Structural and Mössbauer Effect Studies of $0.5Bi_{0.95}Dy_{0.05}FeO_3$-$0.5Pb(Fe_{2/3}W_{1/3})O_3$ Multiferroic

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A polycrystalline ceramic of $0.5Bi_{0.95}Dy_{0.05}FeO_3$-$0.5Pb(Fe_{2/3}W_{1/3})O_3$ was synthesized from a solid-state reaction method. At room temperature material exhibits both magnetic and electric dipolar properties simultaneously. Detailed X-ray diffraction analysis and Mössbauer effect studies have been done to determine the crystallographic structure and magnetic properties of $0.5Bi_{0.95}Dy_{0.05}FeO_3$-$0.5Pb(Fe_{2/3}W_{1/3})O_3$. T_N temperature was estimated at around 600 K.

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1. Introduction

Perovskite-base materials, where coexist in the same phase (ferro)magnetism and ferroelectricity are known as multiferroics. Multiferroics were discovered in 1960s, but during the next several decades a moderated evolution of new magnetoelectrics has been made [1–7]. Essentially, a large attraction of that class of materials revives in 2003, where a few promising reports about new type of multiferroics have been published [8–10]. It was clear, that strong coupling between magnetic and electric subsystems gives incomparable opportunities for changing physical properties and make multiferroics very attractive for practical applications as so called multifunctional materials.

One of the most promising multiferroic material $BiFeO_3$ [8] is a well known ceramic perovskite with relatively high $T_C = 1110$ K and $T_N = 610$ K. Unfortunately, the synthesis of $BiFeO_3$ is difficult due to a high leakage current and the other oxide phases ($Bi_2Fe_4O_9$, $Bi_{25}Fe_2O_{39}$), that could significantly reduce the magnetoelectric effect [2–4]. Therefore, a solid solution of $BiFeO_3$ and $Pb(Fe_{2/3}W_{1/3})O_3$ was synthesized, where $Pb(Fe_{2/3}W_{1/3})O_3$ component is a lead-based complex perovskite with a large dielectric constant, $T_C = 150$ K and $T_N = 350$ K, respectively [7, 11].

2. Sample preparation

High purity powder oxides of Bi_2O_3, Dy_2O_3, Fe_2O_3, PbO_2 and Fe_2WO_3 were weighted in stoichiometric proportions and mechanically activated for 7 h during a ball milling process. Thereafter, mixture was calcined at 780 °C for 4 h, secondly granulated and pressed into disc shaped pellet (1.8 mm height and 1.53 cm in diagonal). Finally, pellet was heat-treated at 545 °C for 2 h and sintered at 850 °C either for 2 h.

3. X-Ray studies

Crystallographic structure of $0.5Bi_{0.95}Dy_{0.05}FeO_3$-$0.5Pb(Fe_{2/3}W_{1/3})O_3$ (BDF-PFW) material was examined by X-ray diffraction technique using Cu K_α radiation and Philips powder diffractometer with graphite monochromater. A fitting program (FULLPROF software [12]) based on the Rietveld method was used to analyse the diffraction pattern — Fig. 1.
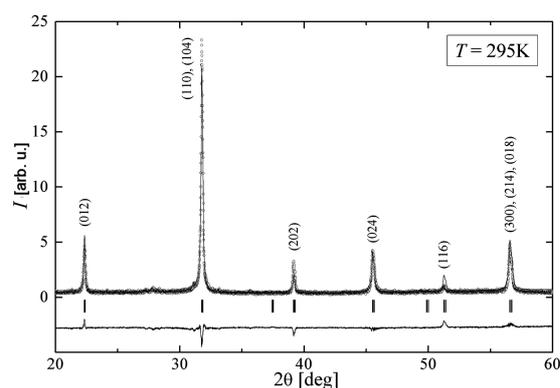
Fig. 1. Observed (open circles), calculated and difference X-ray diffraction profiles of BDF-PFW at 295 K.

In general rule ABO_3-type perovskites crystallise in cubic Pm-$3m$ system. Nevertheless, the ferroelectric

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materials distinctly show off-centre shift of the B-site cation during polarisation ordering and therefore in ferroelectrics a small tetragonal distortion is observed. On the other hand, $BiFeO_3$ perovskite is characterized by a small rotation of the oxygen octahedra leading to a rhombohedral distortion [7].

