# Heat Capacity of Nanostructured Multiferroics $BiFe_{1-x}Zn_xO_3$

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**Abstract**—The heat capacity of ceramic $BiFe_{1-x}Zn_xO_3$ multiferroics has been studied in the temperature range 150−750 K. It is found that the antiferromagnetic transition temperature $T_N$ slightly shifts to lower temperatures as the concentration of the substitutional impurity Zn increases. An excess heat treatment has been observed; it is considered as the Schottky anomaly in three-level states.

In recent years, multiferroics have attracted enhanced interest, since these materials are promising for designing magnetoelectric devices and exhibit a strong correlation of the structure with the magnetic and electrical properties. Despite a great number of the works devoted to studying miltiferroics performed over the last decade, bismuth ferrite-based compounds remain among most perspective and extensively studied magnetoelectric materials. Bismuth ferrite has a perovskite rhombohedral structure with the *G*-type antiferromagnetic ordering below the Néel temperature $T_N \sim 643$ K and is a ferroelectric with a Curie temperature ~1083 K [1]. However, the spin-modulated structure with a period of 0.62 nm revealed in bulk $BiFeO_3$ prevents the appearance of a magneto-electric ordering at room temperature [2, 3]. One of most abundant ways of solving this problem is the substitution of rare-earth element (REE) ions for Bi ions in bismuth ferrite [4−8]. Searching for the most optimal variants of replacing Bi in $BiFeO_3$ led to the use of both nonmagnetic trivalent ions Cr, Ti, and Mn [9−11] and bivalent dopants Ca, Pb, and Sr [12, 13]. In addition, it was shown that the application of two substitutional dopants was effective for an increase in the magnetoelectric interaction as, for example, in the case of the $Bi_{0.87}La_{0.05}Tb_{0.08}FeO_3$ compound doped with La and Tb [14]. The studies in this direction revealed the influence of the concentrations of substitutional ions not only on the megnetoelectric parameters, but also on the structure, the magnetic and the electrical properties of $BiFeO_3$, including the region of phase transitions [15, 16]. The situation in the case of

influence of replacement of Bi on the physical properties of $BiFeO_3$ is to some degree understood; however, the information on the studies of the bismuth ferrite, in which iron ion is substituted, is poor and contradictory. In particular, the high-temperature phase transitions and the physical properties of such materials almost were not studied in detail. Taking into account the aforementioned, we choose for the study ceramic $BiFe_{1-x}Zn_xO_3$ samples, in which bivalent $Zh^{2+}$ ions substituted trivalent $Fe^{3+}$ ions.

The ceramic $BiFe_{1-x}Zn_xO_3$ ($x = 0.05$, 0.1, 0.15, and 0.2) samples were prepared by method of liquid-phase reaction from precursors $Bi(NO_3)_3 \cdot 5H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, and $Zn(NO_3)_2 \cdot 6H_2O$ that were used as oxidizers and ($NH_2CH_2COOH$) was used as a fuel for combustion. The proportions of the oxidizers and the fuel combusted were calculated with allowance made for the valences of the oxidizers of metal nitrates and the glicine deoxidizer, which then were completely dissolved in the stoichometric proportion. Then the mixture was heated up to the evaporation of the water excess and the appearance of the spontaneous combustion. The $BiFeO_3$ powders with different concentrations of Zn additives obtained as a reaction product were grinded 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 granules prepared were sintered at temperatures chosen for each Zn concentration: 943 K ($x = 0.05$), 948 K ($x = 0.1$), 953 K ($x = 0.15$), and 958 K ($x = 2$) for 30 min.
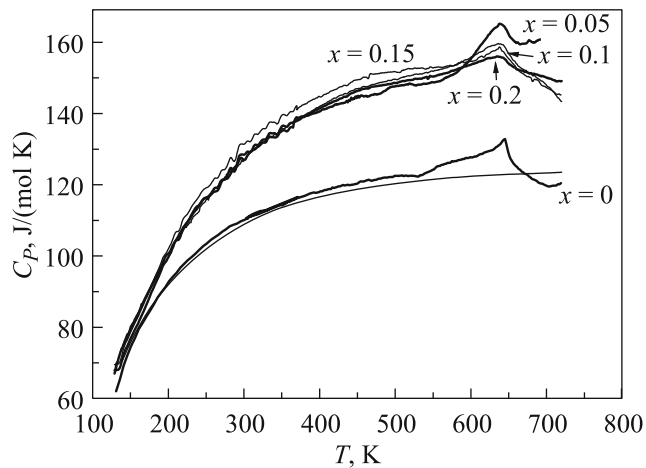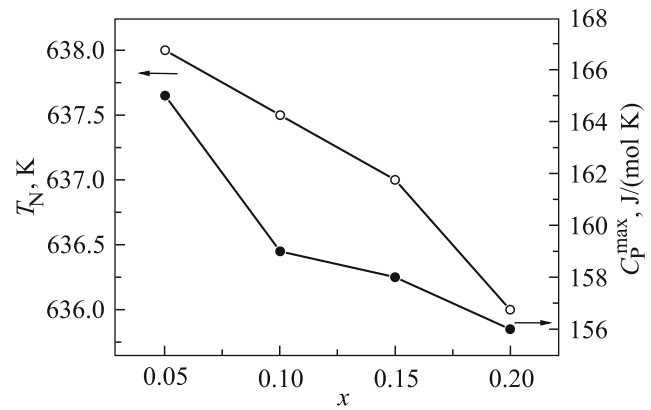
**Fig. 1.** Temperature dependences of the heat capacity of the $BiFe_{1-x}Zn_xO_3$ ($x = 0$, 0.05, 0.1, 0.15, and 0.2) samples: points are the experimental data, the lines are the results of approximating the phonon heat capacity by the Debye function.



