Crystal structure and Mössbauer effect in multiferroic 0.5BiFeO$_3$-0.5Pb(Fe$_{0.5}$Ta$_{0.5}$)O$_3$ solid solution

Abstract. Multiferroic 0.5BiFeO$_3$-0.5Pb(Fe$_{0.5}$Ta$_{0.5}$)O$_3$ solid solution is a material that exhibits ferroelectric and antiferromagnetic orderings in ambient temperature. The solid solution was obtained as a result of a conventional reaction in a solid state. The obtained material is a dense, fine-grained sinter whose surface was observed by scanning electron microscopy (SEM) and stoichiometry was confirmed by energy dispersive X-ray spectroscopic (EDS) analysis. According to the X-ray powder diffraction (XRD) measurements, the main phase is R3c space group with admixture of Pm-3m regular phase. Small contribution of pyrochlore-like phase was also observed. Mössbauer spectroscopy suggested random distribution of Fe$^{3+}$/Ta$^{5+}$ cations in the B sites of ABO$_3$ compound. Reduction of the magnetic hyperfine field with an increase in the substitution of Ta$^{5+}$ in Fe$^{3+}$ neighbourhood was also observed.

Keywords: BiFeO$_3$ • crystal structure • hyperfine interactions • multiferroics • solid solution

Introduction

Materials that exhibit ferromagnetic and ferroelectric ordering in the same phase are named magnetoelectrics, which are part of a larger group of multiferroics. Multiferroics possess at least two ferroic orderings at the same time. Magnetoelectric materials are characterized by a strong coupling between the magnetic and electric subsystems, which means that the magnetic field is able to induce electric polarization and vice versa.

The first single-phase multiferroic perovskite oxides (ABO$_3$) were discovered in early 1960s. However, very limited progress has been made during the past several decades [1–6]. The significant development of multiferroic materials started with the successful synthesis of multiferroic thin films [7].

Magnetoelectrics are widely used as transducers, actuators, detectors, and other sensors that are characterized by high dielectric permittivity and magnetic permeability [1–7]. Strong coupling between electrical polarization and magnetization vectors is desirable for a new class of multifunctional materials, for example, new mass storage devices. Unfortunately, most multiferroic materials are characterized by a low magnetic ordering temperature, considerably below room temperature, what limits their practical applications.

Bismuth ferrite (BiFeO$_3$) is a well-known perovskite compound that simultaneously exhibits...
ferroelectric ($T_C = 1110$ K) and antiferromagnetic ($T_N = 610$ K) orderings at ambient temperature. The stereochemical activity of Bi lone-pair electrons induces ferroelectric polarization, while the partially filled 3$d$ orbitals of the Fe$^{3+}$ ions produce G-type antiferromagnetic ordering. BiFeO$_3$ has a spatially modulated magnetic structure of a cycloidal type with a period of modulation of about 62 nm [4, 7]. One way to suppress the spiral spin modulation is the chemical substitution of magnetically active atoms, especially rare earth trivalent ions, into the Bi sublattice [4].

Lead iron tantalate (Pb(Fe$_{0.5}$Ta$_{0.5}$)O$_3$) is another type of magnetoelectric material where ferroelectrically active Ta$^{5+}$ cations are partially substituted by magnetic Fe$^{3+}$ ions of a different valence state, the so-called paramagnetic substitution [5]. As a consequence, Pb(Fe$_{0.5}$Ta$_{0.5}$)O$_3$ exhibits antiferromagnetic ordering at temperatures below 150–180 K as well as ferroelectric ordering at temperature below 270 K [8–12]. It is considered that the magnetic ordering temperature and magnetic properties of the iron-containing oxides depend on the number of Fe-O-Fe linkages in a crystal lattice [13]. The number of Fe-O-Fe linkages can be governed by changing the Ta$^{5+}$/Fe$^{3+}$ ratio and/or the degree of Fe$^{3+}$ and Ta$^{5+}$ cations ordering. However, no such ordering have been observed and Pb(Fe$_{0.5}$Ta$_{0.5}$)O$_3$ could be considered as a fully disordered in B-site sublattice of perovskite structure [8–10]. On the other hand, for a similar Pb(Fe$_{0.5}$Nb$_{0.5}$)O$_3$ compound, large scattering of magnetic ordering temperature could be explained by local compositional ordering and formation of Nb-poor-Fe-rich and Nb-rich-Fe-poor regions as postulated in [14–16]. Additionally, Pb(Fe$_{0.5}$Ta$_{0.5}$)O$_3$ is a perovskite relaxor, is reported to have a very high dielectric constant, and can be used as a multilayer ceramic capacitor [17].

