Hyperfine interactions and electrical properties of multiferroic 0.5Bi\textsubscript{0.95}Dy\textsubscript{0.05}FeO\textsubscript{3}−0.5Pb(Fe\textsubscript{0.5}Nb\textsubscript{0.5})O\textsubscript{3}

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Abstract. 0.5Bi\textsubscript{0.95}Dy\textsubscript{0.05}FeO\textsubscript{3}−0.5Pb(Fe\textsubscript{0.5}Nb\textsubscript{0.5})O\textsubscript{3} is a multiferroic material, simultaneously revealing ferroelectric and antiferromagnetic ordering, synthesis is rather difficult. In this paper we present a conventional solid state reaction method for synthesis of 0.5Bi\textsubscript{0.95}Dy\textsubscript{0.05}FeO\textsubscript{3}−0.5Pb(Fe\textsubscript{0.5}Nb\textsubscript{0.5})O\textsubscript{3} perovskite. A series of methodological measurements were carried out to determine the basic structural and electromagnetical properties. X-ray diffraction studies have been made in order to determine a crystal structure. Mössbauer effect spectroscopy was used to identify the oxidation state of Fe. Electrical properties of the perovskite ceramic were examined with impedance spectroscopy. The impedance spectra were analysed by means of an equivalent electrical circuit, and results are discussed in the scope of the brick layer model without easy paths.

1. Introduction

Materials, that simultaneously exhibit ferromagnetic and ferroelectric orderings are known as multiferroics. They are widely used as transducers, actuators and the other sensors, as well as the basic components for new mass storage devices.

The first single phased multiferroic perovskites were discovered in the early 1960s. However, during the last several decades a very insular and limited progress has been made [1-5]. A considerable development of multiferroic materials has been started with successful synthesis of multiferroics’ thin films [6] or even more, when a novel class of multifunctional materials has been discovered, where a multiferroic state is not only mutual arrangement of particular subnets but ferroelectricity is exclusively determined by magnetically ordered state [7].

0.5Bi\textsubscript{0.95}Dy\textsubscript{0.05}FeO\textsubscript{3}−0.5Pb(Fe\textsubscript{0.5}Nb\textsubscript{0.5})O\textsubscript{3} is a mixture of two perovskites: Dy-doped BiFeO\textsubscript{3} and Pb(Fe\textsubscript{0.5}Nb\textsubscript{0.5})O\textsubscript{3}. A first component (BiFeO\textsubscript{3}) is a well known perovskite, which exhibits both ferroelectric (\(T_C = 840^\circ C\)) and antiferromagnetic (\(T_N = 340^\circ C\)) orderings. Unfortunately, the synthesis of BiFeO\textsubscript{3} is difficult due to a high leakage current, secondary oxide phases (Bi\textsubscript{2}Fe\textsubscript{2}O\textsubscript{5}, Bi\textsubscript{6}Fe\textsubscript{2}O\textsubscript{7}) and the other harmful effects [2-4]. Nevertheless, there are many reports describing the method how to overcome above problems using a substitution of a rare earth element at A position in typical ABO\textsubscript{3} perovskite structure [8]. Additionally, the substitution of 3\textsuperscript{+} valence ion (for example Dy ion)
considerably increases magnetic exchange interactions, what is observable with extension of hysteresis loop ($M-H$ curve) [9].

A solid solution system of Dy-doped BiFeO$_3$ with Pb(Fe$_{0.5}$Nb$_{0.5}$)O$_3$ was synthesized, where the last component is a lead-based multilayer ceramic capacitor with a high dielectric constant and a low sintering temperature [5]. In this paper, we report the synthesis, crystal structure, m"ossbauer and impedance spectroscopy studies of 0.5Bi$_{0.95}$Dy$_{0.05}$FeO$_3$-0.5Pb(Fe$_{0.5}$Nb$_{0.5}$)O$_3$ multiferroic system.

2. Sample preparation
High purity Bi$_2$O$_3$, Dy$_2$O$_3$, Fe$_2$O$_3$ and Pb(Fe$_{0.5}$Nb$_{0.5}$)O$_3$ powder oxides were weighted in stoichiometric proportions and mechanically activated for 7 h during a ball milling process. In the next step, the obtained powder was calcined at 820°C for 4 h, granulated and then pressed into disc shaped pellet (2.09 mm height and 1.55 cm in diagonal). Finally, the pellet was heat-treated at 545°C for 2h and sintered at 850°C for 2 h.

3. X-Ray diffraction measurements
A purity of the sinter was checked by means of X-ray diffraction (Philips powder diffractometer with Cu K$_\alpha$ radiations, $\lambda = 1.54056$ Å). A fitting program (FULLPROF software [10]) based on the Rietveld method [11] was used to analyse a diffraction pattern – Fig.1. The derived multiferroic crystallize into a tetragonal symmetry with space group $P4mm$. The determined lattice parameters $a = 3.990(2)$ Å and $c = 4.026(8)$ Å indicate, that the structure of the synthesized ceramic is closely related to a simple cubic perovskite structure with a small distortion in $c/a$ ratio of about 0.9 %.

