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Magnetic Properties of the $Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O_3$ Perovskite

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Magnetic properties of polycrystalline multiferroic $Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O_3$ synthesized under high-pressure (6 GPa) and high-temperature (1500 K) conditions were studied using a SQUID magnetometer technique. The temperature dependent static magnetic moment M was measured in both zero-field-cooled and field-cooled modes over the temperature range of 5–300 K in low magnetic field $H = 0.02$ kOe. The field dependent magnetization $M(H)$ was measured in magnetic fields up to 50 kOe at different temperatures up to 230 K after zero-field cooling procedure. A long-range magnetic ordering of the antiferromagnetic type with a weak ferromagnetic contribution takes place below $T_N \approx 220$ K. Magnetic hysteresis loops taken below T_N show a huge coercive field up to $H_c \approx 10$ kOe, while the magnetic moment does not saturate up to 50 kOe. A strong effect of magnetic field on the magnetic properties of the compound has been found. Below $T_N \approx 220$ K the derivatives of the *initial* magnetization curves demonstrate the existence of a temperature-dependent anomaly in fields of $H = 15 \div 25$ kOe. The nature of the anomaly is unknown and requires additional study.

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1. Introduction

The progress in technology and engineering is directly coupled with the advances made in materials science. Within the broad class of materials available today, multiferroics provide unique opportunities for developing novel components and devices. This is due to the fact that their physical and chemical properties are sensitive to the changes in external factors, namely temperature, pressure, humidity, and electromagnetic fields. The origin of the uniqueness of these materials lies in the coupling between different order parameters.

Cross-coupling between electronic and magnetic subsystems in multiferroic materials has attracted considerable attention in recent years [1–3]. These materials combine spontaneous magnetic and polar order parameters offering a unique opportunity of their effective cross-control.

In many type-II multiferroics, a spin-driven electric polarization is generated by inverse antisymmetric Dzyaloshinskii–Moriya interactions [1]. This interaction is also responsible for appearance of a weak ferromagnetism in some antiferromagnets (AFM) including the important class of materials derived from the room-temperature type-I multiferroic $BiFeO_3$ [3]. In addition, antisymmetric exchange is a source of magnetic anisotropy in many magnetically ordered compounds since it is a higher-order perturbation term which removes degeneracy and selects specific ordered states in some geometrically frustrated spin systems [4, 5].

$Bi_{1-x}La_xFe_{0.5}Sc_{0.5}O_3$ perovskites are the rare examples of single-phase multiferroics which were recently obtained under high-pressure conditions [6–8]. The system demonstrates a rich phase diagram. Three consecutive phases with different crystal structures appear as the lanthanum content is increased: the as-prepared phase with $x \leq 0.05$ is an antipolar *Pnma* [6], an incommensurately modulated phase with the $Imma(00\gamma)s00$ superspace group [7] is observed for $0.10 \leq x \leq 0.30$, and a non-polar *Pnma* phase [8] is stable at $x \geq 0.35$.

The $Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O_3$ perovskite is close to the compositional transition between antipolar and non-polar phases. Such boundary compounds are of particular interest because they may possess enhanced electron and magnetic properties [9]. The compound crystallizes into a distorted perovskite structure with the orthorhombic *Pnma* symmetry. A long-range magnetic ordering takes place below 220 K and implies a *G*-type AFM structure [8]. The present study is aimed at the magnetic characterization of the $Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O_3$ perovskite.

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2. Experimental section

High-purity oxides $Fe2O_3$, $Bi2O_3$, $Sc2O_3$ and $La2O_3$ were used as starting reagents to prepare the $Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O_3$ composition. Previously calcined oxides were mixed in the stoichiometric ratio, ball-milled in acetone, dried and pressed into pellets. The pellets were heated in a closed alumina crucible at 1140 K for 10 min and then quenched to room temperature. The obtained material served as a precursor for the high-pressure synthesis. The pressure was generated by an anvil press DO-138A with a press capacity up to 6300 kN. The sample was synthesized at 1500 K and 6 GPa. The high-pressure treatment time did not exceed 5 min.

X-ray diffraction study of the powdered samples was performed using a PANalytical XPert MPD PRO diffractometer (Ni-filtered Cu K_α radiation) at room temperature has shown a single phase perovskite structure of the obtained $Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O_3$ ceramics.

