

Magnetic Properties of Bismuth Ferrite Nanopowder Obtained by Mechanochemical Synthesis

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Multiferroic bismuth ferrite (BiFeO₃) nanopowders have been obtained at room temperature by mechanochemical synthesis. Depending on the post-synthesis processing the nanopowders exhibited differences in the mean sizes, presence of amorphous layer and/or secondary phases. Extended magnetic study performed for fresh, annealed and hot-pressed nanopowders revealed substantial improvement of the magnetic properties in the as-prepared powder.

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1. Introduction

Multiferroics exhibit at least two primary ferroic orders: ferroelectric, ferromagnetic, ferroelastic or ferrotoroidic in a single homogeneous phase and the order parameters can be mutually coupled [1]. Especially interesting are ferroelectromagnets (or magnetoelectric multiferroics) having magnetization and dielectric polarization, which can be modulated and activated by an external electric field and magnetic field, respectively. For this reason, multiferroic materials are being considered for a host of potential applications like magnetic recording media, information storage, spintronics, and sensors (for review of physics and applications of multiferroics see Ref. [2]). Between multiferroics bismuth ferrite (BiFeO₃ denoted as BFO) attracted the most scientific interest because its antiferromagnetic and ferroelectric properties are observed at room temperature and the phase transitions are well above room temperature i.e. $T_N \approx 640$ K and $T_C \approx 1100$ K [2]. At room temperature BFO has rhombohedrally distorted cubic perovskite cell ($R\bar{3}c$) and the antiferromagnetic properties are related to G -type ordering with a cycloid modulation (62 nm) apparent down to 5 K. Recently, it has been reported that BFO nanoparticles show strong size-dependent magnetic properties [2–4]. That effect has been correlated with: (1) increased a suppression of the known spiral spin structure with decreasing nanoparticle size, (2) uncompensated spins with spin pinning and strain anisotropies at the surface [4] and (3) presence of impurities (like γ -Fe₂O₃) and/or oxygen vacancies [5]. The purpose of the current work was to compare the magnetic properties of BFO compound in form of nanopowder prepared by mechanochemical synthesis [6, 7], annealed nanopowder and bulk ceramics made from nanopowder by hot-pressing method.

2. Experimental

Bismuth ferrite nanopowder was synthesized by mechanochemical route. Details of synthesis were published in previous paper [7]. Commercially available oxides (Bi₂O₃ and Fe₂O₃ purchased from Aldrich, 99% purity) in stoichiometric ratio were milled in a SPEX 8000 Mixer Mill for 120 h. The thermal treatment was performed for 1 h in air atmosphere under atmospheric pressure at 500 °C. The ceramic samples were prepared by hot isostatic pressing of nanopowder at 200 MPa and 800 °C for 2 h. Magnetic properties were studied by Oxford Instruments Ltd. MagLab 2000 System at temperature range 2 ÷ 350 K. The temperature dependent measurements were carried out in two different procedures: zero field cooled (ZFC) and field cooled (FC) one. In the case of ZFC measurements the sample was first cooled in absence of external magnetic field and next the field was applied after the sample reached desired temperature. For FC measurements the sample was cooled in presence of applied field (1 mT ÷ 1 T). In both cases data were acquired during the heating cycle.

3. Results and discussion

Earlier X-ray diffraction (XRD) studies [7] confirm that the nanopowder obtained after 120 h milling exhibits rhombohedrally distorted perovskite structure. The mean grain size estimated using the Scherrer formula is 19 ÷ 26 nm. Very broad XRD peaks and also transmission electron microscope (TEM) studies indicate that nanograins of this powder are composed of crystalline core BFO and amorphous shell [7]. Thermal annealing (1 h at 500 °C) causes crystallization of the shell and this leads to the increase of the mean grain size to 26 ÷ 42 nm. This sample contains also substantial amount of Bi₂Fe₄O₉ parasitic phase formed during high temperature processing.