**Fig. 2.** Diagrams of the dependence of the magnetic transition temperature $T_N$ and the molar heat capacity maximum on the Zn addition concentration for the $BiFe_{1-x}Zn_xO_3$ ($x = 0.05$, 0.1, 0.15, and 0.2) samples.

The structural studies performed in [17] showed that the samples were a homogeneous ceramics with the mean granule size 20 nm with insignificant content of the $Bi_{12}(Bi_{0.5}Fe_{0.5})O_{19.5}$ impurity phase.

The heat capacity was measured on using a NETZSCH DSC 204 F1 Phoenix differential scanning calorimeter. The samples for measuring the heat capacity were 1-mm-thick plates 4 mm in diameter. The rate of varying the heat capacity was 5 K/min. The measurement error of the heat capacity was not higher than 3%.

Figure 1 depicts the temperature dependences of the heat capacity of the $BiFe_{1-x}Zn_xO_3$ ($x = 0$, 0.05, 0.1, 0.15, and 0.2) samples measured in the temperature range 150−700 K. As is seen from Fig. 1, the temperature dependences of all the samples had maxima at 635−640 K, which corresponded to the antiferromagnetic phase transition. The antiferromagnetic phase transition in pure bismuth ferrite was observed almost in this range at $T = 644$ K. The increase in the concentration of the substitutional Zn ion led to a decrease in the maximum heat capacity $C_P^{max}$, and the antiferromagnetic transition temperature $T_N$ shifted to lower temperatures (Fig. 2). A comparison of the shift of $T_N$ due to the increase in concentration $x$ with similar shift for the compositions, in which Bi was replaced showed a higher structural sensitivity of solid solutions $Bi_{1-x}A_xFeO_3$ ($A$ = La, Nd, and Gd) as compared to that of Fe-substituted solid solutions $BiFe_{1-x}Zn_xO_3$ [16, 18, 19]. For comparison, according to the data of measurements of $C_P(T)$ in the concentration range $x = 0.05–0.1$, the shift of $T_N$ for $Bi_{1-x}A_xFeO_3$ ($A$ = La, Nd, and Gd) was about 5 K, while it was not higher than 0.5 K for the $BiFe_{1-x}Zn_xO_3$

system. The Zn addition concentration insignificant influenced also the heat capacity value, although the maximum at $x = 0.05$ was noticeable against the background of other $C_P(T)$ dependences. This was related to higher contents of impurity phases revealed as a result of the structural studies than the contents at other concentrations. The absolute values of $C_P$ of pure $BiFeO_3$ and substituted $BiFe_{1-x}Zn_xO_3$ were not compared, since they were obtained by different technologies and had different densities and the microstructures.

To explain the shift of the transition temperature to lower temperatures with the increase in the Zn addition concentration, it is necessary to take into account the following factors.

(1) The consideration of qualitative differences between the cation substitution in the system with tin and the substitutions of rare-earth element cations for bismuth cations in bismuth ferrite; the inclusion of a possible influence of the effect of diamagnetic dilution due to the doping with tin cations. In this case, magnetically active iron cations are substituted in the $B$ sublattice (which must lead to a decrease in the exchange interactions) and the proximity of the values of ionic radii of $Zn^{2+}$ and $Fe^{3+}$ must lead to relatively small distortions of the structure due to the size factor and, therefore, to a lesser degree favor the distortion (fracture) of the spin cycloid in bismuth ferrite.

(2) The consideration of the composition nonstoichiometry (a deficit of positive charge in the formula unit). Oxygen vacancies also can influence the magnetic properties, including the shift of the transition temperature with the change in the composition of the samples.

