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MAGNETIC PROPERTIES OF SOLID SOLUTIONS OF $\text{BiFeO}_3 - \text{SmCoO}_3$ SYSTEM

Solid solutions of $\text{BiFeO}_3 - \text{SmCoO}_3$ were synthesized by a solid-state method. Peculiarities of the influence of isovalent substitution of Bi^{3+} and Fe^{3+} ions in BiFeO_3 by Sm^{3+} , Co^{3+} ions on the crystal structure and magnetic properties of $\text{Bi}_{1-x}\text{Sm}_x\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ solid solutions are found. It is shown that the substitution 3-25% of the Bi^{3+} , Fe^{3+} ions in BiFeO_3 by Sm^{3+} , Co^{3+} ions results in the gradual destruction of the antiferromagnetic and conception of ferromagnetic ordering. In this case replacing up to 10% of Sm^{3+} and Co^{3+} ions in SmCoO_3 by Bi^{3+} and Fe^{3+} ions leads to the stabilization of Co^{3+} ions in a diamagnetic state.

Introduction. BiFeO_3 compound belongs to ferroelectromagnetics (multiferroics), i.e. substances with simultaneous electric dipolar and magnetic spin ordering. Communication between magnetic and electric subsystems in ferroelectromagnetics manifesting itself as magnetoelectric effects, affords ground for controlling magnetic properties of a material by means of the electric field and, on the contrary, for carrying out modulation of electric polarization by means of the magnetic field. All this helps consider multiferroics as possible materials for creating essentially new devices in information and energy saving technologies, magnetic memory devices and spin electronics, magnetic field sensors, etc. [1–3].

Bismuth ferrite BiFeO_3 is the only material showing both ferroelectric and antiferromagnetic ordering (with a weak ferromagnetic contribution) at room temperature, which offers exciting possibilities for its practical application. However, the existence of spatially-modulated cycloid-type spin structure in BiFeO_3 (every iron ion is surrounded with six iron ions with noncollinear antiferromagnetic spin ordering) the modulation period of which is incommensurate with the crystal lattice period, results in almost full suppression of a magnetoelectric effect in volume samples of BiFeO_3 . Application of large magnetic fields (not less than 20 T), substitution of Bi^{3+} ions by ions of rare-earth elements or Fe^{3+} ions by ions of other metals promotes transition to proportional ferromagnetic ordering.

The present paper deals with the study of the magnetic properties of $\text{Bi}_{1-x}\text{Sm}_x\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ solid solutions generated as a result of simultaneous isovalent substitution of Bi^{3+} ions by Sm^{3+} ions in BiFeO_3 and equivalent amount of Fe^{3+} ions by Co^{3+} ions.

Experimental technique. The synthesis of polycrystalline samples of the $\text{Bi}_{1-x}\text{Sm}_x\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ solid solutions ($0 \leq x \leq 1.0$) was carried out by sol-

id-state method from Bi_2O_3 , Fe_2O_3 , Sm_2O_3 and Co_3O_4 . Powders of the starting compounds taken in set molar ratios were mixed and ground for 30 minutes in a planetary mill with the addition of ethanol. The received batch with ethanol in it was pressed under pressure of 50–75 MPa to produce tablets 25 mm in diameter and 5–7 mm high which then were fired in the air at 800°C for 8 hours. After preliminary firing the tablets were crushed, ground and pressed to produce bars 30 mm long with the cross-section of 5x5 mm². Conditions of synthesizing samples of the system in the air depended on the composition and varied greatly: $T = 850\text{--}1250^\circ\text{C}$, lasting from 30 minutes to 8 hours. The more bismuth ions were substituted by rare-earth element ions, the higher the synthesis temperature was.

X-ray diffractograms were received on the D8 ADVANCE diffractometer with the use of $\text{CuK}\alpha$ -radiation. The crystal structure parameters were determined by means of the X-ray diffraction tabular RTP processor and data of the card catalogue of the International Center for Diffraction Data (ICDD JCPDS).

