

Magnetoelectric Properties of 0.3Bi_{0.95}Dy_{0.05}FeO₃–0.7Pb(Fe_{2/3}W_{1/3})O₃ Multiferroic

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Pb-based complex perovskites with Fe³⁺ like Pb(Fe_{2/3}W_{1/3})O₃ were found to be interesting because of their unique properties such as relaxor and magnetoelectric behavior. Pb(Fe_{2/3}W_{1/3})O₃ is ferroelectric with ferroelectric Curie temperature T_C between 150 and 200 K and at the same time is antiferromagnetic with magnetic Néel temperature about 400 K. BiFeO₃ is a well known perovskite compound which exhibits ferroelectric ($T_C = 1103$ K) and antiferromagnetic ($T_N = 643$ K) ordering simultaneously. The polycrystalline sample of 0.3Bi_{0.95}Dy_{0.05}FeO₃–0.7Pb(Fe_{2/3}W_{1/3})O₃ were synthesized using standard sintering procedure. Magnetization vs. magnetic field (at 4.2 K) curves were measured. Magnetoelectric properties of the sample were obtained.

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1. Introduction

Materials that exhibit ferromagnetic and ferroelectric orderings in the same phase are named multiferroics. Magnetoelectric materials are very attractive due to a strong coupling between magnetic and electric subsystems, which means that magnetic field is able to induce electric polarization and vice versa. Magnetoelectrics are quite interesting because of their fundamental aspects in modern physics but also they are very desirable for practical applications. The first single phased multiferroic perovskites were discovered in the early 1960s. However, very rare and limited progress has been made during the last several decades [1–6]. A significant development of multiferroic materials has been started with successful synthesis of multiferroics' thin films [7].

Unfortunately, most of the multiferroic materials is characterized by a low magnetic ordering temperature, considerably below room temperature, and therefore a magnetoelectric effect is relatively small. Bismuth ferrite BiFeO₃ is a well known perovskite compound which simultaneously exhibits at ambient temperature ferroelectric ($T_C = 1110$ K) and antiferromagnetic ($T_N = 610$ K) ordering. Stereochemical activity of the Bi lone-pair electrons induces ferroelectric polarization, while partially field $3d$ orbitals of the Fe³⁺ ions produce G -type antifer-

romagnetic ordering. BiFeO₃ has a spatially modulated magnetic structure of cycloidal type with the period of modulation about 62 nm [4]. One of the way to suppress the spiral spin modulation is a chemical substitution of the magnetically active atoms, especially rare-earth trivalent ions into Bi sublattice. The discovery of magnetoelectricity in BiFeO₃ in a wide temperature range has made the material viable for multifunctional devices. Unfortunately high dielectric loss and high-leakage current due to presence of Fe³⁺ limit their potential applications. In order to solve these problems the rare-earths substitution at the Bi site or BiFeO₃ composites with other ferroelectric materials are being considered [2–4].

Lead iron tungsten Pb(Fe_{2/3}W_{1/3})O₃ is a multiferroic in which magnetically active Fe³⁺ cations are partially substituted by ferroelectrically active W⁶⁺ cations. This compound is characterized by the ferroelectric Curie temperature between 150 and 200 K and at the same time is antiferromagnetic with magnetic Néel temperature about 400 K [8]. A remarkable feature of this compound is that in comparison with other relaxors is high presence of the magnetic Fe³⁺ cations up to 67% of the octahedral sites in perovskite structure. The big advantage of the Pb(Fe_{2/3}W_{1/3})O₃ is that the preparation of pure perovskite phase is not so difficult as in the case of other Pb perovskite relaxors.

To overcome above-mentioned problems the solid solutions of different kinds of relaxors are being considered. The multicomponent system may exhibit better multi-

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functional, especially magnetoelectric properties at room temperature. Therefore, solid solution of the composition of $0.3\text{Bi}_{0.95}\text{Dy}_{0.05}\text{FeO}_3-0.7\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ is reported.

2. Experimental

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 800°C also for 2 h.

3. Magnetic and magnetoelectric properties

Magnetic hysteresis loop $M(H)$ was recorded at 4.2 K and is presented in Fig. 1. The magnetization curve $M(H)$ reveals a typical antiferromagnetic behavior with no magnetic saturation effect up to maximal magnetic field of 56 kOe. More detailed analysis of $M(H)$ curve is showing a slightly ferromagnetic behavior. Evaluated values of remanent magnetization M_R and coercive field H_C are 121.9 emu/mol and 890 Oe, respectively.

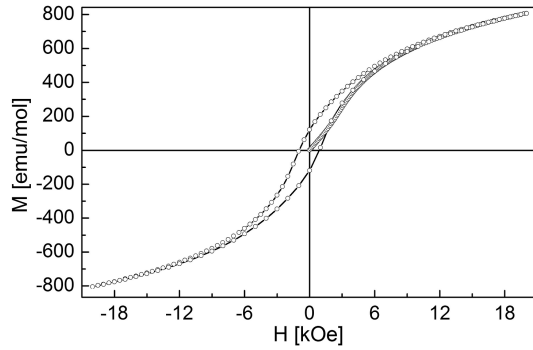


Fig. 1. Magnetization curves $M(H)$ taken at 4.2 K.

