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CRYSTAL STRUCTURE AND PHYSICAL AND CHEMICAL PROPERTIES OF $Bi_{1-x}Nd_xFe_{1-x}Co_xO_3$ SOLID SOLUTION

Solid solutions of the $(1-x)BiFeO_3 - xNdCoO_3$ system were synthesized by a solid-state reactions method. Peculiarities of the influence of isovalent substitution in $BiFeO_3$ of Bi^{3+}, Fe^{3+} ions by Nd^{3+}, Co^{3+} ions on the crystal structure, magnetization and thermal expansion of the forming solid solutions $Bi_{1-x}Nd_xFe_{1-x}Co_xO_3$ are fixed. It is shown that the substitution up to 2% of Bi^{3+}, Fe^{3+} ions in $BiFeO_3$ by Nd^{3+}, Co^{3+} ions leads only to the partial destruction of the antiferromagnetic ordering of the Fe^{3+} ions magnetic moments. According to the results of the magnetic properties investigation it is found that magnetic properties of the samples $Bi_{1-x}Nd_xFe_{1-x}Co_xO_3$ ($0.05 \le x \le 0.15$) are due to the coexistence of the antiferromagnetic and ferromagnetic phases but the samples $Bi_{1-x}Nd_xFe_{1-x}Co_xO_3$ ($0.80 \le x \le 1.0$) reveal paramagnetic properties.

Introduction. In recent decades, the number of publications devoted to the synthesis and study of ferroelectromagnets (multiferroics) properties has greatly increased. Relationship between magnetic and electric subsystems in ferroelectromagnets, manifested in the form of magnetoelectric (ME) effect, allows an electric field to control the magnetic properties of the material and vice versa. This allows you to develop on the basis of fundamentally new multiferroic magnetic memory devices and spintronics, magnetic field sensors, recording and reading information, and others [1–5]. One of the problems of practical use is to search for multiferroic materials exhibiting ME effect at room temperature. Bismuth ferrite $BiFeO_3$ shows the ferroelectric and antiferromagnetic ordering (with a weak ferromagnetic contribution) at room temperature, which opens up broad prospects for its practical application. However, the magnetoelectric interaction in bulk samples of $BiFeO_3$ are low, due to the existence of a complex spatio modulated spin structure of cycloid type. This leads to the absence of a linear MEE in such phases. For the destruction of the incommensurate magnetic structure different techniques are used: the application of a strong magnetic field, the substitution in bismuth ferrite either Bi^{3+} ions, or Fe^{3+} ions, fabrication of thin films of $BiFeO_3$ and others. However, for the observation of ME effect is required a very high magnetic field (~200 kE) [1, 2, 5], so it is difficult to talk about the practical use of such material. It is also worth noting ,that the results for obtaining giant values of ME effect detected on thin films of $BiFeO_3$, were not later confirmed. In this regard, the most promising direction is the substitution of ions in $BiFeO_3$.

The aim of this work was to establish the influence of isovalent substitution regularities in $BiFeO_3$ Bi^{3+} ions by Nd^{3+} ions and Fe^{3+} ions by Co^{3+} ions on the crystal structure, the magnetization and the thermal expansion of the solid solutions.

Experimental procedure. The synthesis of polycrystalline samples of solid solutions $Bi_{1-x}Nd_xFe_{1-x}Co_xO_3$($x$ = 0; 0.02; 0.05; 0.08; 0.10; 0.15; 0.80; 0.85; 0.90; 0.95; 1.0) is carried out by a solid state reactions oxides of of Bi_2O_3, Fe_2O_3, Nd_2O_3 and Co_3O_4. Starting compounds powders taken at predetermined molar ratios, were mixed and milled for 30 minutes in a planetary mill with addition of ethanol. The resulting batch with addition of ethanol was compressed under a pressure of 50–75 MPa into tablets with a diameter of 25 mm and a height of 5–7 mm, which were then calcined at 800°C in air for 8 hours. After prefiring the tablets were crushed, milled, pressed into bars of 30 mm length and a section of 5×5 mm^2. The synthesis conditions in air of samples of a given system depending on the composition varied within wide limits: T = 850–1250°C and duration from 30 minutes to 8 hours. The more ions of bismuth are substituted by rare earth element ions, the higher is the temperature of the synthesis. X-ray diffraction patterns were obtained on a D8 ADVANCE diffractometer using CuK_α-radiation. Specific magnetization (σ_{sp}) of obtained samples at 7 and 300 K in fields up to 14 T and the specific magnetic susceptibility (χ_{sp}) in a magnetic field of 0.86 T in the temperature range of 7–300 K was measured by the oscillation method on a universal high-field measurement system (Cryogenic Ltd, London) and the Faraday method in the temperature range of 77–950 K in the SPC of Belarus NAS of Materials Science. Thermal expansion of the samples was investigated in air in the temperature range of 300–1100 K using quartz dilatometer in dynamic (heating and cooling rates of 3–5 K min^{-1}) mode.