Research workers of the Scientific and Practical Materials Centre of the NAS of Belarus measured specific magnetization (σ_{sp}) of the samples obtained at 7 and 300 K in the fields of up to 14 T and their specific magnetic susceptibility (χ_{sp}) in the magnetic field of 0.86 T at the temperatures ranging from 7 to 300 K by the vibration method, using the universal high-field measuring system (Cryogenic Ltd, London) and Faraday method, the range of temperatures being 77–950 K.

Results and discussion. From the data obtained by the X-ray phase analysis of samples of the $(1-x)\text{BiFeO}_3 - x\text{SmCoO}_3$ system (Fig. 1) it follows that in the system involved solid solutions with perovskite structure, based on both BiFeO_3 and SmCoO_3 , are generated though some of them contain impurity phases of $\text{Bi}_{25}\text{FeO}_{39}$, CoFe_2O_4 ferrites.

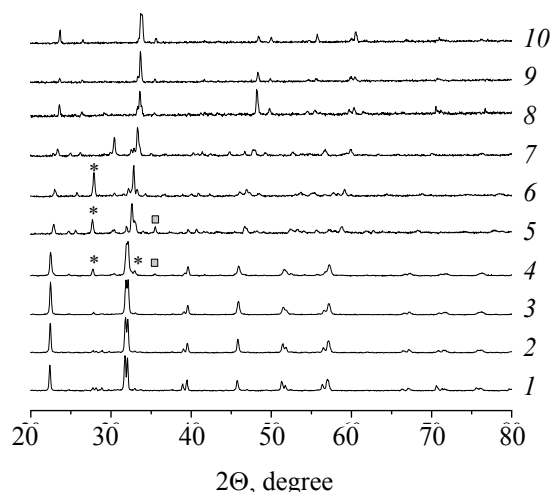


Fig. 1. X-ray diffractograms of $\text{Bi}_{1-x}\text{Sm}_x\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ samples when x values are different:

1 – 0; 2 – 0.03; 3 – 0.05; 4 – 0.1; 5 – 0.25; 6 – 0.5;
7 – 0.75; 8 – 0.9; 9 – 0.95; 10 – 1.0;
* – phase $\text{Bi}_{25}\text{FeO}_{39}$; □ – CoFe_2O_4

The crystalline structure of BiFeO_3 was characterized by a rhombohedrally distorted cell of perovskite with the following parameters: $a = 3.963 \text{ \AA}$ and $\alpha = 89^\circ 44'$ which is coherent with literary data [4]. With the increase in the degree of substitution of Fe^{3+} ions by Co^{3+} ions and of Bi^{3+} ions by Sm^{3+} ions up to 0.1 there is a gradual approach to concentration transition from the rhombohedrally distorted cell of perovskite to the orthorhombically distorted structure of perovskite which $\text{Bi}_{1-x}\text{Sm}_x\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ solid solutions with $0.1 \leq x \leq 1.0$ possess (Fig. 1).

Dependences of specific magnetization (σ_{sp}), measured by Faraday method in the magnetic field of 0.86 T for the $\text{Bi}_{1-x}\text{Sm}_x\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ solid solutions are given in Fig. 2.

Fig. 2 shows that the increase of x substitution degree in diamagnetic ions of Bi^{3+} by paramagnetic ions of Sm^{3+} and of paramagnetic ions of Fe^{3+} by Co^{3+} ions which at temperatures below 300 K are in the diamagnetic low-spin (LS) state, and at higher temperatures - in paramagnetic intermediate (IS) or high-spin (HS) states, results in gradual rise of specific magnetization. For example, at 300 K σ_{sp} for the $\text{Bi}_{1-x}\text{Sm}_x\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ sample when $x = 0.03$ is equal to 0.63 $\text{Gs} \cdot \text{cm}^3/\text{g}$, and for the samples when $x = 0.05$; 0.10; 0.25 it is equal to 1.49; 3.97; 14.34 $\text{Gs} \cdot \text{cm}^3/\text{g}$ respectively. In this case, marked increase in specific magnetization of $\text{Bi}_{1-x}\text{Sm}_x\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ samples with x increasing from 0.03 to 0.25 can be explained by the presence of ferromagnetic phase of CoFe_2O_4 ferrite in samples where $x = 0.1$ and 0.25. The increase of σ_{sp} in growth of a degree of substitution of x can be also a consequence of structural distortion when intro-

