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Sr_2FeMoO_6 nanosized compound with dielectric sheaths for magnetically sensitive spintronic devices

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ABSTRACT

Single-phase agglomerated $Sr_2FeMoO_{6-\delta}$ powders with the iron and molybdenum cations superstructural ordering of 88% were synthesized by sol-gel technique from the $Sr(NO_3)_2$ and $Fe(NO_3)_3 \cdot 9H_2O$ solutions with pH = 4. The ultrasound dispersion enabled us to obtain 75 nm grains. Powders were pressed with 4 GPa to receive the ceramics. The additional annealing at 700 K promoted the appearance of 7.5% $SrMoO_4$ phase. The nanocomposite with dielectric sheaths around the grains was obtained. Magnetization temperature dependences in zero-field cooled mode revealed inhomogeneous magnetic states. At temperature below 19 K, the superparamagnetic state is observed. Temperature increase leads to a realization of the stable superparamagnetic and metastable ferrimagnetic states, blocked by magnetic anisotropy energy. The resistivity temperature dependences have the semiconducting conductivity type. The charge transfer due to the hopping conductivity on the localized states in the energy band near the Fermi level dominates at 260–300 K. At 130–200 K the charge transfer is realized by electrons tunneling through the energy barrier. The electrons inelastic tunneling on conducting channels between grains, through the localized states in the dielectic interlayer dominates at low temperatures. The resistivity decreases in magnetic fields and the negative tunneling magnetoresistive effect reaching 41% occurs.

1. Introduction

Spintronics is based on the fundamental results in the field of the quantum solid state physics and magnetism, combined with the modern technologies of the creation of nanosized materials and structures, where the spin-polarized current-carrying process is dominating at the application of magnetic field. The layers (particles) of ferromagnetic material with the high degree of the charge carriers spin polarization, divided by the dielectric interlayers are at the root of the element base [1,2]. High speed of operation of these devices is not concerned with a transfer of charge and the corresponding mass in space. For the switching over of electron it is sufficient to turn its spin in the opposite direction (Fig. S1).

So far as spintronics was developing, the new magnetics appeared together with the existing ones. These are magnetic semiconductors, being materials, which simultaneously can be magnetics, and semiconductors. Their band structure differs from the two-band structure of the conventional semiconductors, metals and dielectrics by the presence of the third band, which is formed by the electronic d- and f-shells of the atoms of the transitions and rare-earth elements [1–4]. Complex metal-oxide compounds belong to such materials. They have the double perovskite structure the formula unit A2B′B″O6, where A is the two-valent alkaline-earth cation (Sr^{2+}, Ba^{2+}, Ca^{2+}); B′ and B″ are the transition metals cations (Fe, Mo, Mn, Ru, Cr, Ni) [3,4]. The ideal double perovskite crystal structure consists of two mutually penetrating body-centered sublattices with the cubic or tetragonal symmetry, which are shifted relative to each other by a half of a diagonal of the primitive cell basis. The first sublattice is formed by the B′-type cations, and the other one is correspondingly formed by the B″-cations. Each of the B-cations (B′ or B″) is surrounded by six oxygen anions, which in its turn form oxygen octahedrons (B′O6 and B″O6) with common vertices. The A-type cations are placed in the hollows between the oxygen octahedrons (Fig. S2).

The $Sr_2FeMoO_{6-\delta}$(SFMO) compound, where $Fe^{3+}(3d^5)$ and

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$Mo^{5+}(4d^1)$ cations are placed in the B′ and B″ positions, correspondingly, and $Sr^{2+}(5s^2)$ cations are placed in the A positions, is the less studied and very prospective material from the entire double perovskite family. The SFMO possesses a high Curie temperature (Tc) - 400–430 K, and almost 100% degree of the spin polarization [5–10]. Moreover, the compound has high electrical conductivity and a reasonable thermal stability at the increased temperatures in a broad range of partial pressures of oxygen. At temperatures higher than Tc, the SFMO is in a paramagnetic state with the cubic structure (Fm3m, Z = 2). Below Tc the ferrimagnetic ordering is formed with the tetragonal structure (I4/m, Z = 2). It is characterized by the presence of Fe^{3+}-O^{-2} Mo^{5+} chains, with the superstructure ordering of cations [5,8,11]. The strontium ferromolybdate belongs to the half-metals group, where electrons on the Fermi level with the same spin orientation (↓) are placed. When the Fe^{3+} and Mo^{5+} cations are in the 2*g* *g* high-spin state with electron configurations (3 d^5, t ↑ ↑ ↑ e ↑ ↑, S = 5/2) and ($4d^1$, t ↓, S = 1/2), correspondingly, their hybridized orbitals are forming the band structure, where a gap on the Fermi level takes place (∽ 0.8 eV). Electrons with the opposite spin do not give any contribution to the conductivity and the charge carriers have the spin polarization degree P = 100%. As a result, the spin energy band splits to 2 sub-bands: the first sub-band has a semiconducting conductivity nature, and the second sub-band has a metallic one, which influences the processes of current-carrying and magnetization in the SFMO [12–16]. The presence of the “antistructural” point defects ([FeMo] and [MoFe]) destroys the superstructural ordering. This is due to the fact that iron and molybdenum ions can be in different spin states (Fe^{2+}, Fe^{3+} and Mo^{5+}, Mo^{6+}), and thereby renders a considerable effect on the magnetic structure of the SFMO [17–19].