Magnetic properties were measured using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-3). Static magnetic measurements (dc) were performed in applied fields up to 6 kOe under both zero-field-cooled (ZFC) and field-cooled (FC) conditions. Isothermal magnetization measurements were performed between –50 kOe and 50 kOe in the temperature range 5–230 K.

3. Results and discussion

According to the neutron diffraction and magnetic study, a long-range magnetic ordering of the antiferromagnetic type with a weak ferromagnetic contribution driven by the Dzyaloshinskii–Moriya interaction occurs below $T_N \approx 220$ K for $Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O_3$. The ferromagnetic contribution increases with decreasing temperature down to 5 K. ZFC and FC magnetizations measured in low magnetic fields are strongly different (Fig. 1), which can be attributed to significant magnetic anisotropy [10]. Below T_N, field-dependent magnetization measurements showed well-defined hysteresis loops, characterized by a huge coercive field up to $H_c \approx 10$ kOe (Fig. 2). No saturation of magnetization is observed up to $H = 50$ kOe. The unsaturated behaviour of hysteresis loops indicates canted nature of spins [11].

The $Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O_3$ perovskite was found to demonstrate unusual features of its temperature- and magnetic field dependent magnetic behaviour. The temperature dependent ZFC magnetization has an anomaly in temperature range close to 100 K which permits to assume a coexistence of two different magnetic phases with different Néel temperatures T_N (Fig. 1). The assumption is in a good agreement with a naturally phase separated state of the compounds, which are close to the compositional transition of the phase diagrams. Two or more phases may be coexistent in such boundary compounds [9]. The $Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O_3$ appeared to be very sensitive even to small magnetic fields applied, so, no anomaly is seen for FC magnetization curve. However, the neutron diffraction data collected between 1.5 and 300 K (see Ref. [8] for details of the neutron diffraction experiment) did not reveal any evidence of a phase coexistence, indicating that the inhomogeneity can take place in a nanoscale level.

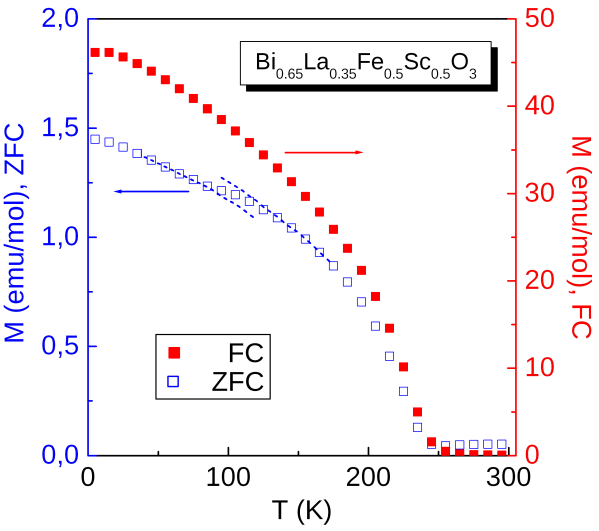

Fig. 1. Temperature dependences of the magnetic moment measured in magnetic field 0.02 kOe after zero field cooling and field cooling procedures. The dashed lines are guides for the eye only.

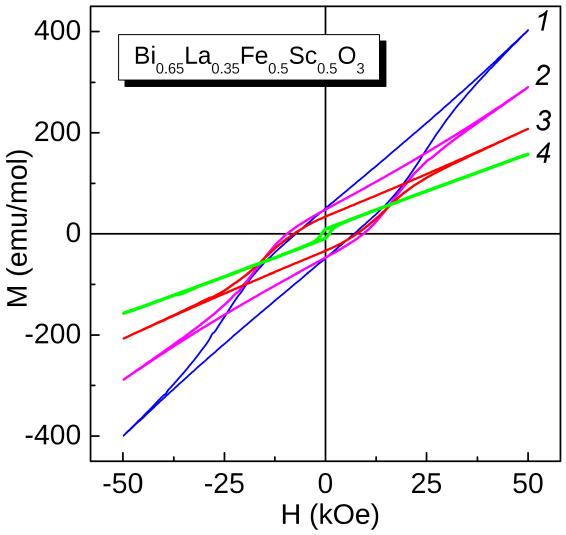

Fig. 2. Magnetic hysteresis loops measured after zero field cooling procedure at temperatures 5, 50, 150, and 230 K (denoted as *1*, *2*, *3*, and *4*, respectively).

