Stoichiometric modification of BiFeO$_3$ / REE to create new materials and methods for their design for artificial intelligence systems

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Abstract. The article discusses the effects of modifying bismuth ferrite BiFeO$_3$ with rare-earth elements, REE, (large-sized, group 1, with 0.94 ≤ R ≤ 1.04 Å – La, Pr, Nd, Sm, Eu, Gd, medium-sized, small-sized Group 2, with R <0.94 Å – Tb, Dy, Ho, Er, Tm, Yb, Lu). The authors describe the study results of the influence of the crystallophysical parameters of stoichiometrically introduced dopants on the type of phase diagrams of Bi$_{1-x}$REE$_x$FeO$_3$ systems, the grain structure of ceramics, the dielectric spectra of samples, and the behaviour of their thermophysical characteristics over a wide temperature range. They show the possibility of using new multiferroic materials in artificial intelligence systems.

1. Introduction
At the current stage of development, science and technology in the Russian Federation are becoming a decisive factor that ensures the country's ability to meet big challenges with significant risks, especially for the economy: exhaustion of raw materials, demographic changes in society, an increase in anthropogenic pressures on humans and the environment, the need to increase Russia's competitiveness in world markets, etc. All this determined the contemporary priorities and prospects of the scientific and technological development of the Russian Federation, including in the material science field, which will create a transition to new materials and methods for constructing them for artificial intelligence systems, to environmentally friendly, resource-saving energy [1]. In this regard, we consider relevant research aimed at establishing correlation relationships: composition – phase state diagrams – grained landscape – dielectric/thermophysical properties of environmentally friendly compositions based on solid solutions, SS, BiFeO$_3$ promising spintronics materials [2].
2. Methods and materials

The objects of the study were following SS: Bi, REE, FeO3 (REE = La, Pr, Na, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu; 0 ≤ x ≤ 0.5; Δx = 0.025; 0.05; 0.10).

The main method for preparing the analyzed SS is double solid-phase synthesis with intermediate grinding and granulation of dispersed crystalline powders, sintering using conventional ceramic technology.

Synthesis and sintering modes: \( T_1 = 1063 \div 1183 \, \text{K}, \, \tau_1 = 5 \, \div \, 10 \, \text{h}; \, T_2 = 1073 \div 1183 \, \text{K}, \, \tau_2 = 4 \, \div \, 10 \, \text{h}; \, T_{\text{sintering}} = 1143 \div 1273 \, \text{K}, \, t_{\text{sintering}} = 1.5 \div 2 \, \text{h}; \) we performed X-ray diffraction studies at room temperature using the powder diffraction method with a DRON-3 diffractometer and vapour pressure apparatus, VPA (Sokol – radiation; Mn – filter; Bragg – Brentano focusing scheme). We used a VPA-1 automatic diffractometer with a VEB Freiberger Praxismechanik goniometer for studying a high-temperature (300–1000) K) study of the crystalline structure of SS. X-ray density \( (\rho_{\text{x-ray}}) \) was determined by the formula: \( \rho_{\text{x-ray}} = 1.66 \times \frac{M}{V}, \) where \( M \) is the weight of the formula unit in grams, \( V \) is the volume of the perovskite cell in \( \text{Å}^3 \).

The measurement errors of structural parameters have the following values: linear \( \Delta a = ab = \Delta c = \pm (0.002 ... 0.004) \, \text{Å}; \) angular \( \Delta \alpha = 3 \, '; \) volume \( \Delta V = \pm 0.05 \text{Å}^3 \) (\( \Delta V / V \times 100 \% = 0.07 \% \)).

We determined the experimental \( (\rho_{\text{exp}}) \) density of the samples by hydrostatic weighing where we used octane as a liquid medium. Relative density \( (\rho_{\text{rel}}) \) was calculated by the formula \( \left( \frac{\rho_{\text{exp}}}{\rho_{\text{x-ray}}} \right) \times 100 \% \).

We studied the grain structure of objects using a Neoophot 21k optical microscope and a Leica DMI-5000M inverted high-precision microscope.

We used a special bench constructed by the Scientific Research Institute of Physics of the Southern Federal University with Agilent 4980A, WayneKerr 6500B precision LCR meters for studying the high-temperature dielectric spectra. We determined specific heat capacity \( (C_p) \) by a capacitive dilatometer developed at the Institute of Physics, DSC RAS; we studied thermal diffusivity \( (\chi) \) by laser flash using an LFA 457 G Microflash installation of the German company NETZSCH; we calculated thermal conductivity \( (\lambda) \) according to the formula: \( \lambda(T) = \chi(T)C_p(T)\rho_{\text{exp}}(T)[3] \).