Recently, interest in half metals has been concentrated on a large intergranular magnetoresistance in granular materials, transport properties of which predominate spin-polarized tunneling through the insulating grain boundaries [20–24]. This is the result of an extended intergrain tunneling through the insulating barrier by reducing the relative magnetization angle in the adjacent grains by applying a magnetic field. Thus, the formation of the tunnel barrier is a key technology for the realization of a suitable device for magnetoresistance. Such a tunneling barrier can be artificially fabricated through a three layer thin film such as $La_{0.7}Sr_{0.3}MnO_3$/(half-metallic)/TiO_2 (insulating)/$La_{0.7}Sr_{0.3}MnO_3$ (half-metallic) [25]. Some previous studies [26–29] reported the tunneling magnetoresistance in SFMO through $SrMoO_4$ grain boundary tunneling barriers. It is well known that the nonmagnetic $SrMoO_4$ impurity is induced to appear at the grain boundaries [30,31]. However, in spite of intensive studies of the magnetoresistive properties of strontium ferromolybdate, there is practically no systematic study of the effect of artificially created intergranular dielectric layers on its magnetotransport characteristics.

Not only the thickness of the barrier (dielectric layer) between magnetic has a significant importance at the creation of spintronic structures. A considerable role here is played by strong magnetic fields occurring around magnetic grains by means of the increase of the magnetostatic energy as compared with the energy of the domains formation [32]. This is achieved by a decrease of the grain sizes, where the quazi-single-domain structure is formed, down to 10–1000 nm [33].

On the base of the stated above information, the goal of the present work is the creation of composite material consisting of the SFMO nanosized granules, divided by the dielectric barriers in the form of thin sheaths around each grain. As previous investigations have shown, the SFMO synthesis according to the standard ceramic technology does not enable one to obtain the SFMO nanosized grains [5,32,34]. Therefore, a modified sol-gel technique has been developed and implemented in the present work. With the use of this technique, not only a powder containing the SFMO granules of the required sized has been obtained, but the composite with dielectric sheaths has been formed as well. The structure of this material, as well as its magnetic and magnetoresistive properties, have been investigated. This research results have confirmed its exploitability for the application in spintronic devices.

2. Experimental

2.1. Material synthesis

The following reagents were used for the synthesis of a single-phase nanosized SFMO powder by the citrate-gel technique (the modified sol-gel technique): $Sr(NO_3)_2$, Fe $(NO_3)_3 \cdot 9H_2O$, $(NH_4)_6Mo_7O_{24}$ and citric acid monohydrate $C_6H_8O_7 \cdot H_2O$. The preparation of the colloidal sol by means of mixing water solutions of strontium nitrate $Sr(NO_3)_2$ an d iron nitrate $Fe(NO_3)_3 \cdot 9H_2O$ at a molar ratio of n(Sr): n(Fe) = 2:1 has been carried out. Citric acid was added to the solution at a molar ratio of n(citric acid): n(Fe) = 6.5:1. After that, the ready water solution with an addition of $(NH_4)_6Mo_7O_{24}$ was added to the general solution containing the strontium and iron nitrates in a molar ratio of n(Mo): n(Fe) = 1:1. Then the ethylenediamine (EDA) was added to the solution under constant stirring using an IKA C-MAG HS 7 magnetic stirrer, until the pH values of the solution reached 4, 6 and 9. After that, the evaporation of the synthesized material was carried out a t 353 K. The resulting substance was placed into a furnace at 373 K. Thereafter the furnace was heated up to 470 K at a rate of 0.4 deg/min. The material was kept at this temperature during 18 h, and then it was cooled inside the switched off heater. As a result, a solid foam was formed. After carefully grinding the latter, a homogeneous powder was obtained which was annealed in the furnace at 773 K in the argon atmosphere, under the pressure $p(O_2) = 0.21 \times 10^5$ Pa for 10 h. The final annealing process, which has made it possible the SFMO compound synthesis, was carried out in the reductive ambient of the 5% H_2/Ar gas mixture in several stages, at the final annealing at T = 1073 K for 4 h. The SFMO sol-gel synthesis diagram is presented in Fig. S3. The subsequent analysis has shown that the single-phase SFMO powder was obtained at pH = 4, and therefore it has been investigated further on. The nanometer grain size has been obtained by the ultrasound dispersion using the Bandelin HD2200 ultrasound homogenizer in the liquid medium with the concentration of 1 g powder per 250 ml of the ethyl alcohol. The SFMO powders were pressed into pellets with a diameter 10 mm and thickness 3 mm at the pressure 4 GPa and temperature 700 K.

2.2. Characterizations

The phase composition and structure of the SFMO powder samples were characterized by X-ray diffraction (XRD) using a Philips X′ Pert MPD diffractometer in conditions of the CuKα – radiation at room temperature with the exposition speed 1°/min. The SFMO crystal lattice parameters has been determined by means of the XRD data using PDF4+ (Release 2013) database and the FULLPROF software. The degree of the superstructural ordering of the Fe and Mo cations was calculated according to the expression:

$$P = (2 \cdot SOF - 1) \cdot 100\%, \quad (1)$$

where SOF is the Seat Occupancy Factor. These data has been obtained by mean s of the modeling of the SFMO XRD patterns using