Therefore, a few probable crystallographic structures of BDF-PFW were examined during the refinement procedure. The best result was obtained for the tetragonal structure $P4mm$. Determined lattice parameters $a = 3.988(3)$ Å and $c = 3.981(3)$ Å indicate that BDF-PFW is closely related to ideal perovskite with a slightly tetragonal distortion $c/a = 0.998$. Fitted lattice parameters and atom positions are summarised in Table I.

TABLE I

Results of the Rietveld refinement for BDF-PFW: W.p. — Wyckoff position in $P4mm$ structure; x, y, z — atom coordinates, B_{iso} — isotropic displacement factor ($B_{iso} = 8\pi^2\langle u^2\rangle$), where $\langle u^2\rangle$ — mean square displacement amplitude), Occ. — stoichiometric site occupancy.

Atom	W.p.	x	y	z	B_{iso} [A^2]	Occ.
Pb, Bi, Dy	1a	0	0	0	2.348(2)	0.500 0.475 0.025
Fe, W	1b	0.5	0.5	0.512(4)	0.534(1)	0.833 0.167
O$_1$	1b	0.5	0.5	0.046(3)	1.362(5)	1.000
O$_2$	2c	0.5	0	0.452(2)	1.362(5)	1.000

$P4mm$ (No. 99): $a = 3.988(3)$ Å, $c = 3.981(3)$ Å

4. Mössbauer spectroscopy measurements

^{57}Fe transmission Mössbauer spectrum of BDF-PFW was measured at 77 K (Fig. 2) using about 20 mCi source of ^{57}Co in Rh matrix. Hyperfine interaction parameters as isomer shift (δ) relative to metallic iron at 300 K, quadrupole shift (ε) and hyperfine magnetic field ($\mu_0 H_{hf}$) were determined from positions of Lorentzian lines and are summarised in Table II. In the investigated case the magnetic interactions are much bigger than quadrupole ones therefore the first-order perturbation approximation was used.

Mössbauer spectrum is dominated by two Zeeman sextets (M1, M2) originating from BDF-PFW sinter. Additionally, there are two small quadrupole doublets Q1 and Q2 (totally of about 3%) of the impurity phases either oxides $Bi_{25}FeO_{39}$, $Bi_2Fe_4O_9$ or $Pb_3(Nb,Fe)_4O_{13}$ [6, 11].

Iron atoms are stochastically distributed among BDF-PFW compound. According to sinter stoichiometry consideration 60% of Fe atoms originate from $Bi_{0.95}Dy_{0.05}FeO_3$ phase, whereas the remainder Fe atoms come from $Pb(Fe_{2/3}W_{1/3})O_3$ component. Therefore,

TABLE II

Characteristic Mössbauer parameters of BDF-PFW at 77 K. δ is the isomer shift with respect to the source of ^{57}Co in Rhodium, (ε) is the quadrupole shift, $\mu_0 H_{hf}$ is the magnetic hyperfine field and A represents the relative areas of the components.

Subspectrum	δ [mm/s]	ε [mm/s]	$\mu_0 H_{hf}$ [T]	A [%]
M1	0.448(1)	0.101(4)	54.2(8)	57.8
M2	0.435(9)	−0.008(2)	52.3(9)	39.1
Q1	0.189(3)	0.418(3)	—	1.5
Q2	0.252(6)	0.810(2)	—	1.6
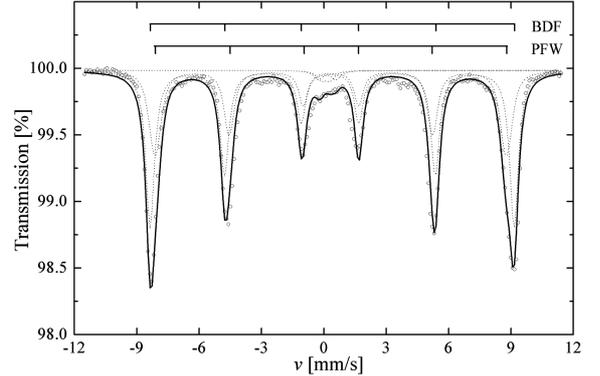
Fig. 2. ^{57}Fe Mössbauer effect spectrum of BDF-PFW sinter at 77 K.

first Zeeman sextet (M1) has surface of about 58%, while the second subspectrum (M1) has area around 39% (Table II).