In order to measure a magnetoelectric voltage coefficient the disc shaped sinter of 0.19 cm height and 1.5 cm in diameter was placed into a static magnetic field H_{DC} , created by electromagnet with additional modulation of magnetic field $H_{AC}(f)$ produced by the Helmholtz coils. Both magnetic fields were oriented perpendicular to the surface of sinter. An electric signal $\delta U(f)$ from the sample was detected by using lock-in amplifier. The voltage δU was measured for different magnitudes of static magnetic field and frequencies of the modulation field in the range 200 Hz–8 kHz. A magnetoelectric voltage coefficient (ME) was derived using formula

$$\text{ME} = \delta U / (\delta H d), \quad (3.1)$$

where d is a height of the investigated sample.

Figure 2 presents dependence of the ME coefficient in function of the H_{AC} frequency at static magnetic field H_{DC} of magnitude 350 Oe. At low values of frequency

the ME coefficient rises rapidly, while with increasing the frequency a monotonical growth of the ME is observed up to about 2 kHz. Further increase of the H_{AC} field frequency causes slower increase of the magnetoelectric response to 9 kHz, which was the maximal value for our experimental setup. At the 9 kHz this increase is stopped, which could suggest existence of the maxima and decrease of the magnetoelectric coupling at higher frequencies. Such a behavior with maxima about 7 kHz was previously observed for the bulk BiFeO_3 [9]. At low frequencies discharging process may occur through the sample resistance; on the other hand, at high frequencies the discharge may occur through the capacitance formed by two surfaces of the sample [10] and it could explain the sudden increase of the magnetoelectric coupling at low frequencies which is then at higher frequencies stopped and probably will be decreasing at higher.

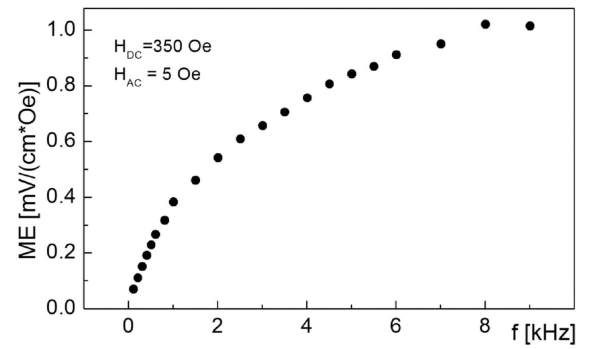


Fig. 2. Magnetoelectric voltage coefficient (ME) vs. frequency for $0.3\text{Bi}_{0.95}\text{Dy}_{0.05}\text{FeO}_3-0.7\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$.

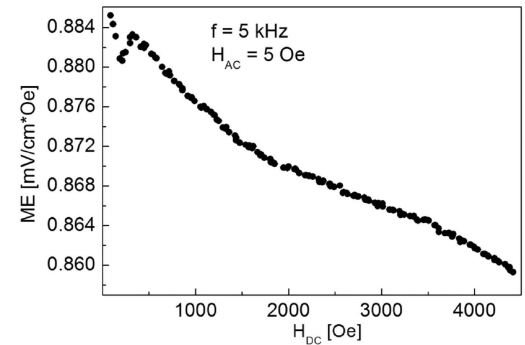


Fig. 3. Frequency dependence of the magnetoelectric coefficient.

Figure 3 shows the ME voltage coefficient vs. static magnetic field for modulated frequency $f = 5$ kHz and $H_{AC} = 5$ Oe. The highest value of magnetoelectric coupling is 0.886 mV/(cm Oe) in absence of the H_{DC} field, increase of the H_{DC} field shows at the beginning decrease of the ME parameter with local minima of about 880 mV/(cm Oe) at 200 Oe, then the ME is increasing with maximal value of about 0.883 mV/(cm Oe) which is obtained for the H_{DC} field of about 880 Oe. Further

increase of the H_{DC} causes decrease of the magnetoelectric coupling. The obtained value of the magnetoelectric voltage coefficient for the sample of almost an order lower than for pure bulk BiFeO_3 [9].

4. Conclusions

$0.3\text{Bi}_{0.95}\text{Dy}_{0.05}\text{FeO}_3-0.7\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ perovskite was synthesized by means of the conventional solid state reaction method. The magnetic hysteresis loop evidenced the antiferromagnetic behavior of the investigated material with slight ferromagnetic behavior where the remanent magnetization M_R and coercive field H_C are 121.9 emu/mol and 890 Oe, respectively. There was observed strong dependence of the ME coefficient vs. frequency of the H_{AC} field. The complicated $\text{ME}(H_{DC})$ dependence was observed.

The obtained results confirmed the magnetoelectric properties of the $0.3\text{Bi}_{0.95}\text{Dy}_{0.05}\text{FeO}_3-0.7\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ solid solution.

Acknowledgments

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