УДК 549.5:54-165:536.21:536.413:537.31/.32

L. A. Bashkirov, D. Sc.(Chemistry), professor (BSTU)**; A. K. Bolvako**, assistant lecturer (BSTU);
G. P. Dudchik, PhD (Chemistry), assistant professor, head of department (BSTU);
L. Y. Krisko, PhD (Chemistry), assistant professor (BSTU)

SYNTHESIS OF Bi$_{1-x}$Pr$_x$Fe$_{1-x}$Co$_x$O$_3$ SOLID SOLUTIONS BY SOLID-STATE REACTIONS METHOD USING BiFeO$_3$ AND PrCoO$_3$ PRECURSORS

Solid solutions of BiFeO$_3$ – PrCoO$_3$ system were synthesized by means of the solid-state reactions method using bismuth ferrite, BiFeO$_3$ and praseodymium cobaltite, PrCoO$_3$ precursors. The temperature-time synthesis regimes of the precursors and the solid solutions were selected. The crystal lattices parameters of the solid solutions of Bi$_{1-x}$Pr$_x$Fe$_{1-x}$Co$_x$O$_3$ composition (x = 0; 0.2; 0.5; 1) were determined. The possible mechanisms of formation of the solid solutions from the precursors were proposed.

Introduction. It is known that a number of crystal dielectrics are characterized by spontaneous polarization (electric ordering) in small substance volumes the linear dimensions of which do not exceed 10^{-6} m. In external electric field such substances called magnetoelectrics, or ferroelectrics (FE), show abnormally high polarization which is 10^4–10^5 times higher than that of conventional dielectrics.

Magnetic analogs of FE are ferromagnetics (FM) – materials with spontaneous magnetization (magnetic ordering) in the same substance volumes which are magnetized 10^{10}–10^{11} times stronger than dia- and paramagnetics in the external magnetic field. The ability of FE to polarize in the electric field and the ability of FM to magnetize in the magnetic one are successfully used in various technical devices (in microelectronics, electrooptics, in magnetic recording and sound reproducing systems, etc.). However, modern technology is in need of devices based on materials of new generation which would combine the possibilities of magnetic recording, storage and high-speed and effective information processing, these needs being one of the reasons for the intensive study of substances having the ability to simultaneously respond to the action of electric and magnetic fields. In such substances called multiferroics, or ferroelectromagnetics (FEM), there is a magnetoelectric effect (ME-effect), i.e. the initiation of magnetization M under the action of electric field with intensity E and electric polarization P under the action of the magnetic field with the intensity of H [1]: $M = \alpha E$ and $P = \alpha H$. In other words, for every FEM there is an unambiguous link between E and H which can be expressed in terms of the dE / dH derivative. The value of the derivative is considered to be a quantitative characteristic of the ME-effect observed. Special attention should be paid to the fact that this effect is caused by the action of the static electric field of constant intensity on FEM, which excludes thermal (power) losses, inevitable when electric current passes through the substance.

Thus, by controlling magnetic properties of the substance via the electric field (or on the contrary, by controlling electric properties via the magnetic field), it is possible to build devices to record or read-out information by transforming magnetic ordering or disordering into the electric signal.

The most prospective FEM which can become common use in various electronic devices of the new generation is bismuth ferrite, BiFeO$_3$. This compound is one of few substances which combine electric and magnetic ordering at extremely high temperatures, its ferroelectric Curie temperature (T_C) being 1083 K, and the temperature of transition from antiferromagnetic into paramagnetic state − (T_N) − 643 K [1]. At room temperatures in thin (50–500 nanometers) films of BiFeO$_3$ ME-effect values are dE / dH = 3 V / (cm · E), which considerably exceeds values measured in other FEM at room temperatures [2].

The problem, however, is that the linear ME-effect in bismuth ferrite bulk samples is practically not observed owing to the presence of spatially-modulated spin structure, i.e. disconformity of its anti-ferromagnetic and crystal structures, it being the reason that on the average by volume the ME-effect and spontaneous magnetization are zero [3].

Numerous examinations of bismuth ferrite have shown that a promising way of suppressing spatially-modulated structure and improving its magnetoelectric properties, equally with applying strong magnetic fields and mechanical stress, is a streamlined synthesis of solid solutions based on BiFeO$_3$, i.e. partial replacement of bismuth ions with ions of other metals [4]. Solid solutions based on bismuth ferrite can be divided into two main groups: those with substitution of bismuth ions and those in which iron ions are substituted. As a rule, in the first case ions of rare-earth elements [3] are used, and iron ions are replaced with those of transition metals having close ionic radii (ions of Ti^{4+}, Ni^{2+}).

