

# Hyperfine interactions in $x\text{Bi}_{0.95}\text{Dy}_{0.05}\text{FeO}_3-(1-x)\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ multiferroics

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**Abstract.** The complex perovskite system  $x\text{Bi}_{0.95}\text{Dy}_{0.05}\text{FeO}_3-(1-x)\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$  was synthesized by the solid-state reaction method and was studied by means of Mössbauer spectroscopy. For different Dy-doped bismuth ferrite (BDF) contents ( $x = 0.1, 0.3, 0.5, 0.7$ ) the formation of single-phase sinters was confirmed using an X-ray diffraction technique. The random distributions of Fe/W cations in crystallographic structures have been proved. A monotonically, saturation-like increase of Néel temperatures with growing BDF contribution was confirmed, and a straightforward dependence between  $T_N$  temperatures and the mean hyperfine magnetic fields at Fe nuclei was shown.

**Key words:** multiferroics • multifunctional materials • Néel temperature

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## Introduction

New materials, which expose two or three simultaneous orderings in one single phase, are mostly preferable in modern sciences as well as in the innovative technical applications. Magnetically and ferroelectrically ordered substances, which are named multiferroics or multifunctional materials could make a great step for the development and engineering design of more user-friendly devices used in ordinary life. Especially, compounds with an electromagnetic coupling are highly interesting for both puzzling fundamental physics at basic level and potential applications, for example, in optoelectronics, spintronics and communications. Also, an improvement of electromechanical characteristics of recent sensors, transmitters, transducers and other electronic components is possible.

Promising candidates for multifunctional materials are natural perovskites, however with slightly modified structures, for example, by doping ferromagnetic lanthanide cations  $\text{La}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Er}^{3+}$  [9] or by combined two-perovskite mixtures with different electromagnetic characteristics of both constituents.

This paper presents the results of magnetic properties of  $x\text{Bi}_{0.95}\text{Dy}_{0.05}\text{FeO}_3-(1-x)\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$  system composed of bismuth ferrite (BFO), which exhibits both ferroelectric ( $T_C = 1143\text{ K}$ ) and antiferromagnetic ( $T_N = 643\text{ K}$ ) orderings at room temperature [7], and a

lead-based complex perovskite  $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$  (PFW) with a large dielectric constant,  $T_C = 150$  K and  $T_N = 350$  K, respectively [1]. Dy doping of  $\text{BiFeO}_3$  (BDF) is involved for avoiding the formation of multiphase structures mainly embracing  $\text{Bi}_2\text{Fe}_4\text{O}_9$ ,  $\text{Bi}_{46}\text{Fe}_2\text{O}_{72}$  oxides and for a better structural stabilization [6, 8].

## Experimental setup

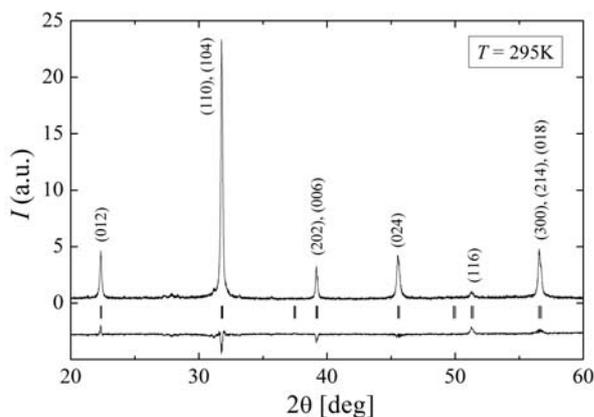
A series of  $x\text{-BDF-(1-x)PFW}$  compounds was synthesized by the solid-state reaction method for a few intermediate concentrations  $x = 0.1, 0.3, 0.5, 0.7$ . Samples were prepared from the high purity powdered oxides  $\text{Bi}_2\text{O}_3$ ,  $\text{Dy}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{PbO}_2$ ,  $\text{Fe}_2\text{WO}_3$  and were finally formed as sintered pellets, according to the description given elsewhere [5].

Crystallographic structures of the sintered materials were examined by a Philips powder X-ray diffractometer with a graphite monochromator. FULLPROF software [4] based on the Rietveld method [3] was used to analyse the diffraction patterns. Measurements of transmission Mössbauer spectroscopy were carried out at 77 K on a WissEl device equipped with a 50 mCi  $^{57}\text{Co}$  source. A velocity range of  $\pm 11$  mm/s was set up, furthermore the Mössbauer spectra were calibrated with a 25  $\mu\text{m}$  pure Fe foil and evaluated by the Voigt-function model.

