OPTICAL SPECTRA OF CERAMIC $Bi_{1-x}Gd_xFeO_3$, $Bi_{1-x}Nd_xFeO_3$, $Bi_{1-x-y}Gd_xLa_yFeO_3$

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The crystal structure and some optical properties of slightly substituted solid solutions of $Bi_{1-x}Gd_xFeO_3$, $Bi_{1-x}Nd_xFeO_3$ and $Bi_{1-x-y}Gd_xLa_yFeO_3$ as ceramic compound samples at $x < 0.2$ and $x + y < 0.2$ have been estimated by means of *X*-ray diffraction and reflection spectroscopy in visible region of spectrum. Mentioned $Bi_{1-x}Gd_xFeO_3$, $Bi_{1-x}Nd_xFeO_3$ compounds show at room temperature the dominant crystal structure with space group of *R3c* type at concentration of the doping element $x < 0.1$ and also detect the presence of the optical absorption due to electronic transitions with wave length of the order of 0.4–0.5 μk, 0.6 μk, 0.8 μk and 1.1 μk due to the transitions of the three-charge iron ions, positioned in the distorted oxygen octahedra.

Key words: solid solutions; ceramic; optical absorption.

INTRODUCTION

The materials being simultaneously both the ferroelectrics and magnetic ones are attractive due to benefits of potential applications for new devices using the multiferroic coupling. The rhombohedrally distorted $BiFeO_3$ perovskite is double ordered material because the ferroelectric and antiferromagnetic orders coexist at room temperature [1, 2]. The *G*-type antiferromagnetic structure of $BiFeO_3$ takes place up to 640 K [3, 4], while the phase transition from para- to ferroelectric state is observed at near 1100 K [5, 6]. An antiferromagnetic domain switching by an external electric field in $BiFeO_3$ films indicates that there is a principal possibility of applying these materials [7]. Its anti ferromagnetic spin configuration, as assumed, can be destructed by any action on to a modulated spin spiral, having a 620 A periodicity [8] by chemical doping [9–11]. Particularly to intensify the macroscopic magnetic properties usually it is proposed to use some rare earth elements for the substitution of Bi. The three charged ion radius of lanthanum, neodymium and gadolinium are close to three-charged ion radius of bismuth. An investigation of the number of changes in physical properties caused by the rare earth elements substitution for bismuth has been studied in [11–15]. It is, nevertheless, desirable to extent the investigation of the mixed system on the base of $BiFeO_3$. Here $Bi_{1-x}Gd_xFeO_3$, $Bi_{1-x}Nd_xFeO_3$ and $Bi_{1-x-y}Gd_xLa_yFeO_3$ polycrystalline ceramic samples with $x < 0.2$ and $x + y < 0.2$ respectively were prepared and identified at room temperatures.

MATERIALS AND METHODS

$Bi_{1-x}Gd_xFeO_3$, $Bi_{1-x}Nd_xFeO_3$ and $Bi_{1-x-y}Gd_xLa_yFeO_3$ ceramic samples were synthesized by usual solid-state reaction. Bismuth (III) oxide (Bi_2O_3), Gadolinium (III) oxide (Bi_2O_3), Lantanum (III) oxide (Bi_2O_3), and Iron (III) oxide (Fe_2O_3) powder ingredients have been used in accordance with the next transformation:

$$xGd_2O_3 + (1-x)Bi_2O_3 + Fe_2O_3 = 2Gd_x^{3+}Bi_{1-x}^{3+}Fe^{3+}O_3^{2-}$$

$$xNd_2O_3 + (1-x)Bi_2O_3 + Fe_2O_3 = 2Nd_x^{3+}Bi_{1-x}^{3+}Fe^{3+}O_3^{2-}$$

$$xLa_2O_3 + yGd_2O_3 + (1-x)Bi_2O_3 + (1-y)Bi_2O_3 + 2Fe_2O_3 = 2La_x^{3+}Gd_y^{3+}Bi_{1-x-y}^{3+}Fe^{3+}O_3^{2-}$$

