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Synthesis and properties of nanostructure composites based on barium titanate and 3D metals

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Abstract. We report the production of a hybrid nanostructure combining ferroelectric and antiferromagnetic ordering based on toroidal nanoparticles of barium titanate and an iron-cobalt nanoalloy. The methods of optical and magneto-optical spectroscopy revealed a change in the coordination of 3D metal ions in the composition of FeCo after high-temperature annealing in the presence of barium titanate, and a study of the magnetic properties showed a change in the predominant alignment of spins from superparamagnetic to antiferromagnetic type. In addition, the sample exhibits optically nonlinear properties.

Keywords: antiferromagnetism, magnetoelectric, magnitooptic

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Материалы конференции
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Синтез и свойства наструктурного композита на основе титаната бария и 3D металлов

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Аннотация. Мы сообщаем о получении гибридной наноструктуры, сочетающей сегнетоэлектрическое и антиферромагнитное упорядочение, на основе тороидальных наночастиц титаната бария и наносплава железо-кобальт. Методами оптической и магнитооптической спектроскопии было выявлено изменение координации ионов 3D металлов в составе FeCo после высокотемпературного обжига в присутствии титаната бария, а исследование магнитных свойств показало изменение преимущественного выстраивания спинов с суперпарамагнитного на антиферромагнитный тип.

Ключевые слова: антиферромагнетизм, магнитоэлектрики, магнитооптика

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Introduction

Ferroelectromagnetics (electromagnetics) are materials and multiphase heterostructures with simultaneous presence ferroelectric and ferromagnetic ordering. They have great potential for practical use in magneto- and optoelectronics, as elements of various sensors, tunable optical elements, and memory devices with magnetic reading or electrical recording [1, 2].

In our work, we investigated a composite that coincides with a combination of lead-free ferroelectric perovskite, $BaTiO_3$ (BTO), and cobalt-iron alloy nanoparticles FeCo.

The BTO nanoparticles are the most studied perovskite-type ferroelectrics because of their excelling optical and electrical properties [3]. But a little part is known about bimetallic nanoparticles. Example, the crystal structure of the $Fe_{100-x}Co_x$ alloy depends on the temperature of the synthesis and the related to ratio of Co and Fe, the ideal stoichiometry with high saturation and the least coercive force belongs to $Fe_{60}Co_{40}$ etc. How are the cations in this nanocrystal interconnected between themselves without oxidation in air? In standard case there is a shell which passivates the surface after calcination [4].

In a report [5] analogy structure (CoFe films on BTO substrates) shows significant change properties during structural phase transitions of BTO. Starting from 300 K, cooling through the tetragonal to orthorhombic phase transition leads to a sharp 90° magnetic switching in the magnetic strip domains, an increase in magnetoelastic anisotropy while preserving the overall structure of the magnetic domains. But the influence of morphology and the ratios of BTO to FeCo and Fe to Co on the current processes is not yet known.

Materials and Methods

Synthesis of BTO nanoparticles. The first step of our composite is based on [6]. 1.26 g of $BaCl_2{\cdot}2H_2O$ and 0.15 g $H_2C_2O_4$ (oxalic acid) were dissolved in 10 mL of distilled water. After that 2.5 mL butyl titanate and 2.5 mL H2O were added into the mixture system. Then, 2.25 g NaOH was added into the solution with continuous ultrasonication. The as-prepared mixture was put into a Teflon-lined stainless-steel autoclave (25 mL) and conducted at 160 °C for 12h.

The solution was finally washed with distilled water and absolute methanol for three times.

Synthesis of FeCo/C alloy nanoparticles. As in paper [7], 16 ml of paraffin oil, 50 μl of oleic acid, and 50 μl of oleyl amine were collected and the mixture was degassed with heating to 140 °C and N_2 for 2 h. At the same time, 4 ml of paraffin oil was degassed at room temperature, and we raised the temperature to 275 °C and kept it at this temperature for 1 h in argon flux. 103.3 mg of $Co(oleate)_2$ and 137 mg of $Fe(CO)_5$ were added in the 4 ml paraffin oil. Following this, this mixture was injected dropwise to the hot reaction mixture for 7 minutes and the reaction was completed after 10 minutes and cooled slowly at room temperature. The sample was washed several times with a mixture of hexane/alcohols and purified by magnetic separation.

Accordingly, we expect to obtain nanoparticles with the formula $Fe_{45}Co_{55}$.

Synthesis of BTO-FeCo/C nanocomposite. We took two solutions of BTO (methanol) and FeCo (hexane) with equal concentrations and volume and placed them together in a preheated oven (~ 500 °C) for 15 minutes. Some part of the sample demonstrated diamagnetic properties (black precipitate), the other was ferromagnetic (beige precipitate) and hydrophilic.

The morphology and microstructure of the NPs were investigated using scaning electron microscope Quantex 70, Bruker, USA with accelerating voltage 3000 V and emission current 10100 nA.