**Temperature-time regimes of sintering samples and unit cell parameters
for solid solutions and $BiFeO_3$ and $PrCoO_3$ precursors**

Composition	Sintering temperature, °C	Sintering time, h	a, nm	b, nm	c, nm	Cell volume $V \cdot 10^3$ nm^3	Angle α, degree
$Bi_{1-x}Pr_xFe_{1-x}Co_xO_3$ $x = 0.5$	770	4	0.3974	0.3910	0.4038	62.75	–
	800	2	0.3881	0.3877	0.3798	57.14	–
	800	14	0.3869	0.3868	0.3826	57.27	–
	830	4	0.3863	0.3866	0.3805	56.83	–
	850	14	0.3873	0.3864	0.3879	58.06	–
$Bi_{1-x}Pr_xFe_{1-x}Co_xO_3$ $x = 0.2$	770	4	0.3944	–	–	61.34	89.19
	800	2	0.3909	–	–	59.64	88.19
	800	14	0.3902	–	–	59.39	89.39
	830	4	0.3898	–	–	59.23	89.37
$PrCoO_3$	1200	1	0.3783	0.3795	0.3779	54.39	–
$BiFeO_3$	800	8	0.3963	–	–	62.23	89.23

Introduction of impurities of other elements into bismuth ferrite, being an analog of mechanical pressure upon the crystal lattice, makes the existence of spatially-modulated structure energetically unfavorable and permits to obtain ME-effect values which are much high than those observed earlier [4].

This idea has been further evolved at the department of physical and colloidal chemistry, systematic studies of regularities of influence of simultaneous isovalent substitution of Bi^{3+} and Fe^{3+} ions in $BiFeO_3$ with pairs of ions such as La^{3+} and Co^{3+}; Pr^{3+} and Co^{3+}; La^{3+} and Ga^{3+}, etc. on the crystal structure and electromagnetic properties of solid solutions formed being conducted during several years.

Solid solutions of $Bi_{1-x}La_xFe_{1-x}Co_xO_3$ [5], $Bi_{1-x}Pr_xFe_{1-x}Co_xO_3$ [6] and a number of others have been first synthesized by various methods with the use of various initial substances, their properties being investigated. There are no data on this problem in the literature.

The present paper also deals with the study of possibilities to synthesize polycrystalline samples of $Bi_{1-x}Pr_xFe_{1-x}Co_xO_3$ solid solutions by ceramic method with the use of bismuth ferrite, $BiFeO_3$ and cobaltite praseodymium, $PrCoO_3$ as precursors.

Experimental. Bismuth oxide, Bi_2O_3, (p.), iron oxide, Fe_2O_3, (p.a.), praseodymium oxide, Pr_6O_{11}, (p.) and cobalt oxide, Co_3O_4, (p.a.) were used to synthesize polycrystalline samples of bismuth ferrite, $BiFeO_3$, and cobaltite praseodymium, $PrCoO_3$, precursors by ceramic method. Powders of the initial oxides taken in the molar ratios corresponding to $BiFeO_3$ and $PrCoO_3$ compositions were mixed with the addition of ethanol and ground in the Pulverizette 6.0 planetary mill for 30 min. The obtained batch containing ethanol

was pressed under the pressure of 50–75 MPas, tablets of 25 mm in diameter and 5–7 mm high being formed. Bismuth ferrite was synthesized by isothermal annealing of the tablets in the air at 800°C for 8 h; praseodymium cobaltite was synthesized at 1200°C during 1 h (table). Samples were slowly cooled from sintering temperature to the room one, at the speed of about 2–3 deg/min. To prevent tablets interaction with substrate material (Al_2O_3) buffering layer of the batch of appropriate composition was applied to the substrate surface.

To synthesize polycrystalline samples of $Bi_{1-x}Pr_xFe_{1-x}Co_xO_3$ solid solutions, tablets of precursors were crushed in an agate mortar and ground in a planetary mill, then the obtained powders were mixed up in the molar ratios required, ground with the addition of ethanol and pressed to form tablets of 8 mm in diameter and 4-5 mm high. The samples prepared were sintered at temperatures from 770 to 850°C, sintering time varying from 2 to 14 h (Table).