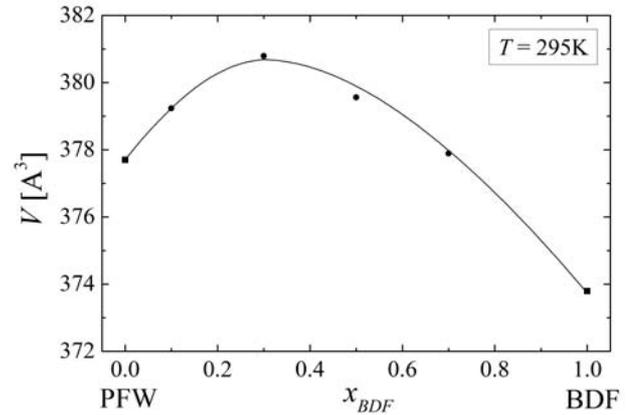
## Results

X-ray diffraction investigations have been made for proving a single-phase and structural homogeneity of the obtained materials (Fig. 1). Additionally, a diffraction technique was used for the monitoring of structural changes induced by sintering of two perovskite constituents with various relative contributions  $x$  that nominally crystallized in different symmetry systems. A room-temperature phase of  $\text{BiFeO}_3$  is classified as rhombohedral  $R3c$  with lattice parameters  $a = 5.579$  Å and  $c = 13.869$  Å [2], whereas  $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$  is crystallized in cubic symmetry  $Pm-3m$  with lattice parameter  $a = 3.978$  Å [1].

As one expected, the substitution of  $\text{Pb}^{2+}$  by  $\text{Bi}^{3+}$  atoms of smaller ionic radius should lead to decreasing the lattice parameters with BDF content. Also, above a certain concentration of BDF a domination of rhombo-



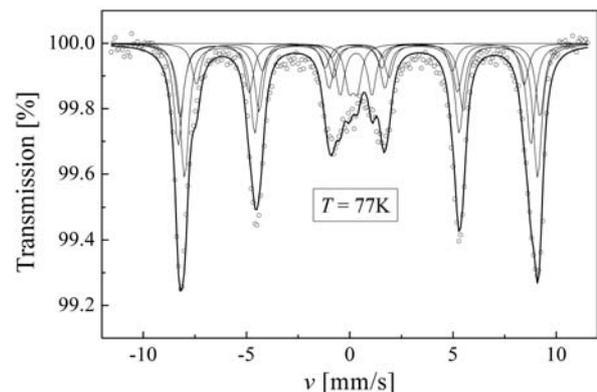
**Fig. 1.** X-ray diffraction pattern of 0.3 BDF-0.7 PFW compound measured at room temperature.



**Fig. 2.** Unit cell volume changes vs. composition of sinters considering a different multiplicity of primitive unit in various crystallographic systems. Solid squares represent the boundary compounds PFW and BDF.

hedral distortion should be visible. However, the volume of unit cell changes parabolically with BDF content and is showing a maximum value at around  $x = 0.3$  (Fig. 2), what suggests a small rearrangement of atoms in the sintered materials. Therefore, a few crystal structures were tested out during a fitting procedure and the determination of proper symmetry was inconvenient. Finally, the best agreement to the experimental patterns of  $x\text{-BDF-(1-x)PFW}$  compounds was found for two structures:  $P4mm$  (No. 99) at  $x = 0.1$  and  $R3c$  (No. 161) for the rest sinters. However, a tetragonal distortion  $P4mm$  is very small, for example, the ratio of the lattice parameters  $c/a$  is almost ideal for the cubic structure and amounts to 1.00(2). It is also clearly seen that the modest content of BDF,  $x = 0.15 \div 0.25$ , is enough to enforce the rhombohedral distortion.

In order to investigate the local crystallochemical environment at atomic scale Mössbauer spectroscopy was used. A typical transmission spectrum of 0.3 BDF-0.7 PFW compound measured at 77 K is presented in Fig. 3. The sample exhibits a magnetic arrangement, nevertheless the characteristic spectral lines for Zeeman splitting are moderately broadened. There was made an assumption that broadening of the resonance lines is a consequence of a different nearest-neighbour surrounding of iron atoms as a result of random substitution of  $\text{Fe}^{3+}/\text{W}^{6+}$  cations. Therefore, a fitting model based on binomial distribution was employed, where  $P(6;n) = 6! / [(6-n)!n!] \cdot (1-x)^{6-n} x^n$  is the probability of individual