3. Results

Figure 1–2 shows the dependence of the structural characteristics and densities of the 1st group objects on the content \( (x) \) of modifiers. All cases of the state diagram contain five concentration regions corresponding to successive structural transformations \( Rh \rightarrow Rh + R \rightarrow Rh + R + R \rightarrow R + R \rightarrow R \) with small variations in the phase filling, and Figure 3 illustrates the position dependences of the boundaries of the existence of the pure \( Rh \) phase, its mixture with the \( R \) – and \( R \) – phases, and the differences between \( R_{\text{Rh}} \) and \( R_{\text{REE}} \), \( V_{\text{exp}} \) and \( V_{\text{theor}} \) (\( \Delta V \)) on the radius, \( R \), REE.

The stabilization of the \( Rh \) phase upon the introduction of La, Pr, Nd (with \( R \geq 0.99 \text{Å} \)) probably results from the creation of the most favourable (dimensional) conditions for the existence of BiFeO3, which, as is known [4], has a boundary position in the perovskite family. At lower \( R \), the shift of the \( Rh \) – boundary toward lower REE concentrations is a consequence of a significant deviation of the conditions from the necessary for the formation of SS substitution (\( \Delta R \) should be less than 15 % [5]). The latter resulted in the stability loss of the region of coexistence of the \( Rh \)– and \( R \) – phases due to the greater instability of the structure of multiphase SSs compared to single-phase ones.
Figure 1. Dependences of the structural characteristics and densities of bismuth ferrite with large REEs: La (a), Pr (b), Nd (c), Sm (d), Eu (e), Gd (f) versus modifier concentration (x). On Figure (a) – 1 – theoretical, 2 – experimental perovskite cell volumes, 3 – 4 – \( \Delta d / d \), 5 – \( \rho \_exp \), 6 – \( \rho \_rel \); on Figure (b) – 1, 2, 3 – \( \lambda \), \( V_{Rh} \), 5, 6 – \( a, c, V_{Rh} \), 8, 9, 10, 11 – \( a, b, c, V_{Rh} \), respectively, 4 – microdeformations, \( \Delta d / d \); on Figure (c) – 1, 2, 3, \( a, \lambda, V_{Rh} \), 4, 5, 6 – \( a, b, c, \lambda, V_{Rh} \), respectively, 7, 8, 9, 10, 11 – \( \alpha, a, b, c, V_{Rh} \), respectively, 12 – \( V_{theor} \) perovskite cell; on fig (d) 1, 2, 3 – \( a, \lambda, V_{Rh} \), 4, 5, 6 – \( a, b, c, V_{Rh} \), 7, 8, 9, 10 – \( a, b, c, V_{Rh} \), respectively; on fig (e) 1, 2, 3 – \( a, \lambda, V_{Rh} \), 4, 5, 6 – \( a, \lambda, V_{Rh} \), 7, 8, 9, 10 – \( a, \lambda, V_{Rh} \), respectively; on Figure (f) 1, 2, 3 – \( a, \lambda, V_{Rh} \), 5, 6, 7, 8 – \( a, \lambda, \lambda, V_{Rh} \), 3 – \( \Delta d / d \), respectively. Straight lines without experimental points are the dependences of \( V_{theor} \) (x) calculated for SS substitution in \( A \) positions.
Figure 2. Dependences of the structural characteristics and densities of bismuth ferrite with medium-sized: Tb (a), Dy (b), Ho (c) and small-sized: Er (d), Tm (e), Yb (f), Lu (g) REEs depend on the concentration \( x \) of the modifier. On Figure (a):

1, 2, 3 – parameter \( a \), angle \( \alpha \), volume \( V \) of the rhombohedral cell, 4, 5, 6, 7 – parameters \( b, a \), angle of the rhombic cell, respectively. On Figure (B-j):

\[ 89.42, 92.02, 3.96 \]

\[ 89.48, 89.54, 3.97 \]

\[ 89.44, 89.50, 3.97 \]

\[ 89.46, 89.52, 3.97 \]

\[ 89.48, 89.54, 3.97 \]

\[ 89.44, 89.50, 3.97 \]

\[ 89.48, 89.54, 3.97 \]

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\[ 89.48, 89.54, 3.97 \]

\[ 89.44, 89.50, 3.97 \]
Figure 3. a – Dependences of the position of the boundary \( x \) of the existence of a pure \( Rh \) phase, its mixture with \( R_{1,2} \) phases, the relative difference between \( \bar{R}_{Bi} \) and \( \bar{R}_{REE} \) (\( \Delta \bar{R} \)) on the radius \( \bar{R} \), REE

\( b-d \) – Dependencies of the difference between \( V_{\text{exp.}} \) and \( V_{\text{Theor.}} \) (\( \Delta V \)) from the ionic radius, \( \bar{R} \), REE in SS with \( x = 0.05 \) (b); 0.10 (s); 0.15 (d)

The reasonableness of the above assumption is also confirmed by the behaviour of \( \Delta V \) (Figure 3, a) which characterizes the structural nonstoichiometry of BiFeO\(_3\) – compounds with a variable valence ion (\( \text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+} \)) and, as a result, it is vacancy-saturated with the defect situation excluded by a crystallographic shift with the development of anion and A – deficiency [6]. At low REE contents (Figure 3, b-d), their effect is minimal, and \( \Delta V_{0.05} \) is practically independent of \( \bar{R} \) REE against the background of a noticeable spread in \( \Delta V \) values.

