Effects of modification of bismuth ferrite with small-sized rare earth elements

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Abstract. The phase and grain structures and the dielectric properties of solid solutions (SS) of bismuth ferrite modified with small-sized rare-earth elements (SRE) are studied. The regularities of the appearance of impurities of various compositions depending on the ion radius and SRE concentration in objects are revealed. Based on the analysis of the dielectric spectra of the SSs, the development of Maxwell-Wagner relaxation associated with the accumulation of fSRE charges at the interfaces between the components was established in them. The conclusion is made about the possibility of using the results obtained when creating a new generation of multifunctional materials.

1. Introduction

Recently, there has been a rapid increase in interest in a wide class of substances – multiferroics based on bismuth ferrite, due to the combination of magnetic (TN ~ 643 K), and ferroelectric (Tc ~ 1083 K) orderings [1]. However, it was most often not possible to synthesize thermally stable powder products suitable for producing ceramics [2]. The introduction of rare-earth elements (SRE) makes it possible to stabilize the structure of bismuth ferrite, optimize its properties, and also strengthen the interaction between magnetic and electrical properties by suppressing the spatially modulated magnetic structure [3]. In this case, in most works, the effects of BiFeO3 modification by large-sized SREs with 0.94 ≤ R ≤ 1.04 Å (La, Pr, Nd, Sm, Eu, Gd) are studied. Information on the effect of small-sized SREs with R ≤ 0.94 Å on the internal structure (crystalline, grain) and the BiFeO3 macroresponses is practically absent in the literature. In this connection, the aim of this work was to establish the features of phase formation, the formation of a polycrystalline (grain) structure and the dielectric properties of ceramic samples of solid solutions (SS) of bismuth ferrite modified with small SREs.

2. Methods and materials

The objects of study were SS binary systems of the form Bi1-xSRExFeO3, где SRE=Tb (0.89), Dy (0.88), Ho (0.86), Er (0.85), Tm (0.85), Yb (0.81), Lu (0.80) (in brackets are given the values of ionic radii SRE, R, in Å according to [4]), x = 0.05–0.20, Δx = 0.05. Samples were obtained using conventional ceramic technology, including two-stage synthesis from oxides Bi2O3, Fe2O3, SRE2O3, BiFeO3.
high purity at temperatures $T_1 = 1070$ K, 10 h; $T_2 = 1070–1120$ K, 5 h (depending on the composition, with an increase in $T_2$ by 10 degSREs for every 5 mol.% SRE), and subsequent sintering without pressure at temperatures $T_{sp} = 1140–1200$ K, 5 h (depending on a composition) [5].

X-ray diffraction studies were performed by powder diffraction using a DRON-3 diffractometer (filtered Co $k_{α}$ radiation, Bragg-Brentano focusing scheme). The calculation of structural parameters (linear parameters of the cell; experimental, $V_{exp}$ and theoretical, $V_{theor}$, volumes) was carried out according to the standard method [6]. The experimental ($\rho_{exp}$) density of the samples was measured by hydrostatic weighing in octane; X-ray density calculation ($\rho_{x-ray}$) were calculated according to the formula: $\rho_{x-ray} = 1.66xM/V$, where $M$ is the weight of the formula unit in grams, $V$ is the perovskite cell volume in $\text{Å}^3$; the relative density ($\rho_{rel}$) was calculated by the formula ($\rho_{exp}/\rho_{x-ray}$)$\times100\%$.

The polycrystalline (grain) structure of multiferroics was studied in reflected light using a Neophot 21 optical microscope and an Leica DMI 5000M inverted high-precision microscope.

The relative permittivity ($\varepsilon/\varepsilon_0$) was studied on a special bench using an Agilent E4980A precision LCR meter in wide temperature ranges (300–800 K) and frequencies ($f$) of an alternating measuring field (20–2$\times$10$^6$ Hz).