**Fig. 3.**  $^{57}\text{Fe}$  transmission Mössbauer effect spectrum of 0.3 BDF-0.7 PFW sinter measured at 77 K.

**Table 1.** The hyperfine interaction parameters of 0.3 BDF-0.7 PFW compound at 77 K.  $A$  represents the area of individual subspectrum relative to the contribution of particular component

Component	$\delta$ (mm/s)	$\Delta$ (mm/s)	$\mu_0 H_{\text{eff}}$ (T)	$A$ (%)
M1	$0.559 \pm 0.014$	$0.098 \pm 0.010$	$52.96 \pm 0.08$	33.8
M2	$0.444 \pm 0.011$	$0.160 \pm 0.011$	$54.01 \pm 0.07$	18.6
M3	$0.502 \pm 0.012$	$-0.161 \pm 0.010$	$52.91 \pm 0.08$	25.7
M4	$0.546 \pm 0.023$	$0.071 \pm 0.015$	$49.17 \pm 0.10$	7.5
S1	$0.416 \pm 0.019$	$0.768 \pm 0.058$	–	6.5
S2	$0.275 \pm 0.021$	$0.198 \pm 0.084$	–	5.1

**Table 2.** Mean values of hyperfine interaction parameters and magnetic ordering temperature  $T_N$  for  $x\cdot\text{BDF}\cdot(1-x)\cdot\text{PFW}$  system

Compound	$\delta$ (mm/s)	$\Delta$ (mm/s)	$\mu_0 H_{\text{eff}}$ (T)	$T_N$ (K)
PFW	0.525	–	50.5	350
0.1 BDF-0.9 PFW	$0.520 \pm 0.008$	$0.013 \pm 0.004$	$50.8 \pm 1.8$	$416 \pm 1$
0.3 BDF-0.7 PFW	$0.516 \pm 0.007$	$0.032 \pm 0.006$	$52.6 \pm 2.1$	$529 \pm 1$
0.5 BDF-0.5 PFW	$0.513 \pm 0.009$	$0.025 \pm 0.004$	$53.4 \pm 1.8$	$590 \pm 1$
0.7 BDF-0.3 PFW	$0.512 \pm 0.007$	$0.028 \pm 0.005$	$53.9 \pm 1.9$	$617 \pm 1$
BDF	0.511	–	54.2	643

neighbourhood of selected iron atom composed of  $(6-n)$  Fe atoms and  $(n = 0, 1, 2, \dots, 6)$  W atoms, and  $x$  corresponds to the stoichiometry of  $x\cdot\text{BDF}\cdot(1-x)\cdot\text{PFW}$  with respect to BDF content. Particular neighbourhoods of iron atoms produce the individual subspectra that contribute to the overall Mössbauer effect pattern. Assuming that the amplitudes of particular Mössbauer subspectra follow the probabilities  $P(6;n)$ , a fitting procedure was performed with a limited number of employed sextets due to postulation that probabilities below 5% were neglected. Therefore, at a final stage of the fitting procedure the free amplitudes of subspectra were also considered.

The hyperfine interaction parameters of 0.3 BDF-0.7 PFW are listed in Table 1. For magnetic components (M1–M4), a mean values of hyperfine interaction parameters were determined for further comparison and analysis.

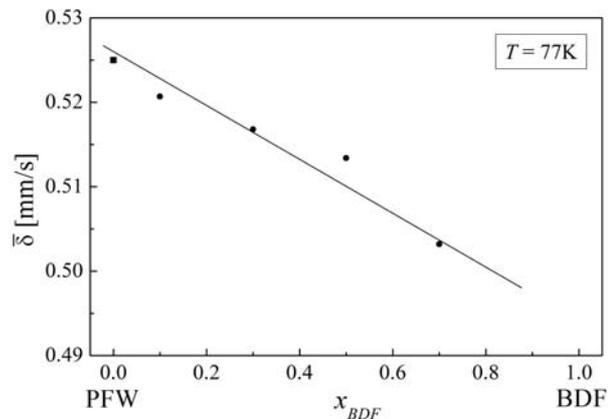
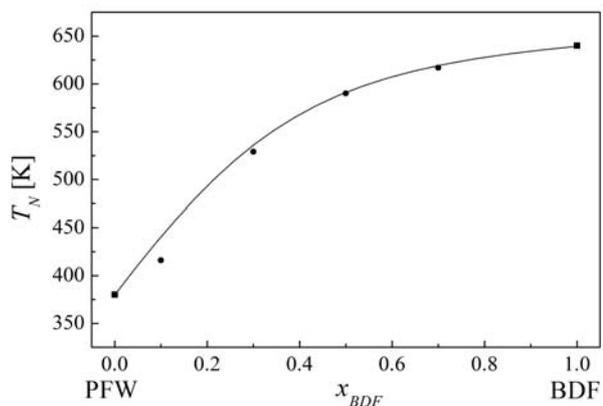
Additionally, two small quadrupole doublets S1 and S2 were detected (Fig. 3, Table 1) and it was characteristic phenomenon for all synthesized BDF-PFW multiferroics. Insignificant non-magnetic components probably arise from impurity oxide phases, which are easily formed during the synthesis of  $\text{BiFeO}_3$ .