ducing samarium ions with a smaller ionic radius ($r_{\text{Sm}^{3+}} = 0.97 \text{ \AA}$) [5], than in bismuth ions ($r_{\text{Bi}^{3+}} = 1.20 \text{ \AA}$) [5] which promotes the destruction of spiral spatially-modulated structure of BiFeO_3 and emergence of weak ferromagnetism. For example, such destruction of the spatially-modulated structure with the formation of solid solutions of $\text{Bi}_{1-x}\text{Sm}_x\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ when Bi^{3+} ions were substituted by Sm^{3+} ions was reported in papers [6, 7].

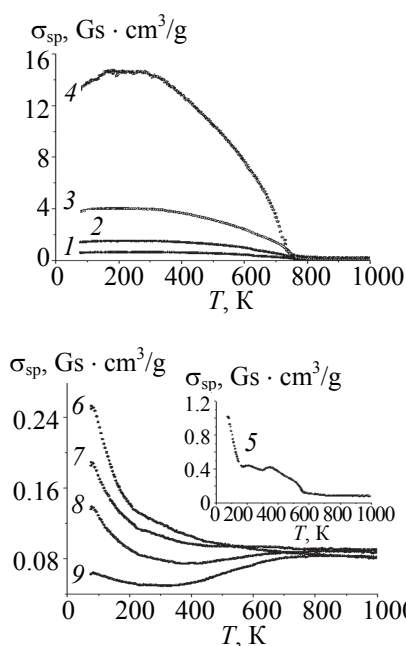


Fig. 2. Dependences of specific magnetization (σ_{sp}) on temperature T for $\text{Bi}_{1-x}\text{Sm}_x\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ samples when x values are different:

1 – 0.03; 2 – 0.05; 3 – 0.1; 4 – 0.25; 5 – 0.5; 6 – 0.75;
7 – 0.9; 8 – 0.95; 9 – 1.0

It should be noted that the type of curves of temperature dependences σ_{sp} for $\text{Bi}_{1-x}\text{Sm}_x\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ solid solutions ($0.03 \leq x \leq 0.5$) (fig. 2, a) is indicative of the presence in the samples of the ferromagnetic phase for which Curie temperature (T_c) changes slightly. So, for solid solutions with $x = 0.03$; 0.05; 0.10; 0.25 T_c is equal to 789; 778; 767; 739 K respectively. However, on roentgenograms of the samples with 10 and 25% degree of substitution there is an X-ray peak of the most intensive reflex of CoFe_2O_4 ferrite ($2\theta = 35.43^\circ$, $d = 2.53144 \text{ \AA}$) for which Curie temperature and specific saturation magnetization (σ_{sp}) at 0 K are equal to 793 K and 90 $\text{Gs} \cdot \text{cm}^3/\text{g}$ respectively [8]. It greatly hinders the interpretation of magnetic properties of the solid solutions under consideration. However, the weight of evidence suggests that ferromagnetism of the samples is caused not only by the presence of the ferromagnetic phase, CoFe_2O_4 , but also by weak ferromagnetism of the main phase, since on roentgenograms of the sam-

ples with $x = 0.03$; 0.05 CoFe_2O_4 impurity is absent, but temperature dependences of specific magnetization of the samples (Fig. 2, *a*) show the presence of a ferromagnetic phase in them.

On temperature dependences of magnetization for the $\text{Bi}_{1-x}\text{Sm}_x\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ samples with the degree of substitution $x = 0.03$ and 0.05 and no CoFe_2O_4 impurity, as well as with $x = 0.1$ and 0.25 and impurity of the ferromagnetic phase, CoFe_2O_4 there were various anomalies observed to show that substitution of 25% of Bi^{3+} , Fe^{3+} ions by those of Sm^{3+} , Co^{3+} in BiFeO_3 did not result in complete collapse of antiferromagnetic ordering of magnetic moments of Fe^{3+} ions in the basic BiFeO_3 compound.