### 3. Results

X-ray phase analysis carried out at room temperature showed (Table 1) that all the studied SSs contain impurity phases $\text{Bi}_2\text{Fe}_4\text{O}_{12}$ (1) (S.G. 123, $a = 10.181$ Å, cubic symmetry), $\text{Bi}_2\text{Fe}_3\text{O}_9$ (2) (S.G. Pbam, $a = 7.965$ Å, $b = 8.44$ Å, $c = 5.994$ Å, rhombic symmetry), usually concomitant formation of $\text{BiFeO}_3$ [7], and phases with a garnet-type structure SRE$_2$Fe$_5$O$_{12}$ (3) (cubic symmetry, space group Ia3d) [8], the concentration of which varies depending on the type of SRE and their concentration. Thus, compound (1) enriched in bismuth is always formed, and (2) enriched in iron, in cases where $I_{m}/I_{exp}$ phases (3) less than 10 % (excluding SS composition $\text{Bi}_{10.85}\text{Y}_{0.15}\text{O}_{12}$, in which a small amount of compound (2) is fixed in the presence of ~ 40% $I_{m}/I_{exp}$ phase (3)). The smallest number of ballast phases (1), (2) is characteristic of TPs with larger SRE cations (Tb), and a larger number of TPs with Lu — the smallest of all SREs. At the same time, a minimum of such impurities is contained in TR phases (1), (2) is characteristic of TPs with larger SRE cations into the base structure $\text{BiFeO}_3$ significantly exceeds the values of parameter $a$ of the SRE$_2$Fe$_5$O$_{12}$. This means that during the synthesis of SS ($\text{Bi}_{1-x}\text{SRE}_x$)Fe$_3$O$_9$ apparently, SSs of the form (SRE$_{1-x}\text{Bi}_x$)$_3$Fe$_5$O$_{12}$ are formed, which is indirectly confirmed by the identity of the dependences of the cubic cell parameters of the SRE$_2$Fe$_5$O$_{12}$ and SS compounds of this type on the ionic radius SRE (Fig. 2). In this case, the stoichiometry of a given composition is violated due to the “departure” of Bi from the base structure. This explains the absence of this impurity in SS with SRE, in which a sufficiently large amount of Bi-containing impurities crystallizes already (1), (2).
Figure 1. Dependence of \( \frac{I_{ip}}{I_{imp}} \) of the impurity phase of the SRE\(_3\)Fe\(_5\)O\(_{12}\) type on the SRE concentration. The inset shows the dependence of the minimum SRE concentration at which phase (3) is already formed on the \( R_i \) of the SRE cation.

Figure 2. Dependencies of the parameters of cubic connection cells SRE\(_3\)Fe\(_5\)O\(_{12}\) according to the JCPDS database) (1) and SS (SRE\(_{1-y}\)Bi\(_y\))\(_3\)Fe\(_5\)O\(_{12}\) (2) from SRE ionic radius.

The table shows that SS (Bi\(_{1-x}\)Tb\(_x\))FeO\(_3\) and (Bi\(_{1-x}\)Dy\(_x\))FeO\(_3\) undergo a transition from the rhombohedral (Rh) phase to the morphotropic area (MA) containing a mixture of Rh and a rhombic (R) with monoclinic (M) subcell (the latter is of the type of GdFeO\(_3\), implemented in SREFeO\(_3\) compound). All other SSs belong to the Rh area (except for the SS composition Bi\(_{0.8}\)Er\(_{0.2}\)FeO\(_3\) with "traces" of the R phase). The absence of MA in these SSs may be due to the formation of garnet-like structures, as a result of which the SRE concentration decreases and the Rh \( \rightarrow \) R transition becomes impossible.

In fig. Figure 3 shows the changes in the volumes of rhombohedrally distorted elementary perovskite cells of the studied SS. In almost all SS V cells decrease with increasing SRE, which corresponds to the logic of decreasing the average radius of the A cation, the exception is SS with Er and Lu, in which V increases, and SS with Yb, in which V remains almost unchanged. This, as well as the fact that, at the same concentration (starting from x = 0.10) of the introduced SRE V does not decrease with a decrease in the average radius of the A cation, is a consequence, as noted earlier, of the crystal chemical features of the formed SS: for small and large x, most likely, SS embeddings are formed, with medium SS substitutions or a combined type. R cell options \((a = c, b, \beta)\) SS composition
Bi$_{0.85}$Tb$_{0.15}$FeO$_3$, Bi$_{0.80}$Tb$_{0.20}$FeO$_3$, and Rh cells (α, α) Bi$_{0.90}$Dy$_{0.10}$FeO$_3$ are equal, so, 3.910 Å, 3.902 Å, 92.02°; 3.911 Å, 3.903 Å, 92.08°; 3.954 Å, 89.48°.

