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

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$0.7\text{Bi}_{0.95}\text{Dy}_{0.05}\text{FeO}_3\text{-}0.3\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ is a multiferroic material which exhibits ferroelectric and antiferromagnetic ordering. In this paper the way of the synthesis of $0.7\text{Bi}_{0.95}\text{Dy}_{0.05}\text{FeO}_3\text{-}0.3\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ is presented. The detailed X-ray and Mössbauer effect studies were done and crystal and hyperfine interaction parameters were obtained.

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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 [1–6].

BiFeO_3 is a well known perovskite compound which exhibits ferroelectric ($T_C = 1110$ K) and antiferromagnetic ($T_N = 643$ K) ordering simultaneously [7].

$\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ 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].

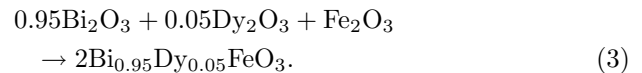
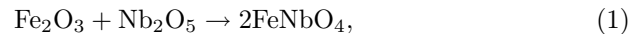
Unfortunately high leakage current, unwanted secondary phases and other defects make BiFeO_3 difficult to obtain [2–4]. To overcome these problems solid solution system of Dy-doped BiFeO_3 with $\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ was synthesized.

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

2. Sample preparation

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

relaxor $\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ and BiFeO_3 doped with 5 mol% Dy_2O_3 was obtained due to following chemical reactions:



High purity Bi_2O_3 , Dy_2O_3 , Fe_2O_3 and $\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ powder oxides were weighted in stoichiometric proportions and than ball milled for 7 h. Powders were calcined at 820 °C for 4 h. The obtained powder was granulated and than pressed into disc shaped pellets. The pellets were heat-treated at 545 °C for 2 h and next sintered at 850 °C for 10 h.

3. X-Ray studies

The crystal structure and purity of the powder samples were checked from the X-ray powder diffraction patterns obtained with a Philips diffractometer using $\text{Cu K}\alpha$ radiation. The crystal structure was refined using the Rietveld method with the FULLPROF software [8]. The ceramic sample was crushed into powder in an agate mortar. The measured XRD pattern at room temperature is presented in Fig. 1.

The simple ABO_3 perovskites crystallize in cubic $Pm\text{-}3m$ crystal structure. Ferroelectric ordering often cause tetragonal distortion and changes the crystal structure to $P4mm$. Simultaneously existence of ferroelectric and antiferromagnetic coupling often induce rotation of the oxygen octahedra and the crystal structure is reduced to rhombohedral $R3c$ [7]. The changes are relatively small and therefore difficult to measure. The $Pm\text{-}3m$, $P4mm$ and $R3c$ crystal structures were fitted to the experimental

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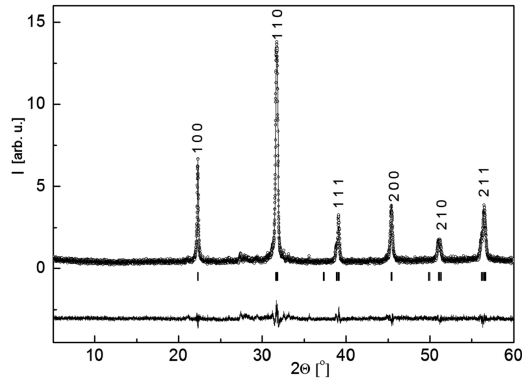


Fig. 1. X-ray pattern of $0.7\text{Bi}_{0.95}\text{Dy}_{0.05}\text{FeO}_3\text{-}0.3\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ at 300 K.

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

$$a = 5.6591 \text{ \AA}, \alpha = 59.694^\circ$$

4. Mössbauer spectroscopy measurements

The ^{57}Fe transmission Mössbauer spectra of $0.7\text{Bi}_{0.95}\text{Dy}_{0.05}\text{FeO}_3\text{-}0.3\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ 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 ($\mu_0 H_{hf}$) 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 $\text{Bi}_{0.95}\text{Dy}_{0.05}\text{FeO}_3$ phase. The obtained hyperfine interaction parameters agreed well with [9]. The hyperfine interaction parameters for the second sextet agreed with parameters obtained previously for $\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ [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 $\text{Bi}_2\text{Fe}_4\text{O}_9$ or $\text{Pb}_3\text{Fe}_4\text{O}_{13}$ which are easily formed during synthesis of

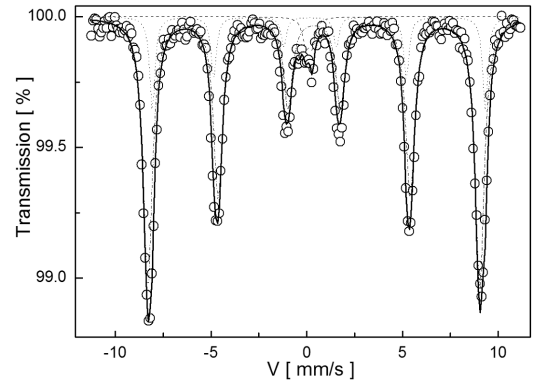


Fig. 2. ^{57}Fe Mössbauer effect spectra at 11 K.

TABLE II

The ^{57}Fe hyperfine interaction parameters at 11 K (Γ — half width, W — weight, IS — isomer shift, $\mu_0 H_{hf}$ — magnetic hyperfine field, QS — quadrupole split).

No.	Γ [mm/s]	W [%]	IS [mm/s]	$\mu_0 H_{hf}$ [T]	QS [mm/s]
1	0.282(1)	80.59(1)	0.475(4)	53.77(2)	-0.011(5)
2	0.161(1)	15.21(3)	0.502(2)	53.94(6)	0.463(1)
3	0.147(3)	2.76(5)	0.224(6)	0	0.333(4)
4	0.150(2)	0.76(9)	0.109(2)	0	0.674(4)

the BiFeO_3 and $\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$. 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 $0.7\text{Bi}_{0.95}\text{Dy}_{0.05}\text{FeO}_3\text{-}0.3\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ 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 splitted 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 Γ 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 $\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$.

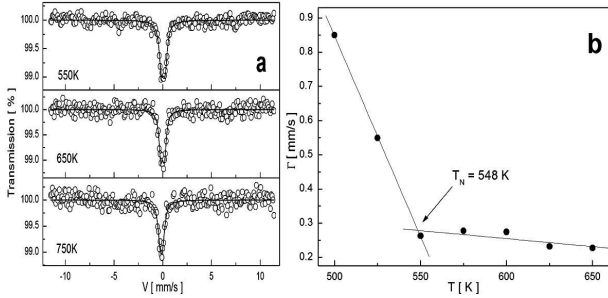


Fig. 3. a) Temperature evolution of the exemplary Mössbauer spectra (550 K, 650 K, 750 K); b) Half width of the Mössbauer line vs. temperature for the $0.7\text{Bi}_{0.95}\text{Dy}_{0.05}\text{FeO}_3\text{-}0.3\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$.

5. Conclusions

The $0.7\text{Bi}_{0.95}\text{Dy}_{0.05}\text{FeO}_3\text{-}0.3\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ 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 $\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ phase and the second one $\text{Bi}_{0.95}\text{Dy}_{0.05}\text{FeO}_3$. 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

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