These three different BFO samples were used for magnetometric measurements. ZFC and FC temperature dependences of magnetic susceptibility $\chi(T)$ were measured

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for all samples and for various applied magnetic fields. The origin of the difference between ZFC and FC susceptibilities in as-prepared nanopowder is domain wall pinning and/or reorientations of weak ferromagnetic domains in bismuth ferrite phase. A spin-glass phase as a source of this difference should be rather excluded because in BFO compounds there is a lack of memory effect common for spin-glass systems [8]. In ZFC susceptibility anomalous, field-dependent maximum about 8 K (for the field 1 T) is observed whereas FC susceptibility decreases monotonously with temperature (see Fig. 1). This low temperature maximum is probably related to spin clusters in amorphous shell of nanograins [9].

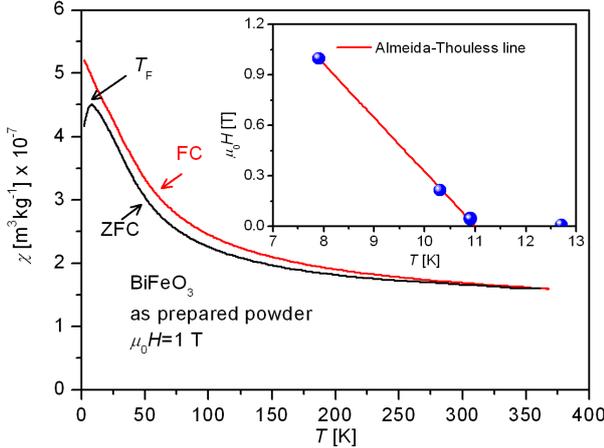


Fig. 1. ZFC and FC magnetic susceptibilities for as-prepared nanopowder. The inset shows freezing temperature dependence on magnetic field fitted with the Almeida–Thouless model.

In this approach, at high temperature the spins are in a paramagnetic state. At lower temperature the ordered spin clusters are formed, which freeze below temperature T_F , into random directions. It is assumed that the freezing temperature T_F corresponds to the maximum of ZFC susceptibility. The validity of the above explanation can be tested using the Almeida–Thouless relation between the freezing temperature and the applied magnetic field [8]: $H = H_0[1 - T_F(H)/T_F(0)]^{3/2}$. In this equation H_0 is magnetic field for which $T_F \rightarrow 0$ and $T_F(0)$ is the freezing temperature for $H = 0$. The best fit to the data is obtained for parameters $\mu_0 H_0 = 3.5$ T and $T_F(0) = 11$ K (inset to Fig. 1).

The annealed sample shows no low temperature anomaly but it exhibits substantial difference between ZFC and FC susceptibilities (Fig. 2a). The absence of maximum in ZFC susceptibility well corresponds to the crystallization of amorphous shell with spin-glass phase after thermal annealing. The thermal processing also leads to the increase of the mean grain size to 26 ÷ 42 nm. We expect enhanced energy barriers for magnetic moment reorientations or pinning of domain walls in nanoparticles with improved crystal structure leading to pronounced irreversibility effects. The anomaly observed

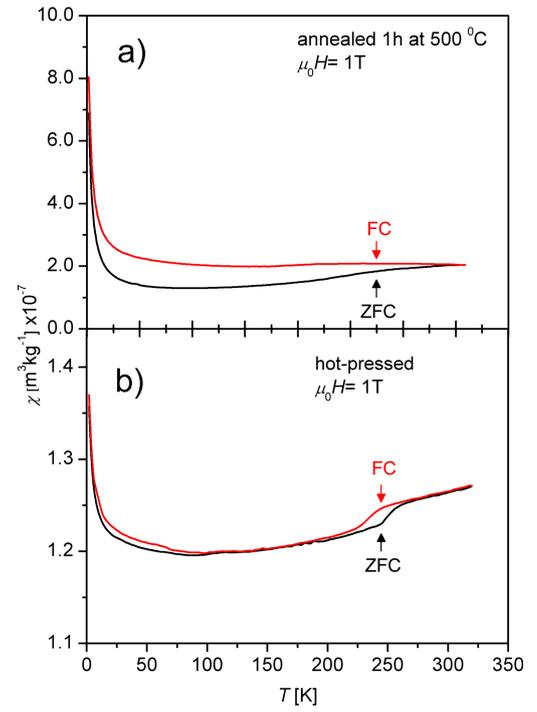


Fig. 2. ZFC and FC magnetic susceptibilities for calcined BFO nanopowder (a) and hot-pressed ceramics (b). The applied magnetic field was 1 T.