Table 1. The relative intensity of the strong line of the impurity phase, (I approx/I first), SS symmetry and density Bi$_1$,$_x$SRE,$_y$FeO$_{3}$, experimental and tabular values of the cubic cell parameter of the SRE$_3$Fe$_2$O$_{12}$ compounds, impurity phases formed during the solid-state synthesis of SS species (Bi$_1$,$_x$SRE,$_y$)FeO$_3$, (25-1-40) relates to Bi$_{32}$FeO$_{40}$; (2-4-9) − Bi$_{32}$Fe$_2$O$_{40}$.

| Chemical formula | I approx/I first | Symmetry | $P_{\text{exp.}}$ r/CM$^3$ | $P_{\text{cent.}}$ r/CM$^3$ | $P_{\text{rel.}}$ % | $d_{\text{exp.}}$ Å | $d_{\text{tab.}}$ Å | JCPDS |
|------------------|------------------|----------|--------------------------|--------------------------|----------------|----------------|----------------|------|
| (Bi$_{0.85}$Tb$_{0.15}$)FeO$_3$ | 7(25-1-40) | Rh | 7.67 | 8.35 | 91.88 | 7.06 | 8.29 | 85.18 | 12.509 |
| (Bi$_{0.90}$Tb$_{0.20}$)FeO$_3$ | 5(25-1-40) | Rh + traces R | 7.61 | 8.32 | 91.56 | 7.10 | 8.19 | 86.67 | 12.498 |
| (Bi$_{0.85}$Tb$_{0.15}$)FeO$_3$ | 3(2-4-9) | ~60 % Rh + ~40 % R (SREFeO$_3$) | 7.06 | 8.29 | 85.18 | 12.509 |
| (Bi$_{0.90}$Dy$_{0.10}$)FeO$_3$ | 6(25-1-40) | ~15% Rh + 85% R | 6.97 | 8.46 | 82.40 | 12.512 | |
| (Bi$_{0.85}$Ho$_{0.15}$)FeO$_3$ | 10(25-1-40) | Rh | 7.48 | 8.36 | 89.44 | 7.06 | 8.31 | 91.95 |
| (Bi$_{0.85}$Ho$_{0.15}$)FeO$_3$ | 10(2-4-9) | Rh + traces R | 7.64 | 8.31 | 91.95 | |
| (Bi$_{0.85}$Ho$_{0.15}$)FeO$_3$ | 21(25-1-40) | ~30 Dy$_3$Fe$_2$O$_{12}$ | 7.41 | 8.25 | 89.79 | 12.500 | 12.404 (23-237) |
| (Bi$_{0.85}$Ho$_{0.15}$)FeO$_3$ | 35(25-1-40) | ~60 Dy$_3$Fe$_2$O$_{12}$ | 7.10 | 8.19 | 86.67 | 12.498 |
| (Bi$_{0.95}$Er$_{0.05}$)FeO$_3$ | 9(25-1-40) | Rh | 7.06 | 8.31 | 88.33 | 7.06 | 8.29 | 86.19 | 12.489 |
| (Bi$_{0.95}$Er$_{0.05}$)FeO$_3$ | 17(25-1-40) | Rh + traces R | 7.10 | 8.24 | 86.19 | 12.489 |
| (Bi$_{0.95}$Er$_{0.05}$)FeO$_3$ | 24(25-1-40) | Rh | 6.86 | 8.19 | 83.78 | 12.487 |
| (Bi$_{0.95}$Er$_{0.05}$)FeO$_3$ | 45Ho$_3$Fe$_2$O$_{12}$ | Rh | 8.35 | 8.35 | 88.03 | |
| (Bi$_{0.95}$Er$_{0.05}$)FeO$_3$ | 9(25-1-40) | Rh | 8.29 | 8.29 | 88.03 | 12.489 |
| (Bi$_{0.95}$Er$_{0.05}$)FeO$_3$ | 17(25-1-40) | Rh | 8.23 | 8.23 | 12.489 |
| (Bi$_{0.95}$Er$_{0.05}$)FeO$_3$ | 26(25-1-40) | Rh + traces R | 8.16 | 8.16 | 12.460 |
| (Bi$_{0.95}$Er$_{0.05}$)FeO$_3$ | 50(Er$_3$Fe$_2$O$_{12}$) | Rh | 8.29 | 8.29 | 12.465 | |
| (Bi$_{0.95}$Tm$_{0.05}$)FeO$_3$ | 6(25-1-40) | ~10(Tm$_3$Fe$_2$O$_{12}$) | 7.26 | 8.35 | 86.98 | 12.423 | 12.327 (23-591) |
| (Bi$_{0.95}$Tm$_{0.05}$)FeO$_3$ | 11(25-1-40) | ~20(Tm$_3$Fe$_2$O$_{12}$) | 7.40 | 8.30 | 89.12 | 12.434 |
| (Bi$_{0.95}$Tm$_{0.05}$)FeO$_3$ | 15(25-1-40) | ~30(Tm$_3$Fe$_2$O$_{12}$) | 7.24 | 8.25 | 87.79 | 12.434 |
| (Bi$_{0.95}$Tm$_{0.05}$)FeO$_3$ | 24(25-1-40) | ~50(Tm$_3$Fe$_2$O$_{12}$) | 7.11 | 8.20 | 86.74 | 12.432 |
| (Bi$_{0.95}$Yb$_{0.05}$)FeO$_3$ | 11(2-4-9) | ~10(Yb$_3$Fe$_2$O$_{12}$) | 7.29 | 8.34 | 87.38 | 12.414 | 12.301 (23-730) |
| (Bi$_{0.95}$Yb$_{0.05}$)FeO$_3$ | 17(25-1-40) | ~20(Yb$_3$Fe$_2$O$_{12}$) | 7.37 | 8.30 | 88.83 | 12.399 |
Table 1. Continuation