In addition, a strong magnetic field effect on the properties of the $Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O_3$ was found and is evidenced in the *initial* magnetization curves taken at fixed temperatures below T_N after ZFC process (Fig. 3, upper part). At first glance, the magnetic responses look almost linear, but the analysis of derivatives of magnetization curves (Fig. 3, lower part) reveal the nonlinear nature. Since the magnetic moment of the antiferromagnetic $Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O_3$ phase [8] has a linear mag-

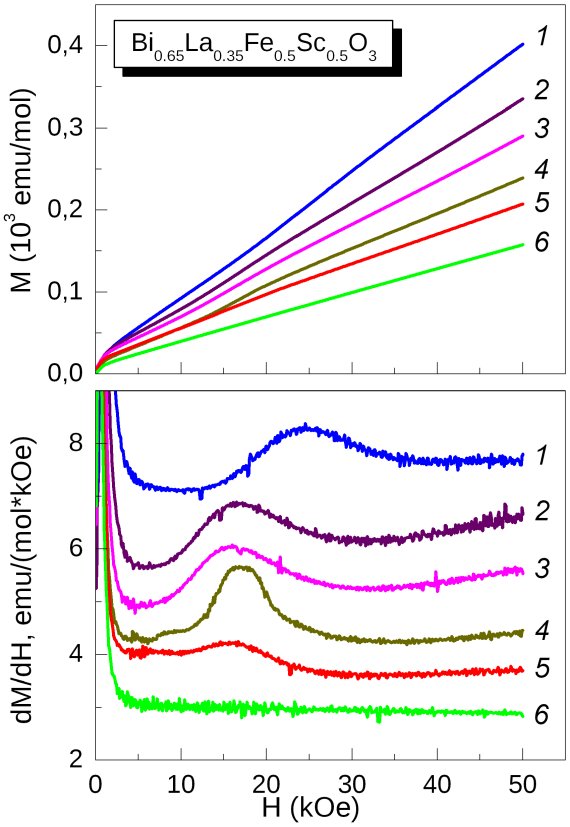

Fig. 3. Initial magnetization curves (upper part) after ZFC procedure at different temperatures (the field step is 0.1 kOe) and the derivative of the magnetization (lower part). Numbers denote the temperatures 5, 25, 50, 100, 150, and 230 K (*1*, *2*, *3*, *4*, *5*, and *6*, respectively).

netic field dependence, no peculiarities of its magnetic field derivative were expected. In our case, the derivative curves of the initial magnetization demonstrate a temperature-dependent anomaly (sort of a hill) in fields 15–25 kOe. The anomaly is shifted to lower magnetic field with increasing temperature and disappears above $T_N \approx 220$ K. The nature of the anomaly is unknown and needs additional study. It is could be associated with a nano-inhomogeneous magnetic state of the studied metastable compound.

4. Conclusions

Magnetic properties of the polycrystalline multiferroic $Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O_3$ compound have been studied in the temperature range of 5–300 K in magnetic fields up to 50 kOe. Below the Néel temperature, $T_N \approx 220$ K, the $Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O_3$ perovskite demonstrates a long-range magnetic order with a weak ferromagnetic contribution which increases with temperature decrease down to 5 K. Its magnetization loops demonstrate a huge hysteresis with coercive field up to 10 kOe. No saturation of the magnetic field dependent magnetization was found. A strong magnetic-field effect on the properties of the $Bi_{0.65}La_{0.35}Fe_{0.5}Sc_{0.5}O_3$ has been observed. Magnetic-field derivatives of the *initial* magnetization curves, taken at temperatures below T_N, demonstrate a temperature-dependent anomaly in fields of $H = 15$–25 kOe, which disappears above the Néel temperature. The anomaly may be associated with a nano-inhomogeneous magnetic state of the compound that is close to the compositional boundary between antipolar and non-polar phases.

Acknowledgments

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