Temperature dependences of specific magnetization for SmCoO_3 and the $\text{Bi}_{1-x}\text{Sm}_x\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ solid solution with $x = 0.95$ (Fig. 2, *b*, Curves 8, 9) show that, indeed, spin transition of Co^{3+} ions from diamagnetic LS to paramagnetic IS and/or HS state in SmCoO_3 occurs over the temperature range of 300 – 650 K (with the increase of temperature, σ_{sp} does not decrease as it should be in the paramagnetic but increases) and in the solid solution with $x = 0.95$ spin transition is observed over the temperature range of 400 – 800 K. Dependence of σ_{sp} on T for the $\text{Bi}_{1-x}\text{Sm}_x\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ sample with $x = 0.9$ (Fig. 2, *b*, Curve 7) already has no region of increasing σ_{sp} when temperature rises. Therefore, in the solid solution involved spin transition of Co^{3+} ions over the temperature range of 77 – 1000 K is not observed and Co^{3+} ions are in the diamagnetic low-spin state at up to 1000 K.

Field dependences of specific magnetization for the $\text{Bi}_{1-x}\text{Sm}_x\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ samples ($x = 0$; 0.03 ; 0.05 ; 0.1) measured at temperatures of 7 and 300 K, are given in Fig. 3.

It is established that in small magnetic fields ($H < 2$ – 5 T), both at the temperature of 7 K and at 300 K, the growth of specific magnetization of cobaltite-ferrites $\text{Bi}_{1-x}\text{Sm}_x\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ in which $0.03 \leq x \leq 0.25$ when the magnetic field increases is not linear. However, with further increase in the field up to 14 T linear dependence of σ_{sp} on H is observed:

$$\sigma_{\text{sp}} = \sigma_0 + \chi H,$$

where σ_0 – the value of spontaneous magnetization obtained on extrapolation of an area of linear dependence of σ_{sp} on H up to $H = 0$; χH – magnetization due to a paraprocess.

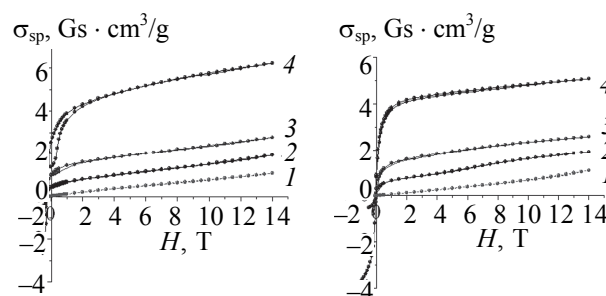


Fig. 3. Dependences of specific magnetization (σ_{sp}) on magnetic field intensity (H) at temperatures of 7 K (*a*) and 300 K (*b*) for $\text{Bi}_{1-x}\text{Sm}_x\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ samples when the degree of x substitution is: 1 – 0; 2 – 0.03 ; 3 – 0.05 ; 4 – 0.1

At the temperature of 300 K demagnetization curves for the cobaltite-ferrites involved show absence of remaining magnetization (σ_r) and coercive force (H_c) which are observed on the field dependences of σ_{sp} at the temperature of 7 K (see the table). It demonstrates the existence of ferromagnetic phase both in samples of $\text{Bi}_{1-x}\text{Sm}_x\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ with $x = 0.03$; 0.05 where there is no impurity of cobaltite-ferrites, CoFe_2O_4 and in samples with $x = 0.1$; 0.25 in which this ferromagnetic phase exists.

Pay attention that in [9] the results of nickel magnetization study are given at temperatures which are slightly higher than the Curie ferromagnetic temperature, in a so-called transitional area. It is shown that transition from ferromagnetic state into paramagnetic one occurs gradually, and in the transitional area of temperatures both states coexist. As the temperature moves off from the Curie temperature, field dependence gradually changes from the curves with nonlinear dependence in weak and linear dependence in strong magnetic fields in which magnetization increases due to a paraprocess, to uniform linear dependence both in small and large fields.