Particularly the dried starting materials for an example Bi_2O_3, Fe_2O_3 and Gd_2O_3 (purity > 0.9999) were measured by using a high-precision balance and have been taken in stoichiometric proportion (such for composition $Gd_{0.1}Bi_{0.9}FeO_3$ the start ingredient quantity was taken: Gd_2O_3 – 0.058914 g, Bi_2O_3 – 0.681553 g, Fe_2O_3 – 0.259533 g, for $Gd_{0.15}Bi_{0.85}FeO_3$ the start ingredient quantity was taken: Gd_2O_3 – 0.089120 g, Bi_2O_3 – 0.649147 g; Fe_2O_3 – 0.261734 g). To carry out the phase control of synthesized samples the *X*-ray diffraction method was applied on the base of high-resolution diffractometer Dron-3 with Cu K_α radiation (1.5406 Å). The experimental data were collected during scanning repeated ten times in a 2Θ range from 20° to 90° with a scanning speed of 10°/6 min. To register optical reflection characteristics the infrared spectra of the samples in tablet powder mixtures were recorded with VERTEX 80v FT-IR spectrometer (Bruker).

RESULTS AND DISCUSSION

X-ray diffraction patterns for the $Bi_{1-x}Gd_xFeO_3$ solid solutions with molar parts of $GdFeO_3$ corresponding to $x = 0.05$, 0.10, 0.15, and 0.20 are presented on Figure 1, and *X*-ray diffraction patterns for the $Bi_{1-x}Nd_xFeO_3$ solid solutions with molar parts of $NdFeO_3$ corresponding to $x = 0.05$, 0.10, 0.15, and 0.20 are presented on Figure 2. It was found that the crystal structure for both the $Bi_{1-x}Gd_xFeO_3$ and $Bi_{1-x}Nd_x$ FeO_3 solid solutions is the rhombohedrally distorted structure of perovskite, *R3c* space group. There is a shift of *X*-ray reflexes that clearly shows the formation of solid solutions in the $BiFeO_3$–$GdFeO_3$ and $BiFeO_3$–$NdFeO_3$ systems.

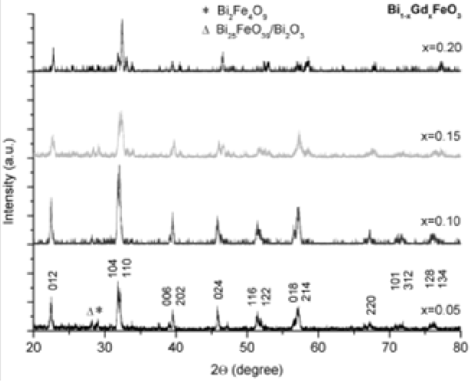

Figure 1. – *X*-ray diffraction patterns for the $Bi_{1-x}Gd_xFeO_3$ solid solutions with molar parts of $GdFeO_3$ corresponding to x = 0.05, 0.10, 0.15, and 0.20

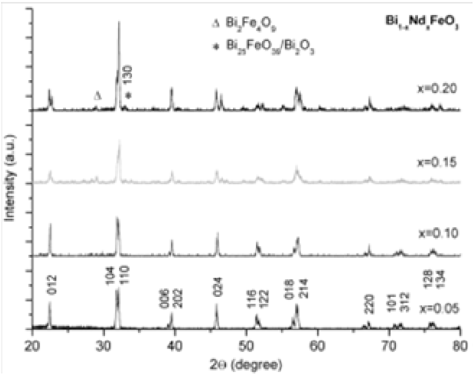

Figure 2. – *X*-ray diffraction patterns for the $Bi_{1-x}Nd_xFeO_3$ solid solutions with molar parts of $NdFeO_3$ corresponding to x = 0.05, 0.10, 0.15, and 0.20

Additional reflexes are detected for solid solutions of both series. These reflexes can be attributed to the phases which are based on ternary compounds $Bi_{25}FeO_{39}$ and $Bi_2Fe_4O_9$ formed in the Bi_2O_3–Fe_2O_3 quasibinary system for the molar ratio of Bi_2O_3 and Fe_2O_3 being 25:1 and 1:2, respectively. The amount of the impurity phases is larger for the Bi(Gd)–Fe–O system and can reach 10 molar %. $BiFeO_3$ exists in the Bi_2O_3–Fe_2O_3 quasibinary system for the molar ratio of Bi_2O_3 and Fe_2O_3 being 1:1 [13, 14]. Its melting occurs in accordance with the peritectoid reaction. This means that this compound in principle cannot be prepared by preparation methods from the melt. Additionally, the high volatility of bismuth oxide Bi_2O_3 has to be taken into account. All of this leads to a thermodynamic instability of $BiFeO_3$ and impossibility to synthesize single-phase $BiFeO_3$ by the solid-state reaction. Synthesis in accordance with the ceramic technology produces the pseudomonophasic composition with accuracy of up to 3% by weight of impurity of $Bi_{25}FeO_{39}$ [11]. It should be noted that the presence of impurity phases affects physical properties and partially changes quantitative values.