Samples of precursors and solid solutions were identified by X-ray phase analysis (XPA). The D8 Advance Bruker AXS X-ray diffractometer (Germany) was employed to obtain diffraction patterns within an angle range of 2Θ 20–80° with the use of CuK_α radiation. Crystal lattice parameters were determined with the RTP X-ray structural table processor and data from the files of the International Centre for Diffraction Data (ICDD JCPDS).

Results and discussion. Diffraction patterns of the precursors polycrystalline samples are presented in Fig. 1 and 2.

The analysis of diffraction patterns showed that within the RFA method accuracy the obtained samples of $PrCoO_3$ are single-phase and do not contain impurities of oxides not taking part in the reaction (Fig. 1, diffraction pattern 2).
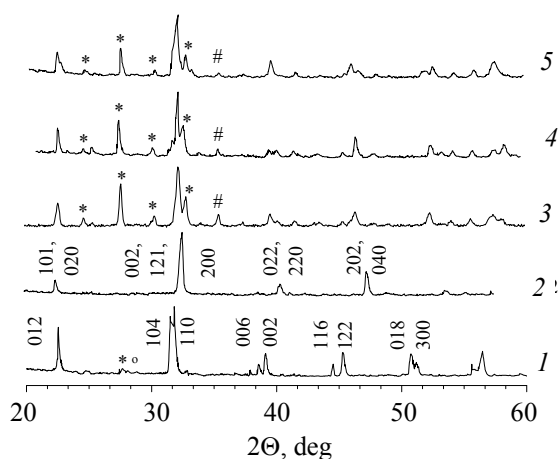
Fig 1. X-ray diffractograms of polycrystalline samples of $BiFeO_3$ (1) and $PrCoO_3$ (2) precursors, $Bi_{1-x}Pr_xFe_{1-x}Co_xO_3$ solid solution ($x = 0.2$) obtained from oxides (3) as in [6] and obtained by us from precursors, where $T = 800°C$, 2 h (4) and $T = 770°C$, 4 h (5).
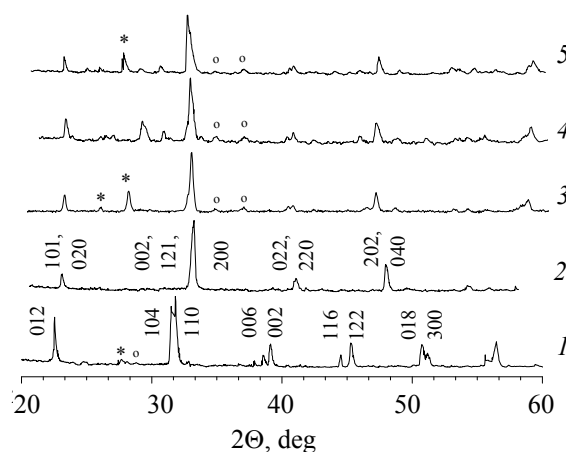– $Bi_{25}FeO_{39}$; o – $Bi_2Fe_4O_9$; # – $CoFe_2O_4$

Fig. 2. X-ray diffractograms of polycrystalline samples of $BiFeO_3$ (1), $PrCoO_3$ (2) precursors, $Bi_{1-x}Pr_xFe_{1-x}Co_xO_3$ solid solution ($x = 0.5$), obtained in [6] from oxides (3) and obtained by us from precursors, where $T = 800°C$, 2 h (4) and $T = 830°C$, 4 h (5).
* – $Bi_{25}FeO_{39}$; o – $Bi_2Fe_4O_9$

On the $BiFeO_3$ diffraction pattern (Fig. 1, diffraction pattern 1) there were small reflexes of impurity phases those of paramagnetic sillenite, $Bi_{25}FeO_{39}$, and anti-ferromagnetic mullite, $Bi_2Fe_4O_9$. Diffraction patterns of $BiFeO_3$ and $PrCoO_3$ are in good agreement with those obtained for these compounds in [6] and with data in the literature on the subject [7] according to which single-phase samples of $BiFeO_3$ can hardly be obtained by solid-phase reaction method.

In Fig. 1 there are also diffraction patterns of polycrystalline samples of the $Bi_{1-x}Pr_xFe_{1-x}Co_xO_3$ solid solution ($x = 0.2$), synthesized at various temperatures and time of sintering (diffraction patterns 4, 5). In Fig. 2 there are diffraction patterns of polycrystalline samples of the $Bi_{1-x}Pr_xFe_{1-x}Co_xO_3$ solid solution ($x = 0.5$). For comparison, in Fig. 1 and 2 there are also diffraction patterns of solid solutions of similar compositions obtained in [6] by sintering appropriate oxides (diffraction patterns 3).