Table

Values of spontaneous specific magnetization (σ_0) and specific magnetization in the magnetic field of 14 T (σ_{14}), specific residual magnetization (σ_r) and coercive force (H_c) at 7 and 300 K for $\text{Bi}_{1-x}\text{Sm}_x\text{Fe}_{1-x}\text{Co}_x\text{O}_3$

Composition x	7 K				300 K	
	σ_0 , Gs · cm ³ /g	σ_{14} , Gs · cm ³ /g	σ_r , Gs · cm ³ /g	H_c , kOe	σ_0 , Gs · cm ³ /g	σ_{14} , Gs · cm ³ /g
0.03	0.6	1.9	0.5	2.0	0.6	1.9
0.05	1.5	2.8	1.0	2.0	1.6	2.6
0.1	4.5	6.3	2.5	2.0	4.0	5.0
0.25	17.2	20.6	11.9	2.0	15.3	16.4
0.5	1.5	4.0	0.7	3.0	0.4	1.7

The obtained field and temperature dependences of specific magnetization for solid solutions of the $\text{Bi}_{1-x}\text{Sm}_x\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ system also show that partial substitution of Bi^{3+} , Fe^{3+} ions in antiferromagnetic bismuth ferrite BiFeO_3 by ions of Sm^{3+} , Co^{3+} results in gradual destruction of antiferromagnetic ordering and in generation of ferromagnetic ordering, and there is an area which is transitional for the degree of x substitution in which both states of magnetic ordering coexist.

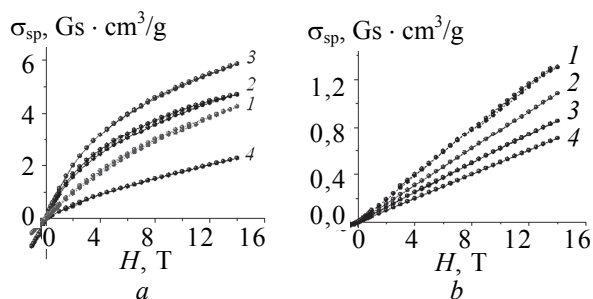


Fig. 4. Dependences of specific magnetization (σ_{sp}) on magnetic field intensity (H) at temperatures of 7 K (a) and 300 K (b) for $\text{Bi}_{1-x}\text{Sm}_x\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ samples with the degree of x substitution: 1 – 0.75; 2 – 0.9; 3 – 0.95; 4 – 1.0

In the $\text{Bi}_{1-x}\text{Sm}_x\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ solid solutions with $0.75 \leq x \leq 1.0$ there is no magnetic ordering of paramagnetic ions, and over the temperature range of 5–1000 K they are paramagnetic (Fig. 2, b). However, linear dependence σ_{sp} on H at up to 14 T is observed at $T = 300$ K (Fig. 4, b), while at 7 K it is absent (fig. 4, a).

Conclusion. Solid solutions of the $(1-x)\text{BiFeO}_3 - x\text{SmCoO}_3$ system were synthesized by solid-state method. It has been established that in the system concerned solid solutions of $\text{Bi}_{1-x}\text{Sm}_x\text{Fe}_{1-x}\text{Co}_x\text{O}_3$, cobaltite-ferrites with the structure of both rhombohedrally distorted perovskite ($0 \leq x \leq 0.05$) and orthorhombically distorted one ($0.1 \leq x \leq 1.0$) are formed. The results of the research show that substitution of 3–25% of Bi^{3+} , Fe^{3+} in BiFeO_3 by Sm^{3+} , Co^{3+} ions leads to gradual destruction of antiferromagnetic ordering and to generation of ferromagnetic ordering, and that there is a transitional by degree of x substitution area in which both states of magnetic ordering coexist. It is established that substitution of 10% of

Sm^{3+} and Co^{3+} in SmCoO_3 by ions of Bi^{3+} and Fe^{3+} promotes the stabilization of Co^{3+} ions in a diamagnetic state, which causes gradual temperature offset of Co^{3+} diamagnetic ions spin transition into the paramagnetic state: from 300 K for SmCoO_3 to 1000 K for $\text{Bi}_{0.1}\text{Sm}_{0.9}\text{Fe}_{0.1}\text{Co}_{0.9}\text{O}_3$ solid solution.

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