At large \( x \), in the region with \( \bar{R} > 0.99 \) Å, \( \Delta V \) changes little contributing to the stabilization of the Rh phase, and at \( \bar{R} < 0.99 \) Å in the case \( x = 0.10 \), \( \Delta V_{0.10} \), grows naturally with decreasing \( \bar{R} \) destabilizing \( Rh \) – \( Rh + R_{1,2} \) phases; in the case of \( x = 0.15 \), the decrease in structural non-stoichiometry, apparently, resulted not so much from size effects as the specifics of other crystallographic characteristics of the introduced REEs.

In the second group of SSs, the Rh phase characteristic of BiFeO\(_3\) either remains in the entire range of REE concentrations (Ho, Tm, Yb, Lu) or coexists with the arising R phase (Tb, Dy, Er). Such a simplification of the phase patterns is due to a large amount of Bi– and Fe-containing impurities usually concomitant with the formation of BiFeO\(_3\) and to ballast phases of the non-perovskite structure with the participation of REEs, the amount of which increases with decreasing \( \bar{R} \) REE. Figure 4 shows it with microphotographs of the grain structures of the studied objects. The accumulation of such phases, grey grains, in the La \( \rightarrow \) Lu ranges leads to loosening of the microstructure, thickening of the crystallite boundaries and deforming the habit of the grains of the main phase.

Figure 5 shows the dependences \( \varepsilon'/\varepsilon_0 \) (T), \( \varepsilon''/\varepsilon_0 \) (T), \( \tan \delta \) (T) on different frequencies of an alternating electric field. The results indicate the formation of a relaxation maximum \( \varepsilon'/\varepsilon_0 \) in BiFeO\(_3\) with all large-sized REEs and some small-sized REEs near (400–450) K and a frequency-dependent maximum \( \tan \delta \) near 600 K. While the position of latter shifts toward lower temperatures in the process of enrichment of BiFeO\(_3\) with introduced REEs. With small-sized REEs, the first maximum is localized near (550 ... 600) K, the second is near (750 ... 800) K.
We developed $ln\omega (1 / T_m)$ graphs, where $T_m$ is the temperatures of the extrema $\varepsilon \prime / \varepsilon_0$ measured at a frequency $f = \omega / 2\pi$, to describe the process of low-temperature dielectric relaxation according to the data obtained from the dependences $\varepsilon \prime / \varepsilon_0 (\omega)$. The obtained dependences satisfy the Arrhenius law with an activation energy $E_a$ close to 1 eV (in BiFeO$_3$ $E_a = 1.007$ eV) and an average time to overcome the potential barrier $\approx 1.06 \times 10^{-16}$ s, which is typical for Maxwell – Wagner relaxation [7], associated with the accumulation of free charges at the interface of components in spatially inhomogeneous media against the background of interlayer, interphase, and intraphase rearrangements. The reason for its development is the natural composite structure of BiFeO$_3$ and Bi$_{1-x}$REE$_x$FeO$_3$ (x = 0.10), which forms based on at least four (except for BiFeO$_3$ itself) Bi-Fe-containing compounds (Bi$_2$O$_3$, Fe$_2$O$_3$, Bi$_{25}$FeO$_{40}$, Bi$_2$Fe$_4$O$_9$) that almost always accompany the formation of BiFeO$_3$, remaining in it (in different quantities) in the form of ballast phases and undergoing a series of bifurcations in the above temperature ranges (Figure 6) [8].

Dependences of thermophysical characteristics (Figure 7-9) on temperature are traditional with maxima and minima near $T_N$. 
Figure 5. Dependences $\varepsilon' / \varepsilon_0 (T)$, $\varepsilon'' / \varepsilon_0 (T)$, $\tan \delta (T)$ at different frequencies of the alternating electric field BiFeO$_3$ (left), Bi$_{0.9}$REE$_{0.1}$FeO$_3$ (bottom), in the frequency range $(25 \div 1, 5 \times 10^6)$ Hz.

Figure 6. Dependences of the unit cell volumes of compounds – components of the naturally – composite BiFeO$_3$ structure (I – III – regions of the invar effect)
Cp, J/g•K

Figure 7. (a). Temperature Dependences of Heat Capacity on Bi$_{1-x}$REE$_x$FeO$_3$ (Several curves in each figure correspond to different REE concentrations in BiFeO$_3$)

χ, mm$^2$/s

Figure 8. Dependences of thermal diffusivity on the temperature of Bi$_{1-x}$REE$_x$FeO$_3$ (Several curves in each figure correspond to different REE concentrations in BiFeO$_3$)
Figure 9. Dependences of thermal conductivity on temperature Bi$_{1-x}$REE$_x$FeO$_3$ (Several curves in each figure correspond to different REE concentrations in BiFeO$_3$)

4. Conclusion
The authors showed the possibility of using multiferroic based on BiFeO$_3$ in artificial intelligence systems.

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