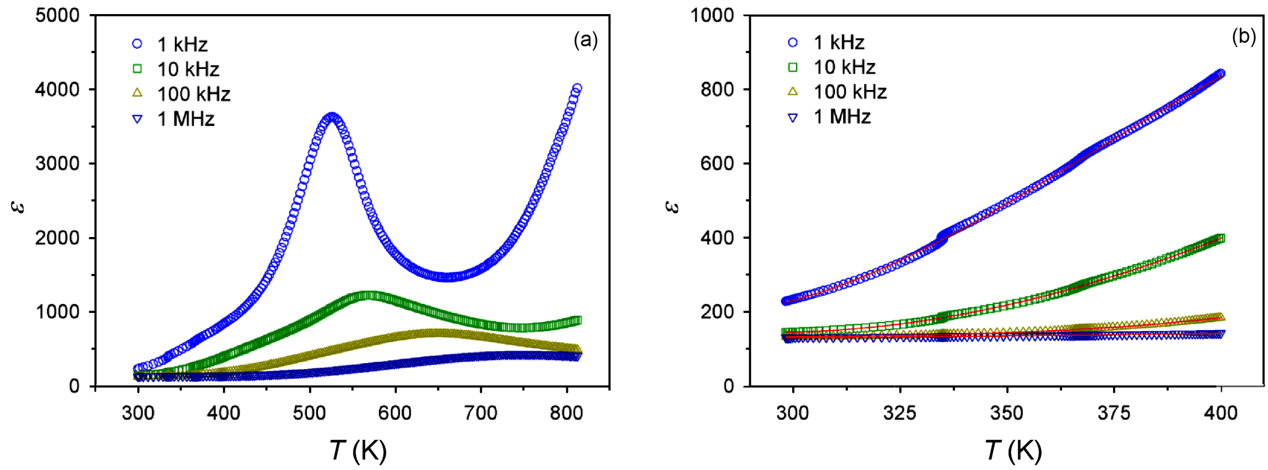

Figure 5. Temperature dependencies of dielectric constant for the Aurivillius type $Bi_7Fe_3Ti_3O_{21}$ material

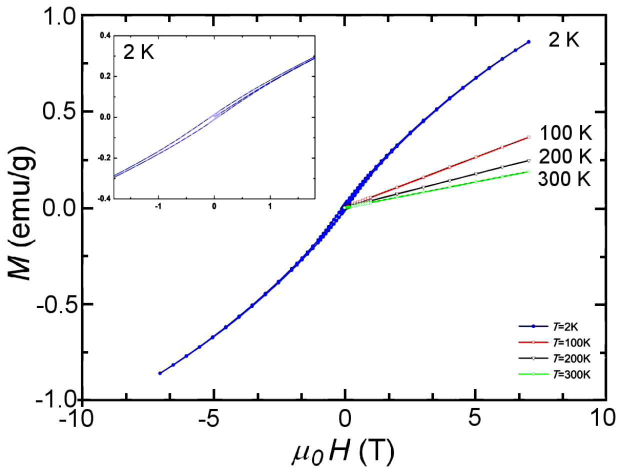

Figure 6. Magnetization as a function of magnetic field for $Bi_7Fe_3Ti_3O_{21}$ ceramics

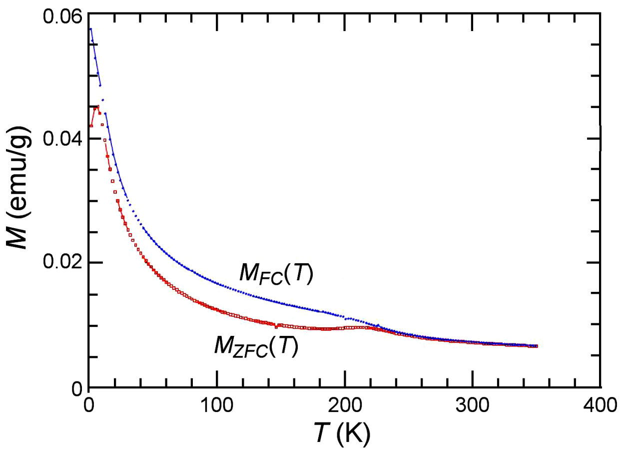

Figure 7. Magnetization of $Bi_7Fe_3Ti_3O_{21}$ ceramics as a function of temperature in ZFC and FC modes ($\mu_0 \cdot H$ = 0.1 T)

vicinity of this temperature a maximum appears, which is a characteristic feature of anti-ferromagnetic materials. These results are consistent with those previously published in the literature [3,20].