about 250 K is very common for orthoferrites [2]. However, the calcined sample contains also $\text{Bi}_2\text{Fe}_4\text{O}_9$ parasitic phase which undergoes near $T_N = 264 \pm 3$ K a transition from paramagnetic to antiferromagnetic state [10] and can be also responsible for this anomaly. For the hot-pressed sample, the ZFC and FC susceptibilities (Fig. 2b) are almost identical, with pronounced anomaly about 250 K. This indicates weak pinning of magnetic domain or domain walls in hot-pressed sample.

The magnetic hysteresis loops presented in Fig. 3 have been recorded at temperatures 4, 50, and 300 K for all samples. The hysteresis loops for nanopowders are not well-saturated which may be related either to antiferromagnetic state or to the spin disorder and spin pinning at the surface [4]. The maximum of magnetization, $M_S = 0.710$ Am²/kg is observed at 4 K and 2 T for the as-prepared nanopowders composed of shell-core nanograins (see Fig. 3a). This value is, depending on temperature range, 2 ÷ 4 times bigger than M_S for the thermal processed ceramics. The increased magnetization is due to size effect and presence of amorphous shell. All recorded loops are superposition of ferromagnetic non-linear and antiferromagnetic or paramagnetic linear contributions. The nonlinear, ferromagnetic contribution is most pronounced at low temperatures and for as-prepared BFO sample (Fig. 3a). This ferromagnetic behaviour can be related to suppression of spin cycloid leading to the lack of spin compensation or to surface spins in BFO nanograins.

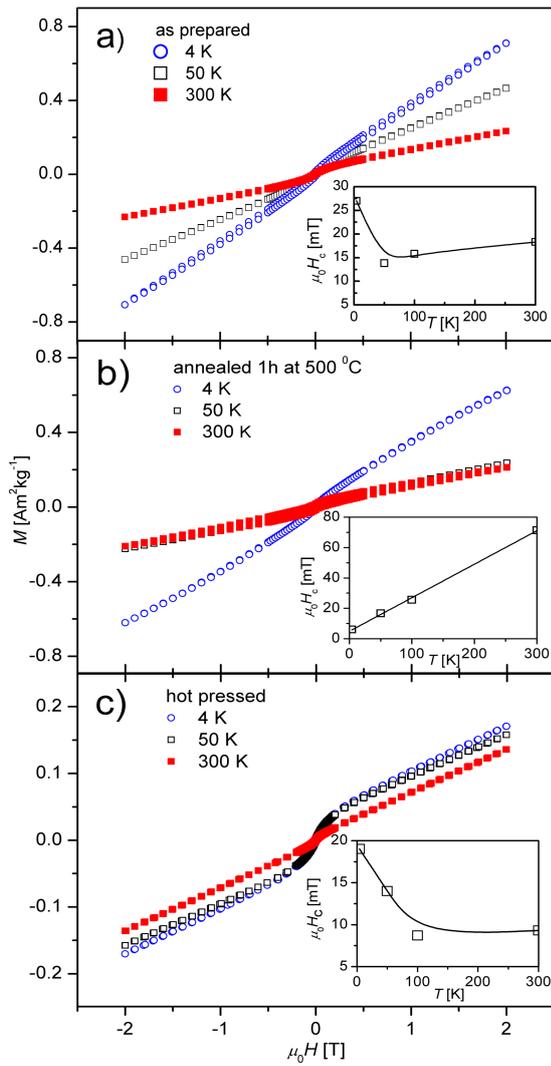


Fig. 3. Hysteresis loops recorded at different temperature for (a) as-prepared, (b) annealed nanopowders, and (c) hot-pressed ceramics made from nanopowder. Insets show temperature dependence of coercive field for each sample.

