==================== **MAGNETISM** ====================

Magnetoelectric Properties of Zinc-Substituted BiFeO$_3$ Multiferroics

D. M. Yusupov[a, b, *], **A. A. Amirov**[a, b], **I. I. Makoed**[c], **Y. A. Chaudhary**[d], **and S. T. Bendre**[d]

[a] *Institute of Physics, Dagestan Federal Scientific Center, Russian Academy of Sciences, Makhachkala, Russia*

[b] *Laboratory of New Magnetic Materials of the Institute of Physico-Mathematical Sciences and Information Technologies, Immanuil Kant Baltic Federal University, Kaliningrad, Russia*

[c] *A. S. Pushkin Brest State University, Brest, Belarus*

[d] *Department of Physics, School of Physical Sciences, North Maharashtra University, Jalgaon, Maharashtra, India*

*e-mail: dibir.usupov@mail.ru

Abstract—The magnetoelectric properties of ceramic samples of BiFe$_{1-x}$Zn$_x$O$_3$ and Bi$_{1-x}$Zn$_x$Fe$_{1-x}$Zn$_x$O$_3$ multiferroics have been studied in magnetic fields from 0 to 80 kOe at room temperature. All the samples have the linear dependences of magnetoelectric coefficient α_{ME} with low hump-like maxima of α_{ME} at 10 kHz and also at 85 kHz. These magnetoelectric studies of the bismuth ferrites with doubly substituted Zn show that the double substitution of Zn^{2+} ions for Bi^{3+} and Fe^{3+} ions does not lead to desired enhancement of the magnetoelectric properties as compared with the ordinary substitution of Zn^{2+}.

1. INTRODUCTION

In recent time multiferroics attract enhanced interest due to the coexistence in them of magnetic and ferroelectric ordering and BiFeO$_3$-based compounds are among promising magnetoelectric materials which are intensively studied now. Bismuth ferrite has the rhombohedral perovskite structure with the *G*-type antiferromagnetic ordering below the Néel temperature $T_N \sim$ 643 K and is a ferroelectric with the Curie temperature $T_C \sim$ 1083 K [1–3]. Most of the works was devoted to the studies of materials in which Bi was replaced by rare-earth elements [4–8]. The studies showed that the replacement of Bi leads to changes in the magnetic and electrical properties of this compound. In addition, one of variants of enhancing the magnetoelectric parameters is the double replacement of bismuth as it is shown in [9]. The studies in this direction have revealed the influence of the concentration of substituting ions not only on the magnetoelectric parameters, but also on the structure, the magnetic and electrical properties of BiFeO$_3$ [10, 11]. If the influence of the replacement of Bi on the properties of BiFeO$_3$ is understood, there is poor information on the studies in which iron ions were substituted. Of specific interest is the study of the properties of bismuth ferrite in which a nonmagnetic ion is used instead of a common rare-earth substitution. In this connection, the aim of this work is to study the magnetoelectric properties of bismuth ferrite in which bivalent Zn^{2+} ion is substituted for trivalent Fe^{3+} ion, and also in the case of the double substitution of Zn^{2+} ions for Bi^{3+} and Fe^{3+} ions.

2. EXPERIMENTAL

The ceramic samples of BiFe$_{1-x}$Zn$_x$O$_3$ (x = 0.05, 0.1, 0.15, and 0.2) and Bi$_{1-x}$Zn$_x$Fe$_{1-x}$Zn$_x$O$_3$ (x = 0.025, 0.05, 0.075, and 0.1) were obtained by the liquid-phase reaction method from precursors Bi(NO$_3$)$_3 \cdot$ 5H$_2$O, Fe(NO$_3$)$_3 \cdot$ 9H$_2$O, and Zn(NO$_3$)$_2 \cdot$ 6H$_2$O which were used as oxidizers, and (NH$_2$CH$_2$COOH) was used as a catalyst for burning. The proportions of the oxidizer and the burnt catalyst were calculated taking into account the valences of the oxidizers (metal nitrides) and the reducing agent (glycine), which then were completely dissolved in the stoichiometric proportion. Then, the mixture was heated up to the evaporation of excess water and appearance of the spontaneous combustion. The BiFeO$_3$ powders with different concentrations of Zn additives obtained as a result of the reaction were ground and baked at a temperature of 650°C for 4 h. Thereafter the powders were granulated by applying a uniaxial pressure and using polyvinyl alcohol as a binder. Lastly, the obtained granules were sintered at temperatures chosen for each Zn concentration for 30 min.

The studies of the structure by X-ray diffraction (XRD) and the Mössbauer spectroscopy confirmed the existence of the bismuth ferrite structure with a low content of a parasitic phase of complex oxides of sillenite $Bi_{25}FeO_{39}$ [12−15].