| Composition                  | Volume Fraction | Yb | Fe | O | Rh  |
|------------------------------|-----------------|----|----|---|-----|
| (Bi<sub>0.85</sub>Yb<sub>0.15</sub>)FeO<sub>3</sub> | 54 (25-1-40)    |    |    |   | 6.93|
|                              | 3 (2-4-9)       |    |    |   | 8.24|
|                              | ~50 (Yb<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub>) |    |    |   | 84.06|
|                              | 12.414          |    |    |   |     |
| (Bi<sub>0.8</sub>Yb<sub>0.2</sub>)FeO<sub>3</sub> | 37 (25-1-40)    | 7.08| 8.20| 86.33|
|                              | ~50 (Yb<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub>) |    |    |   | 12.410|
| (Bi<sub>0.95</sub>Lu<sub>0.05</sub>)FeO<sub>3</sub> | 39 (25-1-40)    | 7.10| 8.34| 85.12|
|                              | 34 (2-4-9)      |    |    |   |     |
|                              | 24 (25-1-40)    |    |    |   |     |
| (Bi<sub>0.9</sub>Lu<sub>0.1</sub>)FeO<sub>3</sub> | 21 (2-4-9)      | 7.37| 8.30| 88.79|
|                              | traces (Lu<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub>) |    |    |   |     |
|                              | 22 (25-1-40)    |    |    |   |     |
| (Bi<sub>0.85</sub>Lu<sub>0.15</sub>)FeO<sub>3</sub> | 16 (2-4-9)      | 7.25| 8.24| 87.94|
|                              | ~20 (Lu<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub>) |    |    |   | 12.388|
|                              | 57 (25-1-40)    |    |    |   | 12.284|
| (Bi<sub>0.8</sub>Lu<sub>0.2</sub>)FeO<sub>3</sub> | 36 (2-4-9)      | 7.27| 8.20| 88.66|
|                              | traces (Lu<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub>) |    |    |   |     |
|                              | 36 (2-4-9)      |    |    |   |     |

Figure 3. Dependence of the volumes of rhombohedrally distorted elementary perovskite cells SS Bi<sub>1-x</sub>SRE<sub>x</sub>FeO<sub>3</sub> on x.

In fig. 4 shows photographs of the microstructure of the studied objects. Black areas of rounded and irregular shape – pores. They are not uniformly distributed on the surface. Etching revealed the boundaries of crystallites: closed dark lines around the lighter areas (grains of ceramics). It was found that the most advanced microstructures of bismuth ferrite are realized with larger SREs. With a decrease in Ri and an increase in x, the amount of the impurity phase (“gray” grains) increases, the structure loosens, intergranular spaces are filled with the liquid phase, grain boundaries become thicker, and their habit is transformed.