Mixtures of powders of precursors in the molar ratio of $BiFeO_3 : PrCoO_3 = 4 : 1$ were sintered at four temperature – time regimes specified in the table for obtaining the $Bi_{0.8}Pr_{0.2}Fe_{0.8}Co_{0.2}O_3$ solid solution ($x = 0.2$), enriched with bismuth. Taking into account rather low, in comparison with $PrCoO_3$, melting temperature of $BiFeO_3$ (1600°C for $PrCoO_3$ and 950°C for $BiFeO_3$ [8]) sintering temperature did not exceed 830°C.

The analysis of diffraction patterns has shown that after batch sintering at $T = 800°C$ (2 h) in the final product of $Bi_{1-x}Pr_xFe_{1-x}Co_xO_3$ ($x = 0.2$) there is small amount of impurity phases, those of $Bi_{25}FeO_{39}$ and $CoFe_2O_4$ ferromagnetic (fig. 1, diffraction pattern 4).

The increase of sintering temperature up to 830°C (4 h) and duration of heat treatment up to 14 h at $T = 800°C$ has not resulted in the formation of a pure product. This can be regarded as evidence of thermal instability of the $Bi_{0.8}Pr_{0.2}Fe_{0.8}Co_{0.2}O_3$ solid solution and complex mechanism of the studied solid-state reaction proceeding at temperatures not exceeding 800°C. The annealing time being 4 hours, the temperature fall to $T = 770°C$ causes essential reduction of the impurity content in the sample, particularly $CoFe_2O_4$ ferromagnetic impurities that negatively influence the properties of the desired product. Fig. 1 (diffraction pattern 5) shows that the content of the impurity concerned is negligibly small.

To obtain $Bi_{0.5}Pr_{0.5}Fe_{0.5}Co_{0.5}O_3$ ($x = 0.5$) solid solution the powdered precursors mixed in the molar ratio of $BiFeO_3 : PrCoO_3 = 1 : 1$ were sintered at five temperature-time regimes specified in the table.
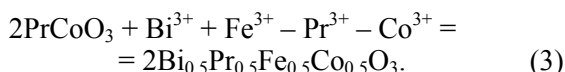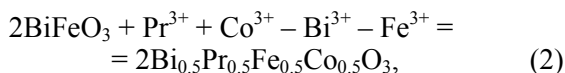
The maximum batch sintering temperature was 850°C, taking into account lowered content of bismuth ferrite in comparison with the previous composition. The samples obtained at $T = 770°C$ (4 h) and $T = 800°C$ (2 h), contained a small amount of anti-ferromagnetic, $Bi_2Fe_4O_9$. The rise of annealing temperature to 830°C (4 h) and 850°C (14 h) lead to almost total disappearance of this impurity phase, however, on the diffraction pattern there is a small reflex caused by the $Bi_{25}FeO_{39}$ paramagnetic. Traces of the $CoFe_2O_4$ ferromagnetic phase were not found in any of the samples concerned (fig. 2). The most optimum regime of synthesizing the $Bi_{0.8}Pr_{0.2}Fe_{0.8}Co_{0.2}O_3$ solid solution should obviously be $T = 830°C$ (4 h).

Comparison of the results obtained with the data given in paper [6] shows (Fig. 1 and 2) that $Bi_{1-x}Pr_xFe_{1-x}Co_xO_3$ solid solutions synthesis from $BiFeO_3$ and $PrCoO_3$ precursors shows more promise as it permits to obtain a product containing minute amount of impurity phases in comparison with samples obtained directly from metal oxides. Besides, the synthesis from precursors makes it possible to reduce sintering temperature from 1000–1200°C [6] to 800 – 850°C as well as the time of heat treatment.