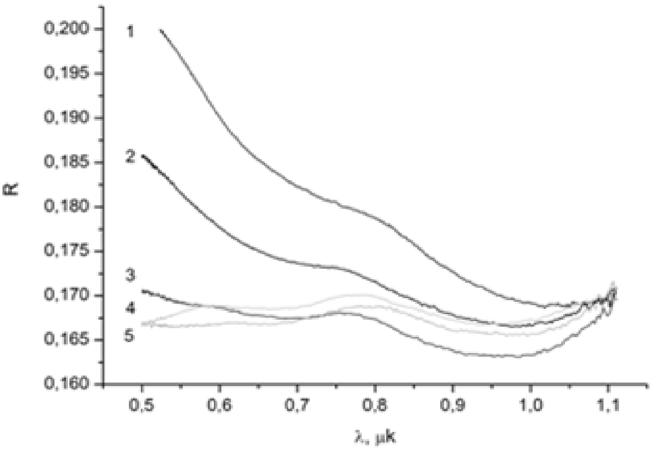

Figure 3. – Reflection spectra for system $Gd_xBi_{1-x}FeO_3$ at Gd^{3+} content in the range $0 \leq x \leq 0.20$ for x: 0 (4), 0.05 (5), 0.10 (3), 0.15 (2), 0.20 (1)

Following to optical experiment the observed total decrease of reflectivity versus of radiation wave length means that for almost all spectrum diapason starting from short wave region of 0.05 nm there takes place a normal dispersion law with consequent changing on to absorption regime near 0.11 nm (Figure 3). The introduction of doping elements activates stronger the high frequent part of spectrum. For undoped sample the reflectivity on the level of 0.165–0.170 corresponds to the value of real part of refractive index of the order of 2.35–2.40. The introduction of doping elements activates stronger the high frequent part of spectrum. Here for undoped sample the imaginary part of refractive index can be accepted as zero because the appearance of absorption is observed only in long wave length range. At least the maximal change of reflective coefficient being of the order of 25% on starting level means that refractive index increases by to 30% in the region of 0.3–0.4 μk that also means the forming of absorption line at 0.1–0.2 μk for material modified by doping of Gd.

The significant transformation of short wave length part spectra probably correlates with the observed *X*-ray spectra indications on the formation of phase structural transitions at Gd^{+3}-content on the level 0.15 and 0.20 at.%. For system on the base of the replacement of bismuth on to neodymium the spectra show that Nd^{3+} content of the level of 0.05 and 0.10 at.% corresponding to the appearance of some phase having a space group *Pnma* are realized in increasing of short wave length reflectivity in comparison with the case of harder doping. The farther increase of Nd^{3+} content in the samples transforms the short

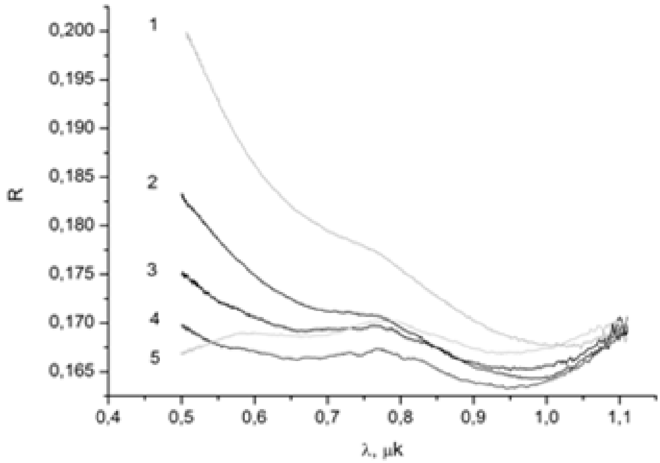

Figure 4. – Reflection spectra for system $Nd_xBi_{1-x}FeO_3$ at Nd^{3+} content in the range $0.05 \le x \le 0.2$ for x: 0 (5), 0.05 (2), 0.10 (1), 0.15 (3), 0.20 (4)

wave length part of spectrum close to that as for the start undoped bismuth ferrite having the space group *R3c.* So the appearance of the strong absorption oscillator in short wave length range is due to structural modification in more degree. The doping activates the appearance of absorption at 0.3–0.4 μk (Figure 4).

