Structural and Mössbauer Effect Studies
of 0.7Bi$_{0.95}$Dy$_{0.05}$FeO$_3$-0.3Pb(Fe$_{0.5}$Nb$_{0.5}$)O$_3$ Multiferroic

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0.7Bi$_{0.95}$Dy$_{0.05}$FeO$_3$-0.3Pb(Fe$_{0.5}$Nb$_{0.5}$)O$_3$ is a multiferroic material which exhibits ferroelectric and antiferromagnetic ordering. In this paper the way of the synthesis of 0.7Bi$_{0.95}$Dy$_{0.05}$FeO$_3$-0.3Pb(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.

PACS: 61.05.cp, 61.66.Fn, 75.50.Ee, 76.08.+y, 77.84.Lf

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 phase multiferroic perovskites were discovered in the early 1960s. However, they are very rare and limited progress has been made during the last several decades [1–6].

BiFeO$_3$ is a well known perovskite compound which exhibits ferroelectric ($T_C = 1110$ K) and antiferromagnetic ($T_N = 643$ K) ordering simultaneously [7].

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, 6]. This compound has the antiferromagnetic ordering at the temperatures below 143 K and is ferroelectric for temperatures lower than 385 K [7].

Unfortunately high leakage current, unwanted secondary phases and other defects make BiFeO$_3$ 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.

In this paper, we report the synthesis, crystal structure, Mössbauer spectroscopy studies of 0.7Bi$_{0.95}$Dy$_{0.05}$FeO$_3$-0.3Pb(Fe$_{0.5}$Nb$_{0.5}$)O$_3$ solid solutions.

2. Sample preparation

Solid solution 0.7Bi$_{0.95}$Dy$_{0.05}$FeO$_3$-0.3Pb(Fe$_{0.5}$Nb$_{0.5}$)O$_3$ of two multiferroic compounds with perovskite structure—

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pattern. The best agreement with experimental points was obtained for the $R3c$ structure. The obtained lattice parameters and atom position are summarized in Table I. The rhombohedral angle is close to 60° which is a value for cubic structure and observed tetragonal distortion is very small.

TABLE I
Crystal structure parameters and atom positions in the $R3c$ structure (rhombohedral coordinates).

| Atom           | $x$    | $y$    | $z$   |
|----------------|--------|--------|-------|
| Bi/Dy/Pb       | 0.2868 | 0.2868 | 0.2868|
| Fe/Nb          | 0.0179 | 0.0179 | 0.0179|
| O              | 0.2582 | 0.2373 | -0.2466|
| $a = 5.6591 \text{Å}$, $\alpha = 59.694^\circ$ |

4. Mössbauer spectroscopy measurements

The $^{57}\text{Fe}$ transmission Mössbauer spectra of 0.7Bi$_{0.95}$Dy$_{0.05}$FeO$_3$-0.3Pb(Fe$_{0.5}$Nb$_{0.5}$)O$_3$ were obtained at 11 K. The measured spectra (Fig. 2) were least squares fitted and the hyperfine interaction parameters like isomer shift ($IS$) relative to metallic iron, quadrupole split ($QS$) and hyperfine magnetic field ($\mu_0H_{hf}$) were obtained and summarized in Table II. The obtained spectrum is composed of two Zeeman sextets and two quadrupole doublet. The first spectra component could be ascribed to Bi$_{0.95}$Dy$_{0.05}$FeO$_3$ phase. The obtained hyperfine interaction parameters agreed well with [9]. The hyperfine interaction parameters for the second sextet agreed with parameters obtained previously for Pb(Fe$_{0.5}$Nb$_{0.5}$)O$_3$ [10]. Ratio of area under the first and the second sextet is about 0.19, which is close to the theoretical value 0.21. This confirms stoichiometry of the measured solid solution. Both of the doublets could belong to impurity phases like Bi$_2$Fe$_4$O$_9$ or Pb$_3$Fe$_2$O$_{13}$ which are easily formed during synthesis of the BiFeO$_3$ and Pb(Fe$_{0.5}$Nb$_{0.5}$)O$_3$. The impurities have lower Bi or Pb content due to their strong evaporation during synthesis. Only 3.5% of the Fe atoms are incorporated into impurity phases which weren’t observed on the X-ray pattern. The achieved $IS$ and $QS$ parameters are typical for Fe$^{3+}$ in octahedral symmetry [9, 10]. The obtained magnetic hyperfine fields are about 50 T and are normal for ferric iron. Thus, a Fe$^{3+}$ charge state for the iron in the 0.7Bi$_{0.95}$Dy$_{0.05}$FeO$_3$-0.3Pb(Fe$_{0.5}$Nb$_{0.5}$)O$_3$ has been confirmed by the isomer shift and hyperfine field values.

Determination of the Neel temperature of the investigated material is quite straightforward. In the paramagnetic state above Neel temperature Mössbauer spectrum consist of well defined quadrupole split line. Lowering temperature below $T_N$ appearing small magnetic hyperfine field which is observed as a broadening of the Mössbauer line and increase of the $QS$. To obtain the average full line width, the Mössbauer spectra was fitted around Neel temperature assuming one quadrupole doublet. On the other hand such the assumption causes coexistence of the two main sublattices. The average half line width is presented in Fig. 3b. As can be clearly seen the magnetic ordering temperature can be estimated as a point of crossection of two lines. The sharper one at lower temperatures and the second at the temperatures above $T_N$.

The Mössbauer Effect spectra were recorded at different temperatures between 500 K and 650 K. An exem-
plary Mössbauer spectra are presented in the Fig. 3a. The obtained $\Gamma$ parameters vs. temperature are shown in the Fig. 3b. The temperature $T_N$ was estimated on 548 K. The $T_N$ temperature of the investigated solid solution is about 100 K lower than pure BiFeO$_3$. On the other hand is much higher than Pb(Fe$_{0.5}$Nb$_{0.5}$)$_3$O$_3$.

Fig. 3. a) Temperature evolution of the exemplary Mössbauer spectra (550 K, 650 K, 750 K); b) Half width of the Mössbauer line vs. temperature for the 0.7Bi$_{0.95}$Dy$_{0.05}$FeO$_3$-0.3Pb(Fe$_{0.5}$Nb$_{0.5}$)O$_3$.

5. Conclusions

The 0.7Bi$_{0.95}$Dy$_{0.05}$FeO$_3$-0.3Pb(Fe$_{0.5}$Nb$_{0.5}$)O$_3$ was synthesized using conventional solid state reaction method. The purity of the obtained material has been confirmed by X-ray and Mössbauer measurements. The X-ray studies showed that the measured compound crystallize in the $R3c$ crystal structure which rhomboedrally distorted ABO$_3$ perovskite structure. The Mössbauer spectroscopy confirmed existence of two Zeeman sextets. One of them belongs to the Pb(Fe$_{0.5}$Nb$_{0.5}$)O$_3$ phase and the second one Bi$_{0.95}$Dy$_{0.05}$FeO$_3$. There is observed small contribution of impurity phases at the level of 3.5%. All iron atoms are a Fe$^{3+}$ iron in octahedral symmetry.

Acknowledgements

The work was partially supported by Polish Ministry of Science and Higher Education project No. NN507347335.

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