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Magnetoelectric properties of $0.5BiFeO_3$–$0.5Pb(Fe_{0.5}Nb_{0.5})O_3$ solid solution

Agata Stoch[a], Pawel Stoch[b,*]

[a] Institute of Electron Technology Krakow Division, Zablocie 39, 30 – 701 Krakow, Poland
[b] AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Mickiewicza 30, 30 – 059 Krakow, Poland

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ABSTRACT

Magnetoelectrics are materials that join magnetic and electric orderings in the same phase. They exhibit magnetoelectric coupling which is important from the fundamental and practical point of view. The subject of the paper is a presentation of magnetic, electric and magnetoelectric properties of $0.5BiFeO_3$–$0.5Pb(Fe_{0.5}Nb_{0.5})O_3$ solid solution. The obtained material belongs to oxide perovskite magnetoelectrics of relatively high magnetic and electric ordering temperatures. Both temperatures are considerably above room what suggests potential application possibilities of the material. The magnetic properties were investigated using Mössbauer spectroscopy and magnetization measurements. The solid solution is an antiferromagnet with incomplete compensated magnetic moments. The electrical properties were determined using impedance spectroscopy analysis. There is an observed change of the electrical properties at the magnetic ordering temperature what indicates magnetoelectric coupling in the system. The electrical conductivity mechanism is also proposed. Magnetoelectric voltage coefficient was determined and possible explanation of its changes was proposed.

1. Introduction

Magnetoelectrics are materials that exhibit magnetic and electric orderings in the same phase. They are interesting from the application and fundamental point of view due to a fact of joining two orderings which tend to exclude each other. Electrical ordering needs the broken spatial inverse symmetry while the time reverse symmetry can be invariant. It means that a spontaneous polarization would not appear unless a structural distortion of the high-symmetry phase brakes the inversion symmetry. Contrary magnetic ordering needs the broken time-reversal symmetry whereas spatial-inverse symmetry can be invariant. This restriction results in the fact that multiferroics are rare in nature. Additionally, all conventional ferroelectric perovskite oxides contain transition metal with an empty d-shell. Magnetism, in contrast, requires transition metals with partially filled a d-shell. The difference in the filling of the d-shells makes these two ordered states mutually exclusive [1–9].

One of the possibility to overcome those problems is to synthesize materials which have two different sublattices like in $BiFeO_3$ which belongs to perovskite (ABO_3) oxides. The A-sites (Bi^{3+}) favor the stability of the ferroelectric distorted structure and the sublattice is responsible for electric polarization. At the same time, the B-sites contains magnetic (Fe^{3+}) ions which provide magnetism. Thus, ferroelectricity is induced by the ions at the A-sites and the B-sites ions induce magnetic order. In this way, the above exclusion rule of ferroelectricity and magnetism can be obeyed [8,10].

Another option is to mix both magnetic and ferroelectric active ions in the same sublattice eg. $Pb(Fe_{0.5}Nb_{0.5})O_3$. There at the B-sites ferroelectric active Nb^{5+} ions, with empty 5d-shell are partially substituted by magnetically active Fe^{3+} ions, which have partially filled 3d-shell. In this system, Nb^{5+} stabilize the off-centrosymmetric distortion of the regular perovskite phase while Fe^{3+} cations work in the opposite way. The magnetic doping counteracts the distortion and therefore cannot be over-concentrated. These systems are called independent. The dilution of the electrical active system leads to a decrease of electric polarization and Curie temperature. Thus, rather low electric and magnetic ordering temperatures can be expected. The coupling between the orderings originate from different kinds of ions and therefore is rather limited [8,11].