Results and discussion. The results of X-ray analysis of the investigated solid solutions based on bismuth ferrite are shown in Fig. 1.

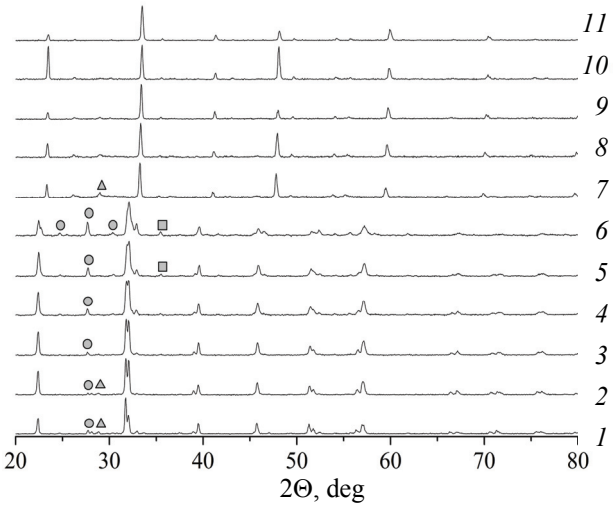

Fig. 1. X-ray diffraction patterns of $Bi_{1-x}Nd_xFe_{1-x}Co_xO_3$samples at different values of *x*: *1* – 0; *2* – 0.02; *3* – 0.05; *4* – 0.08; *5* – 0.10; *6* – 0.15; *7* – 0.80; *8* – 0.85; *9* – 0.90; *10* – 0.95; *11* – 1,0; ● – $Bi_2Fe_4O_9$; ▲ – $Bi_{25}FeO_{39}$; ■ – $CoFe_2O_4$

It has been established that substitution in the $BiFeO_3$ from 2 to 10 mol. % of Bi^{3+} ions by Nd^{3+} ions, and Fe^{3+} ions by Co^{3+} ions formed a continuous series of solid solutions with the structure of the perovskite rhombohedral distortion. The gradual decrease of the parameter *a* and the increase in the angle α of the rhombohedrally distorted perovskite lattice is evident (Table 1).

This is due to a decrease of the effective ionic radius of the ion-substituent (r_{Bi}^{3+} = 1.20 Å [6], r_{Nd}^{3+} = 0.99 Å [6]) for the same anionic environment, with effective ionic radii of the ions Fe^{3+} (r_{Fe}^{3+} = 0.67 Å [6]) and Co^{3+} (r_{Co}^{3+} = 0.64 Å [6]) which are practically identical.

The degree of substitution *x* = 0.15; 0.80; 0.85; 0.90; 0.95; 1.0 forms $Bi_{1-x}Nd_xFe_{1-x}Co_xO_3$ solid solutions with the structure of perovskite orthorhombic distortion. A number of samples of solid solutions contained impurities of ferrites $Bi_{25}FeO_{39}$, $Bi_2Fe_4O_9$ and $CoFe_2O_4$.. Literature data show impossibility of $BiFeO_3$ obtaining without impurities of compounds $Bi_{25}FeO_{39}$, $Bi_2Fe_4O_9$ during the interaction of oxides of bismuth (III) and iron (III) [7–12].