The magnetoelectric effect (ME) is a change in the electric polarization of a material in an external magnetic field (direct ME effect) or a change in the magnetization of a material in an external electric field (inverse ME effect).

The simplest method of measuring the magnetoelectric effect is that based on the measurement of an alternating voltage induced at the ends of a sample as it is placed in an alternating magnetic field; this method is described in [12]. In this method, the magnetoelectric coefficient α_{ME} is determined from expression

$$\alpha_{ME} = \frac{dU}{hdH}, \qquad (1)$$

where h is the sample thickness, dH is the strength of the applied alternating magnetic field, dU is the value of alternating current on the sample ends when the alternating magnetic field is applied. The advantage of this technique is that it enable to measure even low voltages as an alternating magnetic field is applied. The alternating magnetic field amplitude was 10 Oe and, the field was induced by the Helmholtz coils that make it possible to generate a uniform-alternating field over whole length of the sample. The sample voltage modulated by an alternating field is measured by a n SR830 selective nanovoltmeter, that is also the source of the alternating current for modulation coil. The SR830 nanovoltmeter enables one to measure the signal at the frequency of generation of oscillations of a low-frequency oscillator. The studies were performed at two frequencies of the alternating field 10 kHz and 85 kHz. This is related to the fact that frequency 85 kHz is in the region of the electromechanical resonance near which the ME coefficient demonstrates a sharp increase in the signal.

Another important magnetoelectric parameter is the magnetodielectric effect (MDE) or magnetocapacity. The technique of measuring the magnetocapacity is quite simple and is a problem of determining the dielectric permittivity of a flat capacitor placed in the magnetic field source [14]. Dielectric permittivity ε is calculated from the expression of the capacity of a flat capacitor

$$C = \frac{\varepsilon\varepsilon_0 S}{d}, \qquad (2)$$

where ε is the dielectric permittivity of a material, d is the distance between the capacitor plates, S is the capacitor plate area, and $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m.

The sample capacity was measured using an LCR universal digital bridge. The final formula for calculating the magnetocapacity is

$$MC = \frac{\Delta\varepsilon(H)}{\Delta\varepsilon(0)} = \frac{\varepsilon(H) - \varepsilon(0)}{\varepsilon(0)}, \qquad (3)$$

where $\varepsilon(H)$ is the dielectric permittivity in magnetic field, $\varepsilon(0)$ is dielectric field in a zero magnetic field. The magnetocapacity was also measured at room temperature.

3. RESULTS AND DISCUSSION

Figure 1 shows the dc magnetic-field dependence of magnetoelectric voltage coefficient α_{ME} measured for ceramics $BiFe_{1-x}Zn_xO_3$ ($x = 0.05, 0.1, 0.15$, and 0.2) at room temperature. It is clearly seen that the ME coefficient of the sample with concentration $x = 0.15$ is significantly higher as compared to that of the samples with $x = 0.05, 0.1$, and 0.2. This fact can be related to the strong magnetic ordering in the sample with $x = 0.15$ as compared to other concentrations. In particular, the structural analysis performed by X-ray diffraction and the Mössbauer spectroscopy confirmed the formation of an iron-containing impurity magnetic phase as a result of heat treatment [13, 15]. Moreover, the results of the magnetic and dielectric measurements and their theoretical consideration demonstrate a better magnetoelectric coupling in the sample with $x = 0.15$ and this sample has a higher magnetization as compared to other compositions [13, 16]. All the samples have linear dependences of ME-coefficient α_{ME} on dc magnetic field with low maxima of α_{ME} near 20 kOe for the sample with $x = 0.15$ and near 60 kOe for the sample with $x = 0.2$ as at 10 kHz and also at 85 kHz. These anomalies are observed for the first time, they have not been reported yet for Zn-doped $BiFeO_3$ samples and can be explained as a result of changes in the electron and magnetic structure caused by magnetic field and substituting of Zn^{2+} ions for Fe^{3+} ions. The comparison of the field dependences of the ME coefficients of both series of the substituted bismuth ferrites shows that, at the modulation frequency 85 kHz, ME coefficient α_{ME} for the sample with $x = 0.2$ is higher than that at $x = 0.05$ and 0.1, as compared to the case at 10 kHz. This result is due to the fact that α_{ME} of the sample with $x = 0.2$ demonstrates higher values at the resonant frequency. The observed frequencies of the electromechanical resonance for the $BiFe_{1-x}Zn_xO_3$ samples are within the range 83−85 kHz, they have no clear concentration dependence and are determined by individual mechanical properties and geometric sizes of the samples.