Solid solutions are, obviously, formed by diffusion of ions on the border of the $BiFeO_3$ and $PrCoO_3$ interphase. Two possible mechanisms of diffusion can be proposed – two-way (Fig. 3) and one-way (Fig. 4) diffusion. According to the example of forming two formula units of $Bi_{0.5}Pr_{0.5}Fe_{0.5}Co_{0.5}O_3$ solid solutions shown as:

$$BiFeO_3 + PrCoO_3 = 2Bi_{0.5}Pr_{0.5}Fe_{0.5}Co_{0.5}O_3 \quad (1)$$
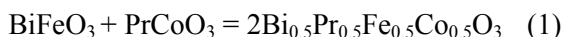
the scheme of two-way diffusion can be expressed in the following way:

$$2BiFeO_3 + Pr^{3+} + Co^{3+} - Bi^{3+} - Fe^{3+} =$$
$$= 2Bi_{0.5}Pr_{0.5}Fe_{0.5}Co_{0.5}O_3, \quad (2)$$

$$2PrCoO_3 + Bi^{3+} + Fe^{3+} - Pr^{3+} - Co^{3+} =$$
$$= 2Bi_{0.5}Pr_{0.5}Fe_{0.5}Co_{0.5}O_3. \quad (3)$$

By adding together the equations (2) and (3) we receive an overall equation (1). The arrows show the direction of ions moving from one crystal lattice to another, the dashed line outlines a new phase generating area, that of $Bi_{0.5}Pr_{0.5}Fe_{0.5}Co_{0.5}O_3$ solid solution (Fig. 3 and 4).
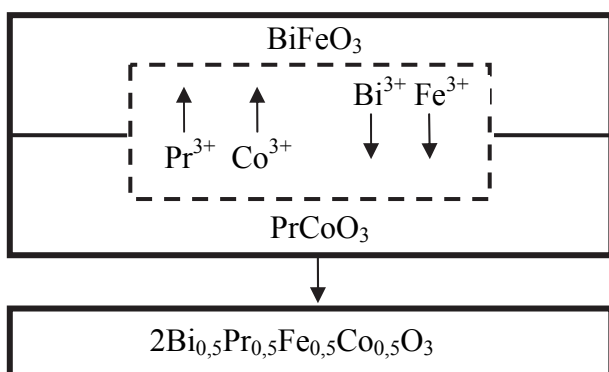
Fig. 3. The scheme of two-way diffusion of Bi^{3+}, Fe^{3+}, Pr^{3+}, Co^{3+} ions, when generating two formula units of the $Bi_{0.5}Pr_{0.5}Fe_{0.5}Co_{0.5}O_3$ solid solution from precursors $BiFeO_3$ and $PrCoO_3$

As the melting temperature of $BiFeO_3$ is much lower than that of $PrCoO_3$, it can be expected that because of higher mobility of bismuth ferrite crystal lattice ions in comparison with that of Pr^{3+} and Co^{3+} ions there can be one-way diffusion of Bi^{3+}, Fe^{3+} and O^{2-} from the crystal lattice of $BiFeO_3$ into that of $PrCoO_3$ according to the scheme shown in Fig. 4.
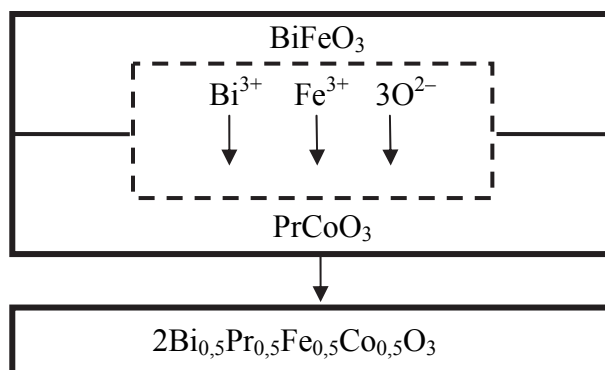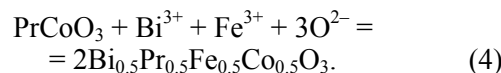
Fig. 4. The scheme of one-way diffusion of Bi^{3+}, Fe^{3+}, O^{2-} ions from the crystal lattice of the $BiFeO_3$ precursor into the lattice of $PrCoO_3$ when generating two formula units of the $Bi_{0.5}Pr_{0.5}Fe_{0.5}Co_{0.5}O_3$ solid solution

The material ionic charge balance corresponds to the scheme given in Fig. 4, according to the equation

$$PrCoO_3 + Bi^{3+} + Fe^{3+} + 3O^{2-} =$$
$$= 2Bi_{0.5}Pr_{0.5}Fe_{0.5}Co_{0.5}O_3. \quad (4)$$