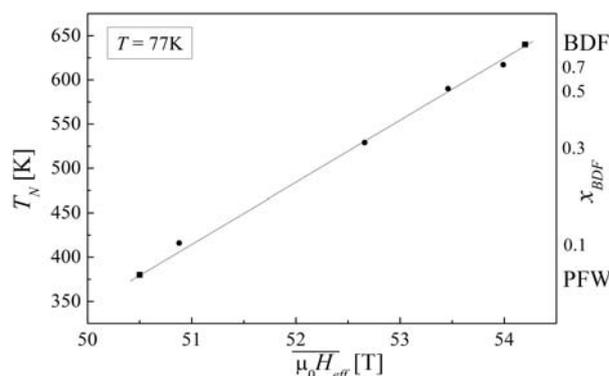
More interesting behaviours are noticeable along the BDF-PFW series. The weighted by subspectra amplitudes  $A$ , the average hyperfine interaction parameters of isomer shift  $\delta$ , quadrupole splitting  $\Delta$  and hyperfine magnetic field  $\mu_0 H_{\text{eff}}$  for all sinters are presented in Table 2. The  $\delta$  parameter is showing inversely proportional dependence on BDF content – Fig. 4a. Substitution of  $\text{W}^{6+}$  by  $\text{Fe}^{3+}$  atoms at B site in  $\text{ABO}_3$  perovskite structure gives rise to an increment of  $s$ -electron density at Fe nucleus involving a reduction in the value of isomer shift parameter (Fig. 4a). The evaluation of quadrupole splitting parameter is important with respect to analyse the local symmetry. Generally, the values of  $\Delta$  are rather small along the BDF-PFW series what means slightly disordered structural atoms in the synthesized materials. One can assume that a maximal value of  $\Delta$  for  $x = 0.3$  coincides with a maximum of the unit cell volume – Fig. 2.

A Mössbauer spectroscopy technique was also used to estimate the magnetic ordering temperatures of

BDF-PFW compounds. A full width at half maximum of a single line was monitored as a function of temperature, and  $T_N$  was defined as an intersection of two trend lines sloping and horizontal below  $T_N$  and in paramagnetic state, respectively.

Predictably, magnetic ordering temperature  $T_N$  is monotonically growing with BDF content and these changes exhibit saturation-like character – Fig. 4b.

**Fig. 4a.** The mean isomer shift parameters determined at 77 K as a function of composition. A solid square represents the boundary compound PFW.**Fig. 4b.** The magnetic ordering temperatures as a function of composition. Solid squares represent the boundary compounds PFW and BDF.



**Fig. 5.** The magnetic ordering temperatures vs. mean values of hyperfine magnetic field at Fe nuclei determined at 77 K. Solid squares represent the boundary compounds PFW and BDF.

Also, a mean magnetic hyperfine field parameter is growing along the BDF-PFW series (Table 2), therefore, the interesting question is about relationship between those two quantities. As one can see in Fig. 5, there is a straight-line dependence between  $T_N$  and  $\mu_0 H_{\text{eff}}$ . This means that with increasing effective hyperfine fields at Fe nuclei the induced magnetic moments are larger and the stronger magnetic coupling are sufficient at higher temperatures to resist the thermal fluctuations.

## Conclusions

The  $x$ -BDF-(1-x)-PFW compounds were synthesized by using a conventional solid state reaction method. The purity of sinters has been confirmed by an X-ray diffraction technique. A related similarity between the probabilities  $P(6;n)$  and contributions of Mössbauer subspectra  $A$  can be treated as evidence of the random distribution of Fe/W cations. The average magnetic

hyperfine fields correspond approximately to the saturated magnetic moments of Fe atoms and indirectly to magnetic ordering temperatures  $T_N$ , which could be linearly modified between 350 K and 640 K, with respect to BDF content. The potential applications of  $x$ -BDF-(1-x)-PFW complex materials involve the supplementary investigations of magnetoelectric properties.

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