According to some authors, the formation of admixture by products $Bi_{25}FeO_{39}$, $Bi_2Fe_4O_9$ occurs not only by solid-phase synthesis method, but also in the preparation of bismuth ferrite by sol-gel technology [13]. To prevent the formation of $Bi_2Fe_4O_9$ we resort to solid phase reactions with a large Bi_2O_3 excess [14]. However, in this case the impurities of antiferromagnetic $Bi_2Fe_4O_9$ and paramagnetic $Bi_{25}FeO_{39}$ are present, which do not disappear even after additional heat treatment or by leaching with dilute nitric acid [14]. According to the study of the magnetic properties of the solid solutions based on bismuth ferrite it has been shown that depending on the concentration of the replaced ion magnetically biphasic solid solutions areformed. Depending on the specific magnetization σ_{sp} from T for $BiFeO_3$ a sharp maximum at the transition point of antiferromagnetic ordering of the magnetic moments of Fe^{3+}ions in the paramagnetic state is observed, which allows to determine the Neel temperature, $T_N \approx 617$ K (Fig. 2).

With a 2% substitution in $BiFeO_3$ Bi^{3+} and Fe^{3+} ions by Nd^{3+} and Co^{3+} ions, respectively, there is only a partial destruction of antiferromagnetic ordering of the magnetic moments of Fe^{3+} ions. This is evidenced by the presence of anomalies in the form of a jump in the temperature dependence of the specific magnetization, similar to that of the ferrite $BiFeO_3$ (Fig. 3, inset).

Neel temperature for the sample T_N = 593 K is near the Neel temperature of bismuth ferrite T_N = 617 K. Therefore, antiferromagnetism of solid solution $Bi_{1-x}Nd_xFe_{1-x}Co_xO_3$ with *x* = 0.02 can be determined precisely by the presence of phase $BiFeO_3$. The data of X-ray phase analysis shows the change in the lattice parameters with negligible ion substitution. Therefore, the substitution up to 2% of the Bi^{3+} and Fe^{3+} ions by Nd^{3+} and Co^3 ions leads only to a partial destruction of the antiferromagnetic ordering of the magnetic moments of the Fe^{3+} ions.

Table 1

Lattice parameters of solid solutions $Bi_{1-x}Nd_xFe_{1-x}Co_xO_3$

The degree of substitution of *x*	*a*, Å	*b*, Å	*c*, Å	angle α, degree	*V*, Å^3	Structure
0	3.9650	–	–	89.437	62.324	*R* (*R3c*)
0.02	3.9624	–	–	89.494	62.205	*R* (*R3c*)
0.05	3.9590	–	–	89.522	62.048	*R* (*R3c*)
0.08	3.9555	–	–	89.529	61.880	*R* (*R3c*)
0.10	3.9527	–	–	89.568	61.752	*R* (*R3c*)
0.15	3.9482	3.9123	4.0332	–	62.299	*O* (*Pnma*)
0.80	5.3739	7.6152	5.3786	–	220.111	*O* (*Pnma*)
0.85	5.3695	7.5999	5.3615	–	218.791	*O* (*Pnma*)
0.90	5.3532	7.5820	5.3589	–	217.505	*O* (*Pnma*)
0.95	5.3456	7.5712	5.3522	–	216.618	*O* (*Pnma*)
1.0	5.3407	7.5653	5.3433	–	215.886	*O* (*Pnma*)

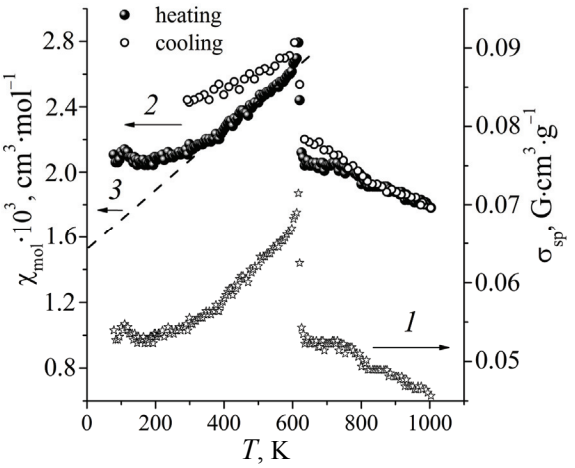

Fig. 2. Temperature dependences of magnetization σ_{sp} (*1*) and molar magnetic susceptibility χ_{mol} (*2*) for $BiFeO_3$ in a magnetic field $H = 0.86$ T. Extrapolation of the linear reduction part χ_{mol} from T to $T = 0$ K (*3*)