4. SEM/EDS studies
X-Ray diffraction results were confirmed by energy dispersive analysis. In Fig.2 the SEM image of a fine grain structure of the synthesized material is shown, where massive microcrystals about 3 μm in diameter are surrounded by smaller grains. According to the EDS studies, both the larger and the smaller grains exhibit the same chemical stoichiometry.

5. Mössbauer spectroscopy measurements
The $^{57}$Fe transmission Mössbauer spectrum of the 0.5Bi$_{0.95}$Dy$_{0.05}$FeO$_3$-0.5Pb(Fe$_{0.5}$Nb$_{0.5}$)O$_3$ sample was measured at 77 K (Fig.3). A full static hamiltonian site analysis was implemented in order to determine the hyperfine interaction parameters as isomer shift ($IS$), quadrupole splitting ($QS$) and a hyperfine magnetic field ($\mu_0H_{hf}$). The derived parameters are summarized in Table 1.

The previous Mössbauer effect studies of BiFeO$_3$ [12-13] and BiFeO$_3$ substituted by Eu [14] assume two different sextets with almost equal values of $IS$ and slightly different values of $\mu_0H_{hf}$ and...
QS (components S₂ and S₃ in Table 1), whereas the hyperfine interaction parameters for subspectrum S₁ agree very well with the values characteristic for Pb(Fe₀.₅Nb₀.₅)O₃ relaxor [15].

Table 1. The $^{57}$Fe hyperfine interaction parameters at 77 K (A – subspectral area, $\Gamma/2$ – half width at half maximum, IS – isomer shift, $\mu_0H_{hf}$ – magnetic hyperfine field, QS – quadrupole split).

| No. | A [%] | $\Gamma/2$ [mm/s] | IS [mm/s] | $\mu_0H_{hf}$ [T] | QS [mm/s] |
|-----|-------|-------------------|-----------|-------------------|-----------|
| S₁  | 15.2(1)| 0.197(3)          | 0.542(4)  | 49.86(10)         | 0.055(1)  |
| S₂  | 50.7(1)| 0.215(3)          | 0.517(4)  | 53.42(4)          | -0.041(1) |
| S₃  | 34.1(4)| 0.199(3)          | 0.518(5)  | 51.78(6)          | -0.012(2) |

The derived values of IS and QS (with respect to the pure iron metal at 300 K) are typical for a Fe$^{3+}$ ion in octahedral coordination [15]. The magnetic hyperfine fields $\mu_0H_{hf}$ ($\mu_0$ – magnetic permeability) of about 50 T are also characteristic for ferric iron.

![Figure 3](image-url)  
**Figure 3.** The $^{57}$Fe Mössbauer effect spectrum at 77 K.

6. Impedance spectroscopy studies

Impedance spectroscopy is a very useful technique to analyse the electrical properties of a wide group of electroceramics. The impedance measurements have been performed in the temperature range 450 – 700 K at frequencies from 10 Hz to 2 MHz.

Fig.4 presents an exemplary impedance spectrum of $0.5\text{Bi}_{0.95}\text{Dy}_{0.05}\text{FeO}_3$-$0.5\text{Pb(Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ recorded at 600 K. The spectrum is dominated by a “grain interior arc”, which is related to a grain interior conductivity, while a second “small arc” originates from the grain boundary conductivity [16].

Recorded impedance spectra were analyzed (solid curve in Fig.4) by LEVM program with implemented an equivalent electrical circuit proposed as a series-parallel connection of two resistors (R) and constant phase elements (CPE) [16,17].

In Fig.5 grain interior ($R_{gi}$) and grain boundary ($R_{gb}$) resistivities are presented in Arrhenius type plot. Conductivity of the investigated material is a thermally activated process with activation energies $E_{gi} = 1.154$ eV and $E_{gb} = 0.961$ eV, which values are typical for electroceramic materials [17].

The slopes of the plots are different, what should be expected on the basis of the brick layer model without easy paths for the systems with tetragonal symmetry [16]. The $R_{gi}$ values are generally lower than the $R_{gb}$ suggesting, that the electrical conductivity along the grains and across the grain boundaries clearly dominates the conductivity along the grain boundaries [16].
7. Conclusions
0.5Bl_{0.5}Dy_{0.5}FeO_{3}·0.5Pb(Fe_{0.8}Nb_{0.2})O_{3} multiferroic was synthesized using the conventional solid state reaction method. The crystallochemical purity of the sinter was checked by X-ray diffraction and Mössbauer effect studies. The analysis of diffractogram confirmed, that the compound crystallizes into a tetragonal system (P4mm) with slightly different lattice parameters. The stoichiometry of investigated material have been proven by SEM/EDS analysis, and the Mössbauer spectroscopy results distinctly exhibit a one charge state of all iron atoms (Fe^{3+}) and octahedral symmetry. Detailed studies of impedance spectra with proposed equivalent electrical circuit show, that temperature dependence of $R_{gi}$ and $R_{gb}$ resistivities fulfill Arrhenius-like behaviour with activation energies of about 1 eV. The different slopes of $R_{gi}$ and $R_{gb}$ dependencies suggest, that the electrical conductivity of the compound can be described in the frame of the brick layer model without easy paths.

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