Represented at Figure 5 reflection spectra for ceramic samples based on the double bismuth replacement show high sensitivity of refractive index to the amount of Gd-content when a structural phase transition had already taken place. From a Figure 5 it is seen that comparatively low level of Gd^{3+}-content decreases the reflectivity coefficient similarly as for single Gd^{3+} substitution.

Indicated peculiarities of the optical properties of these materials is naturally to associate with the presence of the iron ion in chemical structure. Of course the transition from one composition to another do not change the quantity of iron ions per formula unit and per unit of volume because only bismuth ions are replaced. However, one could argue that the modification in some sense of the chemical environment takes place. In other words, oxygen octahedra, which were initially distorted within the space group *R3c*, can be further distorted. It can be argued that unfilled iron electron d-shell is placed so that the crystal field of oxygen ions surrounding the iron ions acts as a intermediate one. The number of sub-levels at the removing of the degeneracy is determined within the framework of the so-called expansion procedure of the continuous representation of the rotation and reflection group into irreducible representations of a finite group, which is characteristic for the point symmetry of the crystal field in the iron ion positions. So the three-charged iron ion is known to contain five *d*-electrons. Electronic energy states for free Fe^{3+} ion in accordance with Hund's rule have the following sequence of term ^6S, ^4G, ^4D, ^4S, ^2J, ^2G, ^2P etc. In these materials iron ions occupy

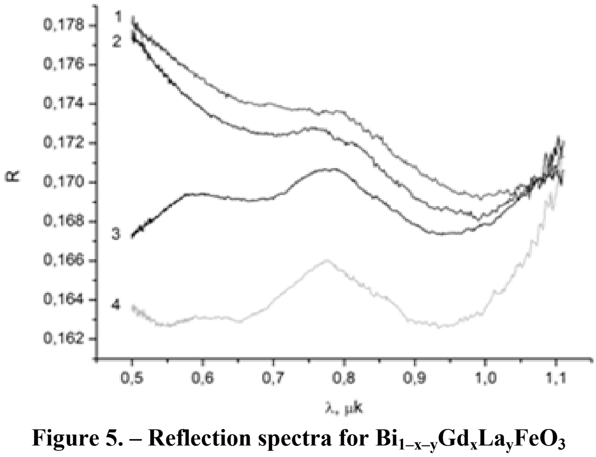

Figure 5. – Reflection spectra for $Bi_{1-x-y}Gd_xLa_yFeO_3$ ceramic samples with double bismuth substitution by Gd(x) and La(y): x = 0, y = 0 (3); x = 0.05, y = 0.15 (4); x = 0.1, y = 0.1 (2); x = 0.15, y = 0.05 (1)

octahedral positions, namely the centers of distorted oxygen octahedra.

So one must display a representation of three-dimensional rotation group $D^{(l)}$ (*l*-orbital quantum number) through a combination of irreducible representations for the octahedral group *O*. Following this procedure, we find that $D^{(l=0)}$ corresponds to Γ_1, $D^{(l=1)}$ corresponds to Γ_4, $D^{(l=2)}$ corresponds to $\Gamma_3 + \Gamma_5$, $D^{(l=3)}$ corresponds to $\Gamma_2 + \Gamma_4 + \Gamma_5$ and $D^{(l=4)}$ corresponds to $\Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5$. Respectively, the *S* and *P* terms are not split, the term *D* is splitted into two energy levels, the *F* term splits into three levels, and the term *G* splits into four levels. The split levels derived from the first excited state term ^4G should be represented as energy increasing in the order of Γ_4, Γ_5, Γ_3, Γ_1. So the observed absorption zones may be ascribed to electron transition from the base state (^6S) to nearest excited ^4G namely to Γ_4 (about 1.1 μk), to Γ_5 – 0.8 μk, to Γ_3 – 0.6 μk and to Γ_1 – 0.4–0.5 μk.

CONCLUSION

The mono Gd or Nd and the double Gd–La substitution of Bi in ceramics samples of BiFeO3 – $Bi_{1-x}Gd_xFeO_3$, $Bi_{1-x}Nd_xFeO_3$ and $Bi_{1-x-y}Gd_xLa_yFeO_3$ have shown the finite sensitivity of crystal structure to small amounts of doping ions when the appearance of 10–20 atomic % of substituting ions transfers space group symmetry from the *R3c* form to another. Respectively for optical absorption three charged iron ions being placed in oxygen octahedra form absorption lines with increasing refractive index somewhat like to the behavior of optical spectra of iron ittrium garnet and of the rare earth orthoferrites.

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