One of the most important and widely studied magnetoelectric is bismuth ferrite $BiFeO_3$ (BFO). It is characterized by high ferroelectric Curie temperature $T_C = 1100\,K$ and antiferromagnetic Néel temperature $T_N = 643\,K$. Both of these temperatures are considerably above room, which is important due to application [12,13]. In magnetoelectric state it adopts non-centrosymmetric $R3c$ perovskite-like structure [14,15]. The structural distortion is stabilized by lone pair electrons of the Bi^{3+} cations. The Bi^{3+} $6s^2$ lone pair hybridizes with 6p oxygen orbitals what produces asymmetric wave function and causes asymmetric bonding between Bi^{3+} and O^{2-}. Thus, off-center displacement of Bi^{3+} with respect to O^{2-} is obtained. The distortion shifts both

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[*] Corresponding author.
E-mail address: pstoch@agh.edu.pl (P. Stoch).

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Bi^{3+} and Fe^{3+} from the center of their coordination polyhedra toward c-axis [14]. The shift is much higher for Bi^{3+} than Fe^{3+} thus, the most of electric polarization is induced by Bi^{3+} cations and they contribute much more to the total polarization of the unit cell [15,16]. Below Néel temperature, BFO has a G-type antiferromagnetic moments alignment [4,7]. In this magnetic ordering, each iron ion magnetic moment is coupled opposite to the moment of the nearest neighbor at the B-site. This ordering is driven by a strong Fe-O-Fe superexchange interaction [17]. Taking into account, only the superexchange interaction would lead to full compensation of magnetic moments and total magnetic moment of the net should not be observed. In fact, BFO has spatially modulated magnetic structure of a cycloid type with a period of modulation of about 62 nm and exhibits at room temperature a residual moment arising from a canted spin structure [4,7]. Therefore can be concluded that there should be another interaction which has a tendency to parallel alignment of the magnetic moments which is much weaker than the Fe-O-Fe superexchange interaction [16,18]. This interaction is an anisotropic exchange interaction due to relativistic spin-orbit coupling called Dzyaloshinskii-Moriya (DM) interaction [19,20]. The interaction favors a spin canting and is a source of weak ferromagnetic behavior in an antiferromagnet. Additionally, the DM interaction stabilizes the observed oxygen displacement which causes net electric polarization what can be called as the inverse DM interaction [21]. Because of this, the interaction can cause symmetry breaking rather than be caused by non-centrosymmetric bonds. Shortening of the selected Bi-O bonds, which is the main source of net electric polarization, forces the FeO_6 octahedra to rotate. The rotation breaks the ideal linear Fe-O-Fe arrangement and gives the possibility to turn on the DM interaction what results in observation of weak ferromagnetic moment. On the other hand, due to the inverse DM interaction, the opposite effect can take place. Thus, electric polarization can induce magnetic polarization and vice versa and magnetoelectric coupling can be achieved [9,22,23].

Lead iron niobate $Pb(Fe_{0.5}Nb_{0.5})O_3$ (PFN) is another type of magnetoelectric material. This material belongs to a group of the independent system multiferroics in which Nb^{5+} sublattice is diluted by Fe^{3+} cations. It is ferroelectric below 370–380 K [24] and is a G-type antiferromagnet below 150 K [25–27]. In a magnetoelectric state, the crystal structure is postulated to be perovskite-like rhombohedral [24,25] or monoclinic [11,28,29]. The magnetic properties and magnetic ordering temperature are dependent on the number of Fe-O-Fe linkages which can be governed by changing Nb^{5+}/Fe^{3+} ratio and/or degree of Fe^{3+} and Nb^{5+} cations ordering. Generally, PFN is considered as a fully disordered in B-site sublattice of perovskite [4,30]. However, a local compositional order and formation of Nb-poor-Fe-rich and Nb-rich-Fe-poor regions were also postulated [31–33]. In PFN system Pb^{2+} cations have also stereochemical active $6\,s^{2+}$ lone pairs which similarly like in BFO can stabilize the non-centrosymmetric distortion of the lattice [34].

Bismuth ferrite forms a solid solution with other perovskite type ferroelectrics or magnetoelectrics like $BaTiO_3$, $PbTiO_3$, PFN, etc [35–40]. This can be done to enhance magnetic and/or electric properties to increase the magnetoelectric coupling and thus, to rise the magnetoelectric voltage coefficient. The increase in this parameter is one of the most important goals leading to the later industrial application of these materials.