The 0.5BiFeO$_3$-0.5Pb(Fe$_{0.5}$Ta$_{0.5}$)O$_3$ solid solution is a mixture of two compounds in which multiferroicity is governed by two different mechanisms such as lone pairs in BiFeO$_3$ and paramagnetic substitution of Fe$^{3+}$ cations by ferroelectrically active Ta$^{5+}$, although the lone pairs mechanism could not be excluded in Pb(Fe$_{0.5}$Ta$_{0.5}$)O$_3$ [18]. In this paper, we report the synthesis, crystal structure, and hyperfine interactions in 0.5BiFeO$_3$-0.5Pb(Fe$_{0.5}$Ta$_{0.5}$)O$_3$ solid solution. The aim of the research was to find the correlation between the structure and the size of hyperfine interactions.

**Experimental**

High-purity Bi$_2$O$_3$, PbO, Fe$_2$O$_3$, and Ta$_2$O$_5$ oxide powders were weighted in stoichiometric proportions, mechanically activated for 7 h during a ball milling process, pressed into pellets, and calcined at 1093 K for 4 h. The molder was then granulated and pressed into a disc-shaped pellet. The pellets were heat treated at 818 K for 2 h and then sintered at 1128 K for 10 h. The pellets were then cooled down to room temperature with the rate of cooling of the furnace.

Crystal structure of the powdered material was checked by Bruker-AXS D8 diffractometer in the Bragg-Brentano geometry at room temperature using CuK$_\alpha$ radiation of wave length $\lambda = 1.5418$ Å.

The surface of the fractured sample was observed by scanning electron microscopy (SEM) using FEI Nova NanoSEM 200 equipped with energy dispersive X-ray spectroscopy (EDS) by EDAX company.

Transmission $^{57}$Fe Mössbauer spectroscopy measurements were performed on a WissEl spectrometer with Oxford cryostat at 77 K. The spectrometer was calibrated using ARMCO foil at room temperature and all isomer shift (IS) values are related to this standard. Share of the particular components was estimated by assuming the same value of Lamba-Mössbauer parameter.

**Results and discussion**

**SEM-EDS studies**

Surface of the 0.5BiFeO$_3$-0.5Pb(Fe$_{0.5}$Ta$_{0.5}$)O$_3$ ceramic sample is presented in Fig. 1. The material is a fine-grained, dense sinter with small grains of few micrometres in size. Energy dispersive analysis was performed at various points corresponding to larger and smaller grains. The EDS profile analysis is close to the theoretical oxide composition within the experimental error range in points 1 and 2 (Fig. 1). In case of point 3, in which the grain size is the smallest, there is a lower concentration of iron. There are no unreacted starting oxides and phases, which can be precipitated as a result of a possible evaporation of Bi$_2$O$_3$ and PbO during the synthesis process.

**Crystal structure**

Crystal structure and phase purity of the sinter were checked by X-ray powder diffraction (XRD). A fitting program (FullProf software [19]), based on the Rietveld method, was used to analyse the diffraction pattern.

![Fig. 1. SEM image of 0.5BiFeO$_3$-0.5Pb(Fe$_{0.5}$Ta$_{0.5}$)O$_3$](image-url)
Crystal structure and Mössbauer effect in multiferroic 0.5BiFeO3-0.5Pb(Fe0.5Ta0.5)O3 solid solution

The simple ABO₃ perovskite crystallizes in a cubic Pm-3m crystal structure, although the ferroelectric materials distinctly show an off-centre shift of the B-site cation during polarization ordering, and, therefore, a small tetragonal distortion is observed. Additionally, the coexistence of ferroelectric and ferromagnetic orderings often leads to the rotations of the oxygen octahedra resulting in rhombohedral distortion [18]. The crystallographic transitions are not distinct and, therefore, difficult to measure. A few probable crystal structures such as Pm-3m, P4mm, R3c, and Cm were examined during the refinement procedure. The XRD pattern is presented in Fig. 2. The best result was obtained by assuming R3c space group for the main phase. The lattice parameters of the phase are \(a = b = 5.6524(4)\) Å and \(c = 13.8489(18)\) Å, and thus the rhombohedral angle is 59.97°, which is close to 60° (the value for a cubic structure in rhombohedral coordinates), thus the observed rhombohedral distortion is very small.