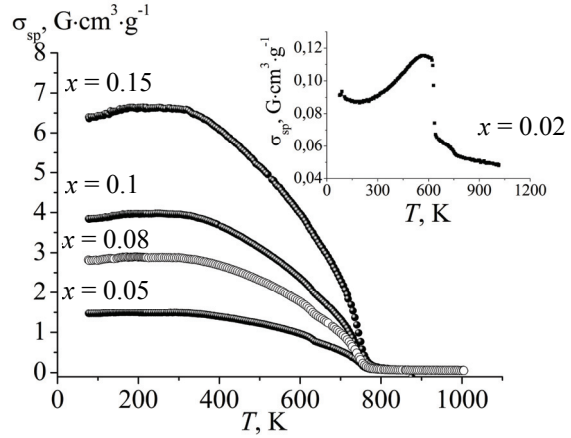

Fig. 3. Temperature dependences of magnetization σ_{sp} for ferroic cobaltites $Bi_{1-x}Nd_xFe_{1-x}Co_xO_3$ samples with varying degrees of substitution x

With increasing degree of substitution of x from 0.05 to 0.15 in $Bi_{1-x}Nd_xFe_{1-x}Co_xO_3$ σ_{sp} increases (Fig. 3). It may be due to structural distortion during the replacement in $BiFeO_3$ of Bi^{3+} ions by ions of rare earth elements with a smaller ionic radius than that of bismuth ions, which leads to the destruction of the spatially modulated spin structure and the appearance of weak ferromagnetism. This behavior is also observed in samples $Bi_{1-x}Ln_xFe_{1-x}Co_xO_3$ (Ln – La^{3+}, Sm^{3+}) at $0.05 \le x \le 0.3$, described in [15–17]. It should be noted that solid solutions $Bi_{1-x}Nd_xFe_{1-x}Co_xO_3$ with $x = 0.10$ and 0.15 contain an admixture of cobalt ferrite $CoFe_2O_4$, which may also contribute to the ferromagnetism of given samples. The presence of admixture cobalt ferrite phase greatly complicates the interpretation of the magnetic properties of these solid solutions. Thus it is reasonable to believe that the ferromagnetism of the samples $Bi_{1-x}Nd_xFe_{1-x}Co_xO_3$ ($0.1 \le x \le 0.15$) is caused not only by the presence of the ferromagnetic phase $CoFe_2O_4$, but by weak ferromagnetism of the main phase as the Curie temperature of given samples (Table 2), and cobalt ferrite differs in 20–50 K (for $CoFe_2O_4$ $T_c = 793$ K [18]), and secondly, even in those samples in which this admixture is missing, there is an increase of the specific magnetization (Fig. 3).

Table 2

The Curie temperature (*Tc*) and the specific magnetization at $T = 300$ K for ferrois cobaltites $Bi_{1-x}Nd_xFe_{1-x}Co_xO_3$

Degree of substitution x	Curie temperature T_c, K	σ_{sp} at $T = 300$ K, $G \cdot cm^3/g$
0.05	772	1.49
0.08	768	2.89
0.1	766	3.96
0.15	765	6.60

It should be said that the temperature dependences of the specific magnetization of the obtained samples (Fig. 3) are characterized by some of the anomalies which are not inherent to ferromagnets: the presence of a diffuse maximum on σ_{sp} from T in the temperature range of 200–350 K, where specific magnetization doesn't increase but decreases with decreasing temperature; as well as the existence at a temperature ~620 K of a small anomaly coincident with the Neel temperature for ferrite $BiFeO_3$. These facts indicate that, in these samples, except the ferromagnetic, there is also an antiferromagnetic phase. Consequently, in the samples $Bi_{1-x}Nd_xFe_{1-x}Co_xO_3$, which dependences σ_{sp} from T have defined above features, the substitution of up to 15% of the ions Bi^{3+}, Fe^{3+} by Nd^{3+}, Co^{3+} ions in the two cation sublattice $BiFeO_3$ does not lead to the complete destruction of antiferromagnetic ordering of the magnetic moments of Fe^{3+} ions in the base compound $BiFeO_3$.

The resulting field dependences of the specific magnetization (Fig. 4) showed the presence of spontaneous and remained magnetization (Table 3), which also confirms the presence of ferromagnetic phase in samples $Bi_{1-x}Nd_xFe_{1-x}Co_xO$ with $x = 0.05$; 0.08, in which there is no admixture of cobalt ferrite $CoFe_2O_4$, and in the samples with $x = 0.10$; 0.15, in which this ferromagnetic phase is present.