Values of δ and ε parameters are typical for Fe^{3+} ion in octahedral symmetry [13]. Both magnitudes of magnetic hyperfine fields about 52 T and 54 T are normal for ferric iron. Thus, a Fe^{3+} charge state for all iron atoms of BDF-PFW perovskite has been confirmed.

Additionally, Mössbauer spectroscopy was used to estimate the magnetic ordering temperature T_N. A series of Mössbauer spectra recorded at different temperatures 525 K ÷ 800 K were fitted by assuming a single doublet
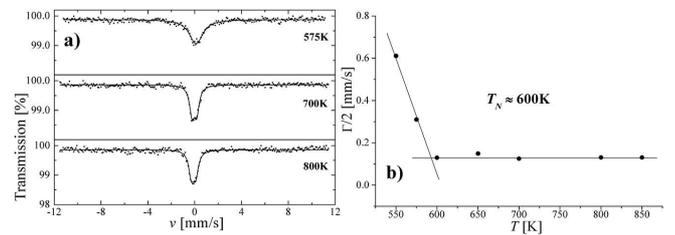
Fig. 3. a) Temperature evolution of the selected Mössbauer spectra: close to T_N in magnetic state (575 K) and above T_N (700 K and 800 K); b) temperature dependence of a half width of Lorentzian line.

with appropriate quadrupole splitting (Fig. 3a). The overall width of the individual Lorentzian line was extracted on the assumption that two main spectrum components of BDF-PFW coexist. Temperature evaluation of a half width of Lorentzian line $\Gamma/2$ is presented in Fig. 3b. T_N was estimated at around 600 K and obtained value is close to the magnetic ordering temperature of pure BiFeO$_3$, although T_N for Pb(Fe$_{2/3}$W$_{1/3}$)O$_3$ compound is relatively lower and amounts about 350 K [11].

5. Conclusions

0.5Bi$_{0.95}$Dy$_{0.05}$FeO$_3$-0.5Pb(Fe$_{2/3}$W$_{1/3}$)O$_3$ perovskite was synthesised by means of the conventional solid state reaction method. The crystallochemical purity of material was checked by X-ray diffraction and Mössbauer effect studies. X-ray analyses confirmed a slightly tetragonal distortion from the ideal perovskite ABO$_3$ structure (Pm-$3m$) to $P4mm$ symmetry. Mössbauer spectroscopy has been verified, that all iron atoms are Fe^{3+} in octahedral symmetry. Furthermore, Mössbauer technique detects a small contribution of impurity phases of about 3% and let us estimate the magnetic ordering temperature, which is comparable with T_N of pure BiFeO$_3$ compound.

Acknowledgements

References

[1] E. Asher, H. Rieder, H. Schmid, H. Stossel, *J. Appl. Phys.* **37**, 1404 (1966).

[2] H. Paik, H. Hwang, K. No, S. Kwon, D.P. Cann, *Appl. Phys. Lett.* **90**, 042908 (2007).

[3] G.L. Yuan, S.W. Or, J.M. Liu, Z.G. Liu, *Appl. Phys. Lett.* **89**, 052905 (2006).

[4] S.T. Zhang, Y. Zhang, M.H. Lu, C.L. Du, Y.F. Chen, Z.G. Liu, Y.Y. Zhu, N.B. Ming, X.Q. Pan, *Appl. Phys. Lett.* **88**, 162901 (2006).

[5] Y. Yang, J.M. Liu, H.B. Huang, W.Q. Zuo, P. Bao, Z.G. Liu, *Phys. Rev. B* **70**, 132101 (2004).

[6] J. Kulawik, D. Szwagierczak, *J. Eur. Ceram. Soc.* **27**, 2281 (2007).

[7] K.F. Wang, J.M. Liu, Z.F. Ren, *Adv. Phys.* **58**, 321 (2009).

[8] J. Wang, *Science* **299**, 1719 (2003).

[9] T. Kimura, *Nature* **426**, 55 (2004).

[10] N. Hur, *Nature* **429**, 392 (2003).

[11] S.A. Ivanov, S.G. Eriksson, R. Tellgren, H. Rundolf, *Materials Research Bulletin* **39**, 2317 (2004).

[12] J. Rodríguez-Carvajal, *IUCR Newsl.* **26**, 12 (2001).

[13] S.A. Ivanov, P. Nordblad, R. Tellgren, T. Ericsson, H. Rundlof, *Solid State Sci.* **9** 440 (2007).