Structural, Electrical and Mössbauer Effect Studies of $0.5Bi_{0.95}Dy_{0.05}FeO_3-0.5Pb(Fe_{0.5}Nb_{0.5})O_3$ Multiferroics

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$0.5Bi_{0.95}Dy_{0.05}FeO_3-0.5Pb(Fe_{0.5}Nb_{0.5})O_3$ is a multiferroic material which exhibits ferroelectric and antiferromagnetic ordering. (The synthesis of such compounds is rather difficult.) In this paper the way of the synthesis of $0.5Bi_{0.95}Dy_{0.05}FeO_3-0.5Pb(Fe_{0.5}Nb_{0.5})O_3$ is presented. The detailed X-ray and Mössbauer effect studies were done and crystal and hyperfine interaction parameters were obtained. To measure electrical properties of the compound the impedance spectroscopy measurements were performed. The obtained impedance spectra were fitted using a proposed equivalent electrical circuit and the results were discussed in the scope of the brick layer model without easy paths.

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1. Introduction

Materials that exhibit ferromagnetic and ferroelectric orderings simultaneously are known as multiferroics. They are used widely as transducers, actuators, other sensors and as a material for the next generation computer memories. The first single phased multiferroic perovskites were discovered in the early 1960s. However, they are very rare and limited progress has been made during the last several decades [1–5].

$BiFeO_3$ is well known perovskite compound which exhibits ferroelectric ($T_C = 840°C$) and antiferromagnetic ($T_N = 340°C$) ordering simultaneously. Un-
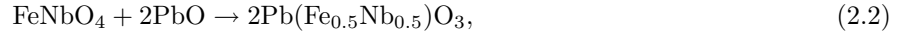
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fortunately, high leakage current, unwanted secondary phases and other defects make it difficult to obtain [2–4]. To overcome these problems solid solution system of Dy-doped $BiFeO_3$ with $Pb(Fe_{0.5}Nb_{0.5})O_3$ was synthesized. $Pb(Fe_{0.5}Nb_{0.5})O_3$ is a lead-based complex perovskite relaxor which is considered as a dielectric for multilayer ceramic capacitors with high dielectric constant and low sintering temperature [5].

In this paper, we report the synthesis, crystal structure, Mössbauer and impedance spectroscopy studies of $0.5Bi_{0.95}Dy_{0.05}FeO_3 - 0.5Pb(Fe_{0.5}Nb_{0.5})O_3$ solid solutions.

2. Sample preparation

Solid solutions $0.5Bi_{0.95}Dy_{0.05}FeO_3 - 0.5Pb(Fe_{0.5}Nb_{0.5})O_3$ of two multiferroic compounds with perowskite structure — relaxor $Pb(Fe_{0.5}Nb_{0.5})O_3$ and $BiFeO_3$ doped with 5 mol% Dy_2O_3 was obtained due to following chemical reactions:

$$Fe_2O_3 + Nb_2O_5 \rightarrow 2FeNbO_4, \tag{2.1}$$

$$FeNbO_4 + 2PbO \rightarrow 2Pb(Fe_{0.5}Nb_{0.5})O_3, \tag{2.2}$$

$$0.95Bi_2O_3 + 0.05Dy_2O_3 + Fe_2O_3 \rightarrow 2Bi_{0.95}Dy_{0.05}FeO_3. \tag{2.3}$$

High purity Bi_2O_3, Dy_2O_3, Fe_2O_3 and $Pb(Fe_{0.5}Nb_{0.5})O_3$ powder oxides were weighted in stoichiometric proportions and then ball milled for 7 h. Powders were calcined at 820°C for 4 h. The obtained powder was granulated and then pressed into disk shaped pellets. The pellets were heat-treated at 545°C for 2 h and next sintered at 850°C for 2 h.

3. X-ray studies

The crystal structure and purity of the powder sample was checked from the X-ray powder diffraction patterns obtained with the Bruker AXS D8 Advance
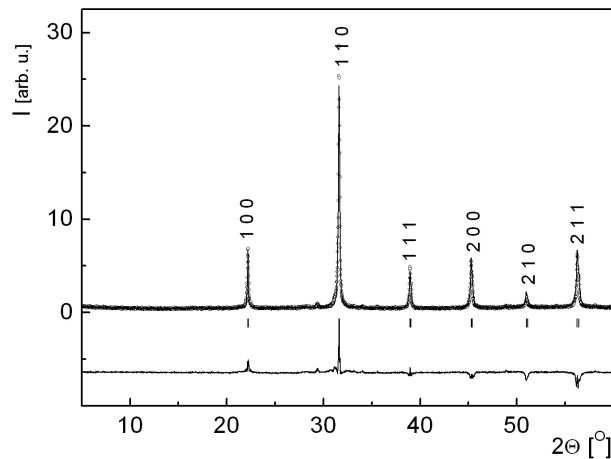