Figure 2 shows the magnetic-field dependences of the magnetoelectric voltage coefficient α_{ME} for $Bi_{1-x}Zn_xFe_{1-x}Zn_xO_3$ ($x = 0.025, 0.05, 0.075$, and 0.1) with double Zn substitution at room temperature. From Fig. 2, it can be noted that all the samples have
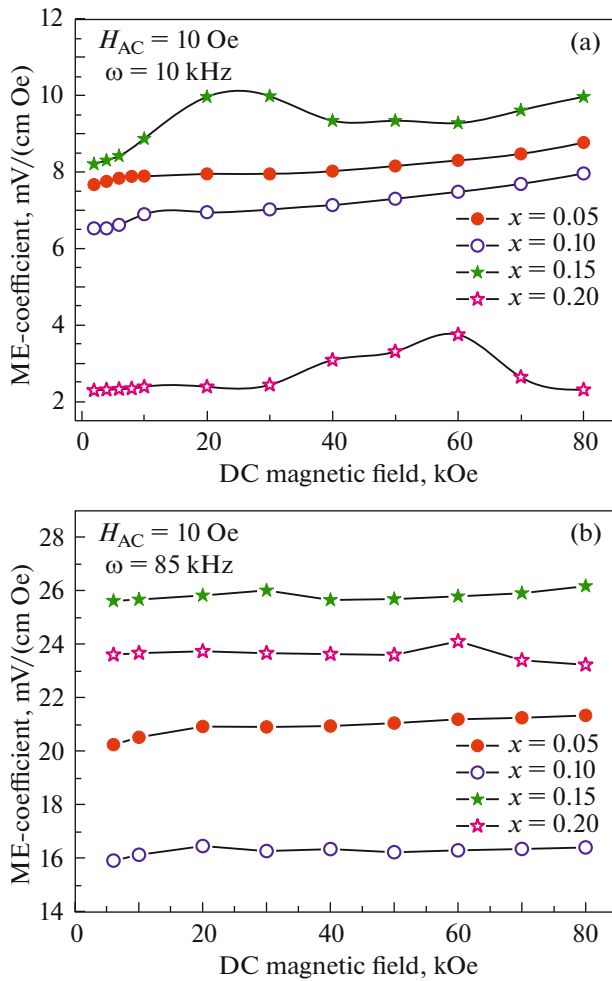
Fig. 1. Magnetic-field dependences of the magnetoelectric coefficient for BiFe$_{1-x}$Zn$_x$O$_3$ (x = 0.05, 0.1, 0.15, and 0.2) samples at room temperature: (a) at 10 kHz, (b) at 85 kHz.

Fig. 2. Magnetic-field dependences of the magnetoelectric coefficient for Bi$_{1-x}$Zn$_x$Fe$_{1-x}$Zn$_x$O$_3$ (x = 0.025, 0.05, 0.075, and 0.1) samples at room temperature: (a) at 10 kHz, (b) at 85 kHz.