Thus, the analysis of the temperature and field dependences of the specific magnetization for samples $Bi_{1-x}Nd_xFe_{1-x}Co_xO_3$ ($0.05 \le x \le 0.15$) shows that their magnetic properties are determined by the coexistence of antiferromagnetic and ferromagnetic phases in them.

Field dependences of the specific magnetization of ferroic cobaltites $Bi_{1-x}Nd_xFe_{1-x}Co_xO_3$ with $x = 0.80$; 0.90 and 1.00 at a temperature of 300 K (Fig. 5*b*) indicate that when the magnetic field intensity is increased up to 14 T specific magnetization of samples increases linearly.

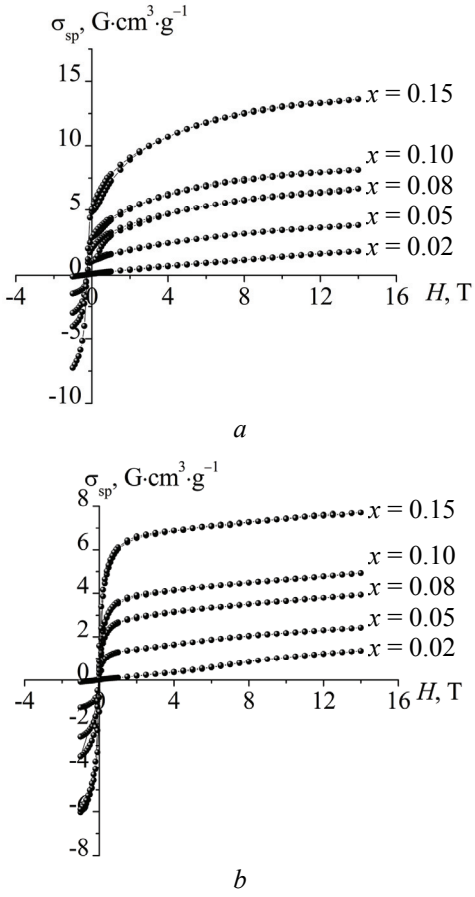

Fig. 4. The dependence of the specific magnetization (σ_{sp}) on the magnetic field intensity (H) at 5 K (*a*) and 300 K (*b*) for $Bi_{1-x}Nd_xFe_{1-x}Co_xO_3$ samples ($0.05 \le x \le 0.15$) with different degree of substitution *x*

Table 3

The values of the spontaneous specific magnetization (σ_0) and the specific magnetization in the magnetic field of 14 T (σ_{14}), the specific residual magnetization (σ_r) at 7 and 300 K for $Bi_{1-x}Nd_xFe_{1-x}Co_xO_3$

Composition *x*	7 K			300 K	
	σ_0, G · cm³/g	σ_{14}, G · cm³/g	σ_r, G · cm³/g	σ_0, G · cm³/g	σ_{14}, G · cm³/g
0.02	0.2	1.8	0.02	0.3	1.4
0.05	2.4	3.8	1.0	1.5	2.4
0.08	4.8	6.7	2.0	2.9	3.9
0.10	6.5	8.1	2.8	3.9	4.9
0.15	11.3	13.6	5.0	6.6	7.7

At a temperature of 5 K in the fields above 2 T (Fig. 5, *a*) there is a trend to magnetization saturation. In this way, for the samples with $x = 0.8$; 0.9; 1.0 in fields 2−12 T magnetic hysteresis is observed, indicating the presence of a phase with the properties of a weak ferromagnet, but with a decrease of the magnetic field from 14 T to zero residual specific magnetization is absent.