Bismuth ferrite, $BiFeO_3$, has a rhombohedral and praseodymium cobaltite – orthorhombic perovskite structure respectively [1, 4]. Diffraction patterns of samples of the $Bi_{0.8}Pr_{0.2}Fe_{0.8}Co_{0.2}O_3$ solid solution enriched with bismuth have shown that it has the structure of a rhombohedrally distorted perovskite unit cell. The parameters of a lattice unit cell of the $BiFeO_3$ precursor calculated by us as well as those of solid solutions are specified in the table. There is good agreement of parameter values of a unit cell of $BiFeO_3$ with data in work [5]. For a solid solution the most preferable parameter values a and α are those corresponding to the sample obtained by sintering at $T = 770°C$ for 4 h (Table). As noted above, this sample is practically free from such impurity as the $CoFe_2O_4$ ferromagnetic.

$Bi_{0.5}Pr_{0.5}Fe_{0.5}Co_{0.5}O_3$ solid solutions with equimolar content of precursors had an orthorhombic crystal structure. We consider that the most reliable parameter values are those corresponding to the sample obtained by sintering precursors at $T = 830°C$ for 4 h (Table).

Conclusion. Solid solutions of $Bi_{1-x}Pr_xFe_{1-x}Co_xO_3$ compositions ($x = 0$; 0.2; 0.5; 1) were first synthesized by the solid-phase reaction method in the $BiFeO_3$ – $PrCoO_3$ dual system with the use of precursors – bismuth ferrite, $BiFeO_3$ and praseodymium cobaltite, $PrCoO_3$. The precursors are obtained preliminarily by sintering appropriate oxides. Temperature and time regimes of synthesizing precursors and solid solutions are established. Crystal lattice parameters of solid solutions synthesized are determined.

In comparison with the $Bi_{1-x}Pr_xFe_{1-x}Co_xO_3$ solid solutions synthesis directly from metal oxides, the method to obtain them from the $BiFeO_3$ and $PrCoO_3$ precursors is more advanced as the final product contains only minute amounts of impurity phases. Moreover, the synthesis from precursors makes it possible to substantially reduce the sintering temperature of initial samples.

Studying the conditions of the synthesis of the $Bi_{25}FeO_{39}$ paramagnetic precursor enriched with bismuth ferrite can be the next step forward in the trend under development i.e. obtaining advanced ferroelectromagnetics based on bismuth ferrite. Solid-phase interaction of the precursor involved with iron oxide according to the following reaction

$$Bi_{25}FeO_{39} + 12Fe_2O_3 = 25BiFeO_3$$

is likely to permit obtain bismuth ferrite with improved ferroelectromagnetic characteristics.

The work is performed within a complex task 1.02 of GIP "Functional materials and technologies, nanomaterials".

References

1. Макоед, И. И. Получение и физические свойства мультиферроиков: монография / И. И. Макоед. – Брест: БрГУ, 2009. – 181 с.

2. Epitaxial $BiFeO_3$ multiferroic thin film heterostructures / J. Wang [et al.] // Science. – 2003. – Vol. 299. – P. 1719–1722.

3. Звездин, А. К. Фазовые переходы и гигантский магнитоэлектрический эффект в мультиферроиках / А. К. Звездин, А. П. Пятаков // Успехи физических наук. – 2004. – Т. 174, № 4. – С. 465–470.

4. Пятаков, А. П. Магнитоэлектрические материалы и мультиферроики / А. П. Пятаков, А. К. Звездин // Успехи физических наук. – 2012. – Т. 182, № 6. – С. 593–620.

5. Физико-химические свойства твердых растворов $Bi_{1-x}La_xFe_{1-x}Co_xO_3$, синтезированныхс использованием различных методов / А. А. Затюпо [и др.] // Труды БГТУ. – 2012. – № 3 (150): Химия и технология неорган. в-в. – С. 37–41.

6. Синтез, структура и физико-химические свойства твердых растворов в квазибинарной системе $BiFeO_3 – PrCoO_3$ / А. И. Клындюк [и др.] // Вести Нац. акад. наук Беларуси. Сер. хим. наук. – 2012. – № 4. – С. 5–9.

7. Морозов, М. И. Особенности образования $BiFeO_3$ в смеси оксидов висмута и железа (III) / М. И. Морозов, Н. А. Ломанова, В. В. Гусаров // Журнал общей химии. – 2003. – Т. 73, Вып. 11. – С. 1772–1776.

8. Портной, К. И. Кислородные соединения редкоземельных элементов / К. И. Портной, И. И. Тимофеева. – М.: Металлургия, 1986. – 480 с.