Pure BiFeO₃ is formed only when Bi₂O₃ to Fe₂O₃ ratio is equal 1:1. Small inhomogeneities lead to the formation of Fe rich phase Bi₂Fe₄O₉ and/or Bi rich phase Bi₂₀Fe₂O₆₃ [20]. Additionally, frequently observed impurity phases are pyrochlores, which could be a solid solution of (Pb,Bi)₂(Fe,Ta)₂O₇. In the obtained material, the pyrochlore phase was also added during the fitting procedure and is represented by asterisk in Fig. 2. The fitted secondary phase is similar to pyrochlores of reference codes 00-014-0318 and 00-034-0871 from ICDD database. The quantity of this phase according to the Rietveld refinement is approximately 10 mass%.

The calculated Goldschmidt tolerance factor for the studied solid solution is 0.95, which is close to unity, and thus ideal cubic perovskite structure is privileged. On the other hand, ferroelectrically active cations such as Pb²⁺ and Ta⁵⁺ enforce distortion of the unit cell but we cannot exclude the existence of the cubic symmetry. Closer look at the Bragg reflex at the higher angle of about 56° showed more complex structure of the peak, which is presented in Fig. 3.

At approximately 56.1°, another peak that originated from the regular cubic phase can be observed. Thus Pm-3m space group was also added to the fitting procedure. The existence of the cubic centrosymmetric phase excludes possibility of electric and magnetic orderings [18]. Therefore, it could be assumed that the obtained material is in paramagnetic and paraelectric state. On the basis of the EDS analysis, both phases should have a similar stoichiometry. Therefore, we conclude, at this moment, that the obtained material is in paramagnetic and paraelectric state. On the basis of the EDS analysis, both phases should have a similar stoichiometry. Therefore, we conclude, at this moment, that the 0.5BiFeO₃-0.5Pb(Fe₀.₅Ta₀.₅)O₃ solid solution is a mixture of two very similar crystal phases. One is a perovskite-like R3c (about 70 mass%) in which the material could possess magnetic and electric orderings. The second is the regular perovskite Pm-3m (about 20 mass%) in which, based on the fundamental symmetry consideration, electric and magnetic orderings are forbidden [18].

Mössbauer spectroscopy

In order to investigate the local crystallochemical environment at atomic scale, Mössbauer spectroscopy was used. A typical transmission spectrum of the obtained solid solution measured at 77 K is presented in Fig. 4. The obtained spectrum is a composition of four Zeeman sextets and two paramagnetic doublets. For the 0.5BiFeO₃-0.5Pb(Fe₀.₅Ta₀.₅)O₃ compound, the Goldsmith tolerance factor is smaller than unity, what suggests random distribution of Fe³⁺/Ta⁵⁺ cations at the B site of the ABO₃ perovskite structure. In the perovskite, every iron octahedron is neighboured by....
The obtained IS value is in the range 0.40–0.49 mm/s, which was previously reported for pyrochlores of similar composition [23].

The use of binominal distribution in fitting of the spectra gives us the possibility to ascribe the magnetically splitted components to the different surroundings of the studied iron nuclei. According to the obtained probabilities, components no. 1–4 (Table 1) could be assigned to the configurations (6,0), (5,1), (4,2) and (3,3), respectively, where the first number in the bracket is the number of surrounded octahedrons with Fe³⁺ in the middle and the second one with Ta⁵⁺. It can be seen that increasing the number of Ta⁵⁺ in the local surrounding of iron lead to the reduction of the μHN field. This dependence is presented in Fig. 5 and the linear behaviour is evidenced.

Conclusions

The 0.5BiFeO₃-0.5Pb(Fe₀.₅Ta₀.₅)O₃ perovskite was synthesized by means of a conventional solid-state reaction method. The obtained material is a dense, fine-grained sinter. According to the XRD analysis, the main crystal phase is rhombohedral R3c with the addition of some regular Pm-3m space group. The Mössbauer spectroscopy confirmed the existence of magnetic ordering of the R3c structure with a possible random distribution of the Fe³⁺/Ta⁵⁺ cations in the unit cell of the 0.5BiFeO₃-0.5Pb(Fe₀.₅Ta₀.₅)O₃. This substitution decreases the number of Fe-O-Fe linkages, what lead to the decrease in the magnetic hyperfine field.

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References