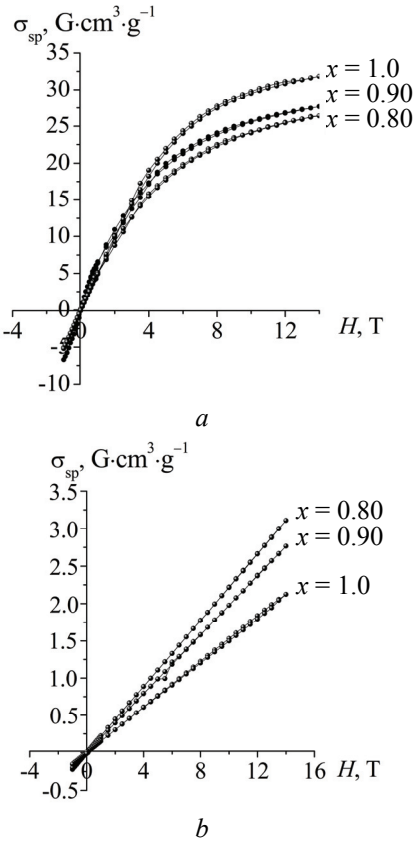

Fig. 5. The dependence of the specific magnetization (σ_{ud}) on the magnetic field intensity (*H*) at 5 K (*a*) and 300 K(*b*) for samples $Bi_{1-x}Nd_xFe_{1-x}Co_xO_3$ with varying degrees of substitution *x*

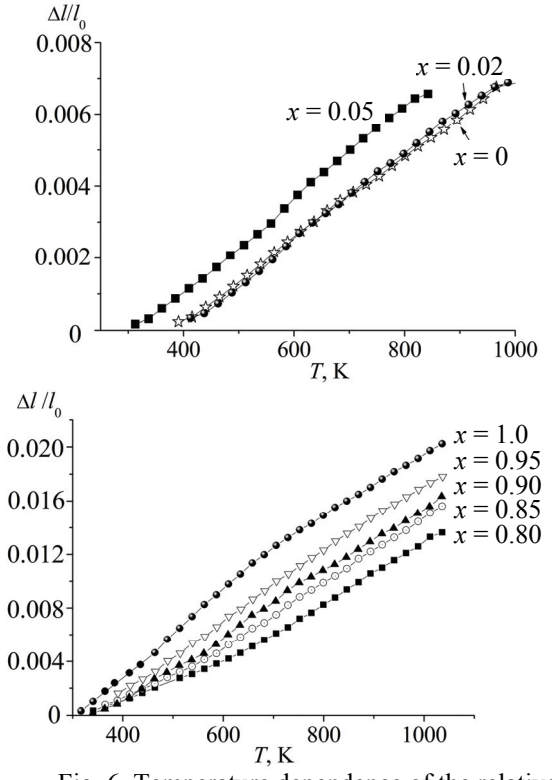

Fig. 6. Temperature dependence of the relative elongation $\Delta l / l_0$ for $Bi_{1-x}Nd_xFe_{1-x}Co_xO_3$ samples with varying degrees of substitution *x*

For more information about the possibility of further practical use of the obtained samples of $(1-x)BiFeO_3 - xNdCoO_3$ system dilatometric studies were conducted. It is shown that for solid solutions $Bi_{1-x}Nd_xFe_{1-x}Co_xO_3$ with minor substitution of bismuth and ironions, dependences of the elongation on the temperature are practically linear (Fig. 6*a*). At the concentration of ions substituents the temperature dependences on the elongation of samples $Bi_{1-x}Nd_xFe_{1-x}Co_xO_3$ $(0.80 \le x \le 1.0)$ become non-linear (Fig. 6, *b*). It is shown that the coefficient value of linear thermal expansion of the samples $Bi_{1-x}Nd_xFe_{1-x}Co_xO_3$ in the temperature range of 400−1000 K with increasing degree of substitution x increases gradually from 11.8×10^{-6} K^{-1} for $BiFeO_3$ to 34.1×10^{-6} K^{-1} for $NdCoO_3$, which may be due to the transition of cobalt ions from the low-spin in the intermediate and the high-spin state.

Conclusion. The solid solutions of $(1-x)BiFeO_3 - xNdCoO_3$ sistem are synthesized by solid-phase reactions method. It is found that the rhombohedral phase is stable at a degree of substitution of $x \le 0.1$, and with a further increase in the concentration of ions substituents solid solutions $Bi_{1-x}Nd_xFe_{1-x}Co_xO_3$ have orthorhombic distortion of the perovskite structure. The studies of the magnetic properties showed that the samples $Bi_{1-x}Nd_xFe_{1-x}Co_xO_3$ $(0.05 \le x \le 0.15)$ are magnetically inhomogeneous; They have both ferromagnetic and antiferromagnetic phases, and they are ferromagnetic materials promising for practical use in various fields of science and technics. Thus the character of the influence of the nature and concentration of substitutional ions on the crystal structure, magnetic properties and thermal expansion of obtained solid solution are identified, which will allow to obtain functional materials with desired properties.

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