Previously, we have shown that 0.5BFO-0.5PFN solid solution can be obtained using conventional sintering method [34]. The proposed synthesis method gives the possibility to obtain pure materials without even small amounts of secondary phases which can be easily formed during synthesis. The solid solution adopts at the room temperature rhombohedral perovskite-like *R*3*c* crystal structure with randomly placed Fe^{3+} and Nb^{5+} cations. No segregation of the cations and formation of the iron or niobium reach regions was observed. Dilution of iron sublattice by niobium decrease the exchange interaction and also decrease iron magnetic moment at low temperature. From theoretical observations, it was shown that electric polarization of the material is the mostly governed by the shift of Bi^{3+} and Pb^{2+} cations from the middle of the coordination polyhedra [34]. Therefore, it is interesting to study electric, magnetic and magnetoelectric properties of the solid solution and compare the obtained results with our previous structural and theoretical considerations

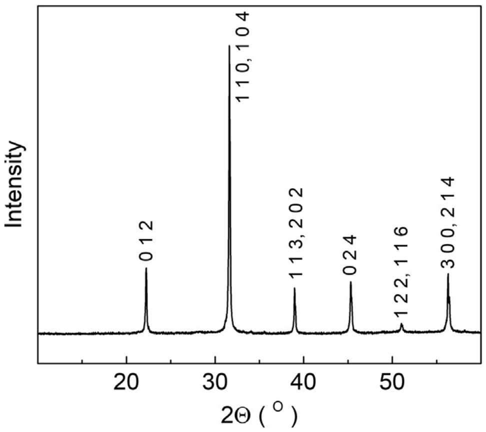

Fig. 1. XRD pattern of the obtained material.

2. Material and methods

The solid solution was prepared using the conventional ceramic method of reaction in the solid state in the same way as described previously [34]. The stoichiometry and the phase composition of the obtained material were discussed previously in [34,41]. The crystal phase purity was checked on powdered samples with application of X-ray diffraction using CuKα radiation. The XRD pattern is presented in Fig. 1. The composite is a fine-grained (a few microns grain size) dense ceramic material of perovskite-like rhombohedral (*R*3*c*) crystal structure without evidence of any secondary phases. Details concerning the crystal structure parameters are given elsewhere [34].

Thermal properties of the powdered sample were measured by differential thermal analysis (DTA) method with the heating rate of 10 $K\,min^{-1}$. Measurements were carried out using Netzsch STA449 F3 Jupiter. Powdered samples weighing 60 mg were heated in Al_2O_3 crucibles in a dry argon atmosphere up to 1350 K.

The ^{57}Fe Mössbauer effect measurements were performed using the standard technique at temperatures above and below magnetic ordering point in a transmission mode using a conventional constant-acceleration spectrometer and a 25 mCi ^{57}Co source in Rh matrix. The velocity scale was calibrated using α-Fe foil. The obtained spectra were least square fitted using conventional Lorentzian line shape and the hyperfine interaction parameters such as: relative area of the subspectrum component (A), isomer shift relative to α-Fe (IS), quadrupole split (QS), magnetic hyperfine field (μ_0H_{hf}) and half line width at half maximum (Γ) were obtained. From Mössbauer spectroscopy point of view the materials are difficult to measure because of bismuth and lead have a very high absorption coefficient of 14.4 keV radiation and only very little resonant absorption could be obtained. Therefore the effect is a very little what results in elongation time of measure.

Impedance spectroscopy measurements were conducted on polished pellets of 20 mm diameter and 5 mm height. On the pellet surface, a conductive silver paste was applied. The paste was dried in the air and then heated at 800 K by 20 min. The measured sample was located between two platinum electrodes and placed in an electric furnace with precise temperature control. The temperature of the measure was increased by 10 K from room temperature. After the temperature increase, the sample was kept at the temperature by 30 min to stabilize the measurement conditions. The impedance spectra were measured in