Magnetization dependence on the magnetic field for paramagnetic materials can be described by the Brillouin function [21,22]:

$$B_J(x) = \frac{2J+1}{2J}\coth\left(\frac{(2J+1)x}{2J}\right) - \frac{1}{2J}\coth\left(\frac{x}{2J}\right) \quad (4)$$

where:

$$x = \frac{g \cdot J \cdot \mu_B \cdot B}{k_B \cdot T} \quad (5)$$

and it is expressed by the formula:

$$M = N \cdot g \cdot J \cdot \mu_B \cdot B_J(x) \quad (6)$$

In these formulas: N means the number of magnetic ions, J is a quantum angular momentum, g is the spectroscopic splitting factor, μ_B is Bohr's magneton, B is magnetic field induction, k_B is the Boltzmann constant, T is the temperature and $\cosh(x)$ is a hyperbolic cotangent. To determine the number of magnetic ions (Fe^{3+}) involved in the formation of magnetic properties, magnetization measurement data were approximated (Fig. 8).

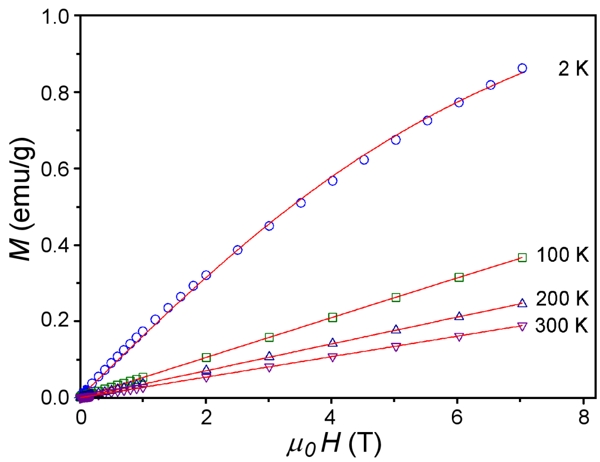

Figure 8. Approximation measurement data of magnetization, as a temperature function for $Bi_7Fe_3Ti_3O_{21}$ ceramics

Based on approximation parameters, the molar concentration of magnetic ions Fe^{3+} was determined and it is equal to 9.36 mol%.

IV. Conclusions

Multiferroic Aurivillius type structure $Bi_7Fe_3Ti_3O_{21}$ ceramics material was obtained by conventional, mixed oxides method. The temperature of synthesis and sintering were equal to 1123 and 1263 K, respectively. The XRD measurements confirmed that the material shows face-centered orthorhombic structure, which was used for determination of the lattice parameters. SEM results showed plate-shaped grains and its anisotropy which is typical feature of compounds consisting of the Aurivillius phases. The EDS investigations revealed high compliance between the theoretical and experimental content of elements. Dielectric measurements manifested strong dependence of the maximum of the dielectric constant ε' on the measurement field's frequency. It testifies to the relaxation processes taking place in the sample. In order to check the relationship between electrical and magnetic properties, the magnetic coupling coefficient γ was determined. For this purpose the Alcantara, Gehring and Janssen theory was taken into consideration. Using the mean field approximation of the dielectric results at room temperature and several frequencies, the magnetoelectric coupling coefficients were calculated. These values are in the range of 0.0226–0.0869 and they are consistent with the measured magnetoelectric coupling values for similar Aurivillius type structure materials. Magnetic measurements for the multiferroic $Bi_7Fe_3Ti_3O_{21}$ ceramics showed that the investigated sample exhibits an antiferromagnetic behaviour. Hysteresis loop was observed at 2 K with a coercivity less than 0.1 T. The molar concentration of magnetic Fe^{3+} ions in the multiferroic $Bi_7Fe_3Ti_3O_{21}$ compound was determined and it was equal to 9.36 mol%.

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