Fig. 1. X-ray pattern of $0.5Bi_{0.95}Dy_{0.05}FeO_3 - 0.5Pb(Fe_{0.5}Nb_{0.5})O_3$ at 300 K.

diffractometer using Cu K_α radiation. The crystal structure was refined using the Rietveld method with the FULLPROF software [6]. The ceramic sample was crushed into powder in an agate mortar. The measured X-ray diffraction (XRD) pattern at room temperature is presented in Fig. 1. The obtained crystal structure of the compound is a pure simple cubic perovskite structure with space group Pm3m. The lattice parameter was 4.002(1) Å.

4. Mössbauer spectroscopy measurements

The ^{57}Fe transmission Mössbauer spectra of $0.5Bi_{0.95}Dy_{0.05}FeO_3-$ $0.5Pb(Fe_{0.5}Nb_{0.5})O_3$ was obtained at 77 K. The measured spectra (Fig. 2) was least squares fitted and the hyperfine interaction parameters like isomer shift (IS) relative to metallic iron, quadrupole split (QS) and hyperfine magnetic field ($\mu_0 H_{hf}$) were obtained and summarized in Table. The Mössbauer studies of $BiFeO_3$ [7, 8] assume two different sextets with two different values of QS and one Zeeman sextet
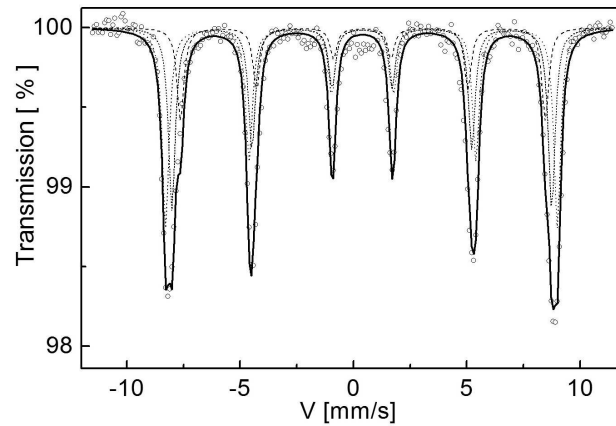

Fig. 2. ^{57}Fe Mössbauer effect spectra at 77 K (circles — experimental points, dotted lines — constituent subspectra, solid line — fitted resultant spectra).

TABLE

The ^{57}Fe hyperfine interaction parameters at 77 K (Γ — half width, W — weight, IS — isomer shift, $\mu_0 H_{hf}$ — magnetic hyperfine field, QS — quadrupole split).

No.	$\Gamma/2$ [mm/s]	W [%]	IS [mm/s]	$\mu_0 H_{hf}$ [T]	QS [mm/s]
1	0.181(1)	19.6(1)	0.540(4)	49.93(13)	0.035(1)
2	0.181(1)	42.0(4)	0.521(3)	53.58(5)	−0.043(1)
3	0.181(1)	38.4(3)	0.519(3)	51.96(6)	0.003(1)
weighted average			0.523(3)	52.24(7)	−0.010(1)

for $Pb(Fe_{0.5}Nb_{0.5})O_3$ phase [9]. The hyperfine interaction parameters for subspectra 1 (Table) agreed with parameters obtained previously for $Pb(Fe_{0.5}Nb_{0.5})O_3$ [9]. The components 2 and 3 of the measured spectra have almost equal values of IS and slightly different values of $\mu_0 H_{hf}$ and QS which was observed previously for $BiFeO_3$ compound [7, 8].

The achieved IS and QS parameters are typical of Fe^{3+} in octahedral symmetry [9]. The obtained magnetic hyperfine fields are about 50 T and are normal for ferric iron. Thus, an Fe^{3+} charge state for the iron in the $0.5Bi_{0.95}Dy_{0.05}FeO_3-0.5Pb(Fe_{0.5}Nb_{0.5})O_3$ has been confirmed by the isomer shift and hyperfine field values.