linear dependences of ME-coefficient α_{ME} on dc magnetic field. At x = 0.05 and 0.1, analogous "humps" are observed in fields 40 kOe and 50 kOe both at 10 kHz and 85 kHz, and the ME coefficients for the samples with double substitution are significantly lower than for the samples, in which only iron is substituted. It seems likely that such a behavior is due to the following factor: the Zn^{2+} substitution leads to local structural distortions and is dependent on the ratio of the ionic radii of Zn^{2+} and Bi^{3+}, and the degree of substitution larger than x = 0.2 leads to a degradation of the dipole ordering. Similar effect seems likely to take place in the case of double Zn^{2+} substitution, leading to a degradation of the electric properties of the compound. This problem was studied in detail in [17] for the case of the rare-earth substitution; the case with double Zn^{2+} substitution is scantily known and needs the confirmation using detailed structural and magnetic measurements.
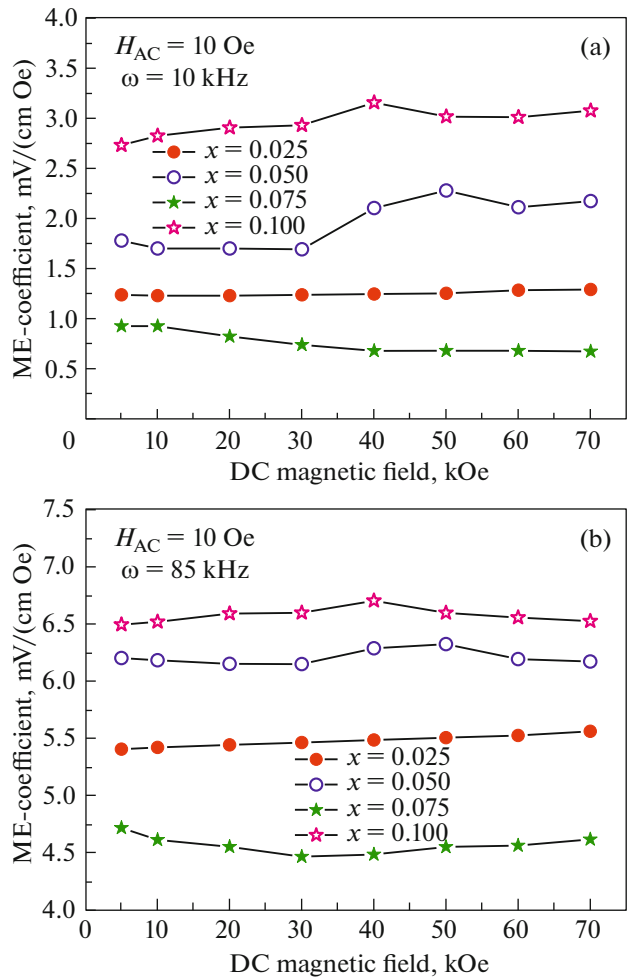
Figure 3 shows the concentration dependences of the magnetocapacity of the bismuth ferrite samples with ordinary and double zinc substitution measured in magnetic field 70 kOe at room temperature. All the samples, except for the composition with concentration x = 0.05 with ordinary Zn substitution, demonstrate negative magnetocapacities. A comparatively high magnetocapacity of 10% is likely to relate to the response of the magnetic parasitic impurity phase with a high magnetic moment that is observed in substituted samples of bismuth ferrite with low concentrations of the substitution. The magnetocapacity of the BiFe$_{1-x}$Zn$_x$O$_3$ series with x > 0.05 is slightly dependent on the concentration, while, for Bi$_{1-x}$Zn$_x$Fe$_{1-x}$Zn$_x$O$_3$, an increase in x leads to the fact that, at x = 0.1, the dielectric permittivity of the sample only slightly dependent on magnetic field.
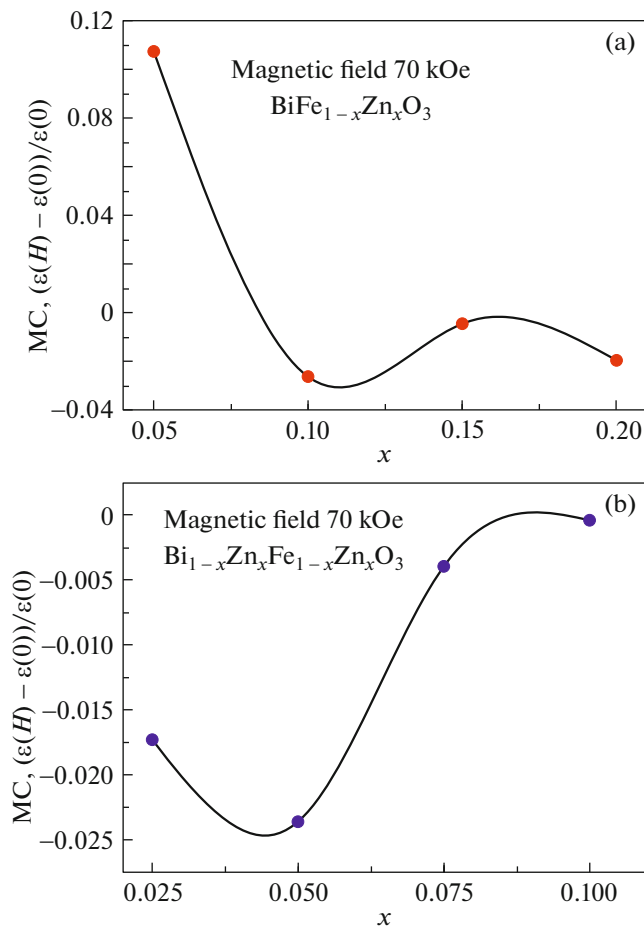
Fig. 3. Dependences of the magnetocapacity on the Zn substitution concentration for samples: (a) $BiFe_{1-x}Zn_xO_3$ ($x = 0.05, 0.1, 0.15,$ and 0.2) and (b) $Bi_{1-x}Zn_xFe_{1-x}Zn_xO_3$ ($x = 0.025, 0.05, 0.075,$ and 0.1).

4. CONCLUSIONS

Thus, the magnetoelectric studies performed for the samples of bismuth ferrite with the ordinary and double Zn substitution show that the double substitution of Zn^{2+} ions for Bi^{3+} and Fe^{3+} ions do not give desired enhancement of the magnetoelectric properties, and an increase in the substitution concentration up to $x = 0.1$ in the case of the double substitution leads to the fact that the dielectric permittivity is only slightly dependent on magnetic field.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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