The complex relation of coercive field $H_c(T)$ on temperature found in the BFO samples has different origins. For the as-prepared BFO sample (inset to Fig. 3a) the coercivity $H_c(T)$ exhibits non-monotonic behaviour with the highest value 25 mT at the temperature 4 K. This dependence is a superposition of strong pinning of spin clusters below freezing temperature T_F and pinning of weak ferromagnetic domains prevailing at higher temperatures. The temperature dependence of coercivity for calcined BFO sample (inset to Fig. 3b) is also unusual because $H_c(T)$ linearly increases with temperature. The increase of coercivity with temperature sometimes takes place in granular systems if intergranular coupling decreases with temperature [11]. In this case, the coercivity $H_c(T)$ is described by a phenomenological formula: $\mu_0 H_c = \alpha_{\text{ex}} \alpha_K \mu_0 H_a - N_{\text{eff}} J_s$, where: α_K is the Kron-

muller parameter, α_{ex} is the intergrain coupling, N_{eff} — the magnetostatic parameter, J is a magnetization and H_a denotes the anisotropy field. For the nanopowders the intergranular coupling is obviously very weak. This coupling is temperature dependent and can be further suppressed at higher temperatures. For dense, hot-pressed ceramic the intergranular coupling is very strong and the coercivity reflects only decrease of anisotropy field with temperature (see inset to Fig. 3c).

4. Conclusions

The studies of the magnetic properties of BFO nanopowder obtained by mechanochemical synthesis have shown the improvement of magnetization. The improvement in the magnetization of nanosized particles we would like to relate to the suppression of cycloidal order, i.e., incomplete rotation of the spins along the direction of the wave vector and also to an increase in spin canting, due to the lattice strain which gives rise to weak ferromagnetism. The presence of the core-shell structure in the BFO grains obtained by mechanochemical synthesis may be important from the application point of view because of possibility to improve magnetic properties of nanomaterials.

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References

- [1] H. Schmid, *J. Phys. Condens. Matter* **20**, 433 (2008).
- [2] G. Catalan, J.F. Scott, *Adv. Mater.* **21**, 2463 (2009).
- [3] T.-J. Park, G.C. Papaefthymiou, A.J. Viescas, A.R. Moodenbaugh, S.S. Wong, *Nano Lett.* **7**, 766 (2006).
- [4] R. Mazumder, P. Sujatha Dev, D. Bhattacharya, P. Choudhury, A. Sen, M. Raja, *Appl. Phys. Lett.* **91**, 062510 (2007).
- [5] H. Bea, M. Bibes, S. Fusil, K. Bouzehouane, E. Jacquet, K. Rode, P. Benco, A. Barthélémy, *Phys. Rev. B* **74**, 020101(R) (2006).
- [6] I. Szafraniak, M. Połomska, B. Hilczer, A. Pietraszko, L. Kepiński, *J. Eur. Ceram. Soc.* **27**, 4399 (2007).
- [7] I. Szafraniak-Wiza, W. Bednarski, S. Waplak, B. Hilczer, A. Pietraszko, L. Kepiński, *J. Nanosci. Nanotechnol.* **9**, 3246 (2009).
- [8] B. Andrzejewski, K. Chybczyńska, K. Pogorzelec-Glaser, B. Hilczer, B. Łęska, R. Pankiewicz, P. Cieluch, *Phase Transit.* **86**, 748 (2013).
- [9] S. Nakamura, S. Soeya, N. Ikeda, M. Tanaka, *J. Appl. Phys.* **74**, 5652 (1993).
- [10] N. Shamir, E. Gurewitz, H. Shaked, *Acta. Crystallogr. A* **34**, 662 (1978).
- [11] Ch.-B. Rong, H.-W. Zhang, B.-G. Shen, J.P. Liu, *Appl. Phys. Lett.* **88**, 042504 (2006).