5. Impedance spectroscopy studies

Impedance spectroscopy (IS) is a very useful technique to analyze the electrical properties of a wide variety of electroceramics. The IS measurements have been performed in the temperature range 450–700 K in frequencies from 10 Hz to 2 MHz. An exemplary impedance spectra at 600 K is presented in Fig. 3. The spectrum is dominated by a grain interior arc which is caused by grain interior conductivity. The second small arc originated from grain boundary conductivity [10]. The IS spectra were fitted by LEVM program [10] using an equivalent circuit showed in Fig. 3. The proposed equivalent circuit is a series connection of parallel connected
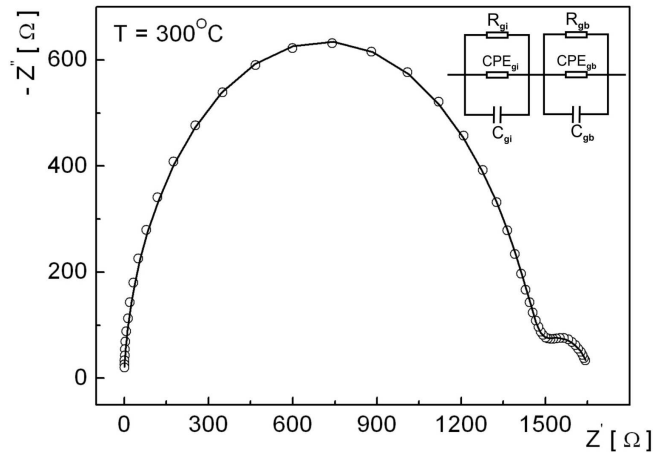

Fig. 3. An exemplary impedance spectra at 600 K with the equivalent electrical circuit.

R, C and constant phase elements (CPE), defined in [10, 11]. The modeled circuit fits very well to the experimental data (solid line in Fig. 3). The R_{gi} and R_{gb} are, respectively, grain interior and grain boundary resistivities. In Fig. 4 R_{gi} and R_{gb} resistivities are presented in the Arrhenius type plot. Conductivity of the investigated material is a thermally activated process which fulfill the Arrhenius

law. The obtained activation energies are $E_{gi} = 1.00(4)$ eV and $E_{gb} = 1.34(9)$ eV for grain interiors and grain boundaries, respectively, which are typical values of various electroceramics [11]. The Arrhenius plots of R_{gi} and R_{gb} are linear over the temperature range 450–750 K. The fact that the activation energies for grain interior and grain boundary are different and the slopes are different and higher for R_{gb} implies that the brick layer model without easy path is appropriate for this material.
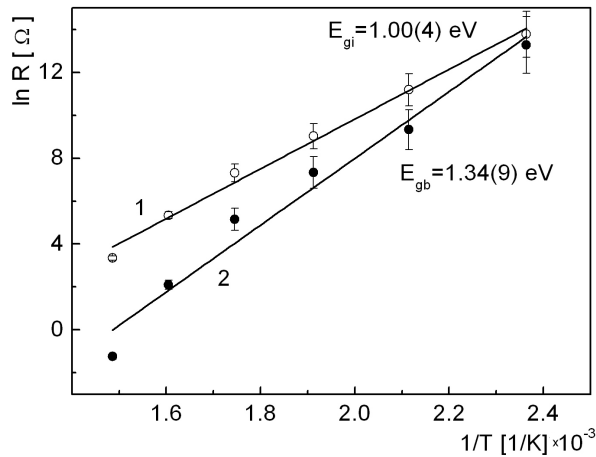

Fig. 4.   The Arrhenius plots of the R_{gi} and R_{gb} resistivities.

The grain interior capacitance C_{gi} is about 3.2(3) nF and the grain boundaries capacitance C_{gb} is about 3.3(9) μF. The both capacitances are almost temperature independent.

6. Conclusions

$0.5Bi_{0.95}Dy_{0.05}FeO_3 - 0.5Pb(Fe_{0.5}Nb_{0.5})O_3$ was synthesized using conventional solid state reaction method. The X-ray studies showed that the measured compound crystallizes in the $Pm3m$ crystal structure which is a typical ABO_3 perovskite structure. The Mössbauer spectroscopy confirmed existence of three Zeeman sextets. One of them belongs to the $Pb(Fe_{0.5}Nb_{0.5})O_3$ phase and two to $Bi_{0.95}Dy_{0.05}FeO_3$. There is no evidence of existence of secondary phases and all iron is an Fe^{3+} iron in octahedral symmetry. To described impedance spectra there was proposed the equivalent electrical circuit and the obtained R_{gi} and R_{gb} resistivities temperature dependences fulfill Arrhenius-like behavior with the activation energy about 1 eV. The different slopes of the above dependences suggest that the conductivity of the compound can be described using brick layer model without easy path.

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