The results of studying the temperature dependences ε/ε<sub>0</sub> of ceramic samples are shown in Fig. 5, 6. As can be seen from the figures, in the areas of 400–500 K two strongly dispersed maxima ε/ε<sub>0</sub> are formed, the peculiarity of which is a shift to the high temperature region, a decrease and smearing of their peak values with increasing frequency. Similar phenomena, known as Maxwell-Wagner relaxation, were observed earlier in [9–10] and were associated with the accumulation of free charges on the component interfaces on the background of interlayer, interphase, and interphase interplanes. The development of such effects is due to the natural composite with the BiFeO<sub>3</sub> state.
Figure 4. Microstructures of ceramic samples Bi$_{0.9}$SRE$_{0.1}$FeO$_3$ (SRE = Tb, Dy, Ho, Er, Yb, Tm) at room temperature. SRE is indicated in the lower left corner of the photos.

Figure 5. Temperature dependences $\varepsilon/\varepsilon_0$ of Bi$_{1-x}$SRE$_x$FeO$_3$ ceramic samples and $f$ at $x = 0.05$ и 0.20, SRE = Tb (a, b), Dy (b, r), Ho (d, e), Er (f, g), respectively.
4. Conclusion

As a result of the studies, it was found that during the synthesis of all the studied SS, impurity phases are formed, while bismuth enriched (Bi$_{25}$FeO$_{40}$) are always formed, and iron-enriched (Bi$_2$Fe$_4$O$_9$) phases are formed when I$_{imp}$/I$_{rep}$ phases with a garnet type structure (SRE$_3$Fe$_{5}$O$_{12}$) are less than 10 %. The crystal chemical features of the formed SSs were revealed: at small and large x, most likely SS interstitials are formed, and at medium x SS substitutions or a combined type. The deterioration of the grain structure of ceramics was established with a decrease in the radius of the introduced SRE. It is shown that the dielectric spectra of SS indicate the development of Maxwell-Wagner relaxation in the studied objects.

The results obtained in this paper must be taken into account when creating a new generation of multifunctional (combining ferroelectric, magnetic, and ferroelastic properties) materials that can find promising applications in areas such as sensory technology, diagnostics, processing and storage of information, and many others.

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References

[1] Smolensky G A and Chupis I E 1982 Ferroelectromagnets Physics-Uspekhi pp 137, 415
[2] Carvalho T T and Tavares P B 2008 Synthesis and Thermodynamic Stability of Multiferroic BiFeO$_3$ Mater. Letters 62 3984
[3] Zalessky A A V, Frolov A A, Khimich T A and Bush A A 2003 Concentration transition of a spin-modulated structure to a homogeneous antiferromagnetic state in the Bi$_{1-x}$La$_x$FeO$_3$ system system according to $^{57}$Fe NMR data Phys. of the solid state 45 134

[4] Bokiy G B 1954 Introduction to Crystal Chemistry (Moscow: Moscow State Univer. Publ. House)

[5] Razumovskaya O N, Verbenko I A, Andryushin K P et al 2009 Fund. Probl. of Radioelectr. Instrumentat. 9 126

[6] Fesenko E G 1972 The perovskite family and ferroelectricity (Moscow: Atomizdat) 248 p

[7] Denisov V M, Belousova N V, Foal V P et al 2012 J. of Siber. Fed. Univer. Chem. 2 146

[8] Smith J and Wayne H 1962 Ferrites (Moscow: Foreign Liter.) 504 p

[9] Khasbulatov S V, Pavelko A A, Reznichenko L A et al 2017 Dielectric and Thermal Properties of Multiferroic Bismuth Ferrite Doped with Praseodymium and Neodymium Advanced Materials – Techniques, Physics, Mechanics and Applications vol 193 Chapter 11 pp 109–124 (Heidelberg; New York; Dordrecht; London: Springer) 570 p

[10] Khasbulatov C C V, Pavelko A A, Shilkina L A et al 2016 Crystal and grain structure, thermophysical and dielectric properties of multiferroic Bi$_{1-x}$Dy$_x$FeO$_3$ Thermophys. and Aeromech. 23(3) 461–6