The estimation of the anharmonic contribution to the phonon heat capacity showed that it was not less than 1%, which was provided by a low linear thermal
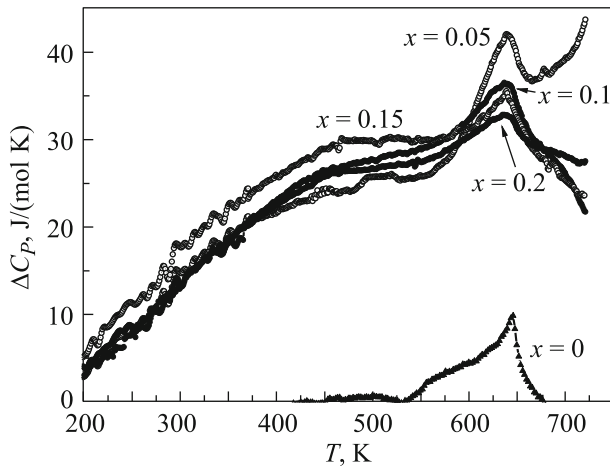
**Fig. 3.** Temperature dependences of the anomalous component of the heat capacity of the BiFe$_{1-x}$Zn$_x$O$_3$ ($x = 0$, 0.05, 0.1, 0.15, and 0.2) samples: points are the experimental data, the lines are the results of approximating by Eq. (3).

expansion coefficient of bismuth ferrite; since this value was small, the difference between $C_P$ and $C_V$ cannot be taken into account when further analyzing the temperature dependence of the phonon heat capacity. In most cases, the quantitative analysis of the temperature dependence of the heat capacity and the separation of the phonon and the anomalous contributions are performed using the simple model describing the phonon heat capacity by the Debye function

$$C_P^0 \sim D(\Theta_D / T), \qquad (1)$$

where $\Theta_D$ is the characteristic Debye temperature. The analysis of our data on the heat capacity of BiFeO$_3$ and BiFe$_{1-x}$Zn$_x$O$_3$ gave values $\Theta_D \approx 550$ and

500 K, respectively. The Debye temperature $\Theta_D$ is known to be dependent on the values of the bonding forces between the lattice sites; because of this, the decrease in $\Theta_D$ due to substitution of Zn ions for Fe ions demonstrated the decrease in the bonding forces between the crystal lattice atoms. The results of approximation of the phonon heat capacity by the Debye function are shown in Fig. 1 by the solid lines for $x = 0.05$–0.20. The compositions of BiFeO$_3$ with a partial substitution of tin for iron demonstrated the deviation of the experimental data from the calculated phonon heat capacity, which indicated the existence of the excess heat capacity (Fig. 1).

The excess component of the heat capacity was determined for each composition as the difference between the measured and calculated phonon heat capacities $\Delta C = C_P - C_P^0$. Figure 3 shows the temperature dependence of anomalous heat capacity $\Delta C(T)$ of BiFe$_{1-x}$Zn$_x$O$_3$. The character of thus-determined heat capacity made it possible to interpret the Schottky anomaly for three-level states separated by the energy barriers $\Delta E_1$ and $\Delta E_2$ from the ground state. These can be the atoms of the same and other types separated by barriers $\Delta E_1$ and $\Delta E_2$ in three structurally-equivalent positions. The three-level system of the Zn substitution can appear due to a distortion of the lattice parameters because of polar displacements of iron ions from the initial positions and the change in the bond angle between oxygen octahedral FeO$_6$ [20].

In the general case, the expression of the Schottky heat capacity can be obtained, differentiating the mean energy of particles at energy levels [21]:

$$\Delta C_P = (KT^2)^{-1}(\langle \Delta E_i^2 \rangle - \langle \Delta E_j \rangle^2). \qquad (2)$$

The expression of the Schottky heat capacity in the framework of three-level model (at arbitrary mass of a material) has the form [22]

$$\Delta C_P = \frac{\nu R \left[ D_1 (\Delta E_1 / kT)^2 \exp\left(-\dfrac{\Delta E_1}{kT}\right) + D_2 (\Delta E_2 / kT)^2 \exp\left(-\dfrac{\Delta E_2}{kT}\right) \right]}{\left[ 1 + D_1 \exp\left(-\dfrac{\Delta E_1}{kT}\right) + D_2 \exp\left(-\dfrac{\Delta E_2}{kT}\right) \right]^2}, \qquad (3)$$

where $D_1$ and $D_2$ are the ratios of multiciplities of degeneration of levels, $R$ is the universal gas constant, and $\nu$ is the number of moles. By comparing the heat capacity calculated by Eq. (1) and the excess heat capacity $\Delta C$ separated experimentally, the following model parameters were obtained: $D_1 = 106.72$, $D_2 = 9.25$, $\Delta E_1 = 0.345$ eV, and $\Delta E_2 = 0.0636$ eV. As is seen from Fig. 3, the experimentally separated $\Delta C(T)$ agreed well with the calculated temperature dependence of the anomalous heat capacity.

Thus, the results of the study of the heat capacity showed an insignificant shift in the temperature of the

antiferromagnetic transition with the increase in the Zn substitution concentration and an insubstantial difference in the heat capacity near the transition for compositions $x = 0.1$–0.2, which can be related to the proximity of Fe$^{3+}$ and Zn$^{2+}$ ion radii, the decrease in the exchange interactions and the formation of oxygen vacancies due to the substitution of Zn$^{2+}$ ions for Fe$^{3+}$ ions in bismuth ferrite. The formation of additional contribution to the heat capacity in the temperature range 140–750 K due to substitution with Zn ions can be related to the Schottky anomaly for three-level states.

## ACKNOWLEDGMENTS

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