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Optical and magneto-optical spectra were registreted on spectrometer of circle dichroism Jasco J-1500 with electromagnet MCD-581. Measurements were carried out in the range 200—800 nm in field 1.5T.

The magnetic properties were measured with the vibrating sample magnetometer Lakeshore 7400 series VSM (Lake Shore Cryotronics, Inc., Westerville, OH, USA).

Results and Discussion

As a result of SEM (Quantex 70, Bruker, USA), the mean size of the completed sample is 0.5 μm. Its form and dimensions in Fig. 1 can be explained by agglomeration during the heat treatment. Another reason is the specifics of hydrothermal processing of $BaTiO_3$ nanotorus synthesis.

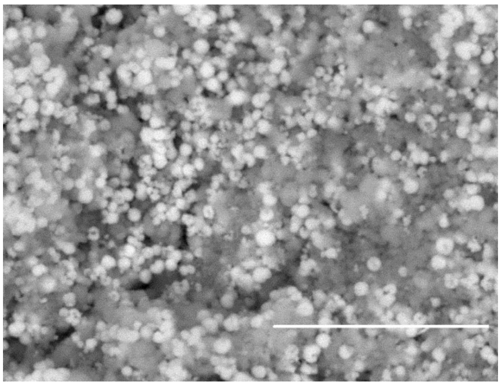

Fig. 1. Bright-field SEM image of the FeCo-enveloped BTO nanoparticles. Scale — 10 μm

Since the absorption spectra do not show any significant features, magnetic circular dichroism spectra were studied to study the excited electronic states of iron and cobalt ions. The MCD spectra of the initial sample of FeCo nanoparticles undergo a significant shape change, apparently associated with the interaction of FeCo and BTO nanoparticles To identify the energies of electronic transitions and study the redistribution of band intensities, the MCD spectra of the initial FeCo nanoparticles and the composite were decomposed into Gaussian components (Fig. 2). As a result of decomposition, the transitions presented in Table 1 were identified. Similar to those observed in works [7—10]. In the same way, the bands were defined on 1) 1.8, 2) 1.95, 3) 2.1, 4) 2.3, 5) 2.4, 6) 2.6, 7) 2.85, 8) 3, 9) 3.3, 10) 4, 11) 4.3 eV in the $BaTiO_3$/FeCo spectrum (Fig. 2, *a*). The main spectral feature is transitions at 1.8 eV (peak 1), which are not observed for FeCo/C and change intensity during each measurement. It can also be a splitting band with a center of 1.5 eV as an effect arising in a magnetic field [7]. In addition, there are bands that can belong to BTO nanoparticles: 3, 4 or 5, 9, 10, 11.

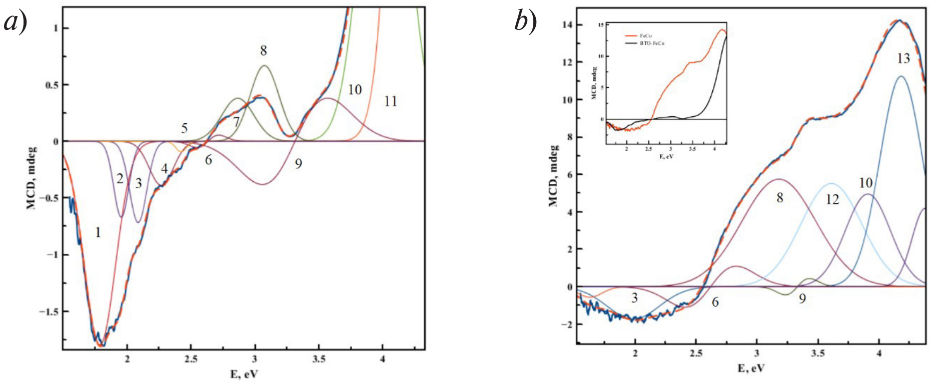

Fig. 2. MCD spectrum of $BaTiO_3$/FeCo nanostructure (*a*) and FeCo/C nanoparticles (*b*)

Fig. 3, *a*, shows that a loop of FeCo nanoparticles behaves like a classical superparamagnetic one with a saturation magnetization of 1.35 emu/g and a complete absence of coercivity. In a composite consisting of magnetic and non-magnetic nanoparticles, the Ms value is 5 times

Table 1

Transitions indicated in Fig. 2

Peaks	Designation	Peaks	Designation
1	-	6	$p(O^{2-}) \rightarrow e_g(Co^{3+})$ or $^6A_g(^6S) \rightarrow {}^4A_g, {}^4E_g(^4G)(Fe^{3+}, O_h)$
2	$^6A_{1g}(^6S) \rightarrow {}^4T_2(^4G)$ (Fe^{3+}, O_h) or $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (Co^{2+}, O_h)	7	$^6A_{1g}(^6S) \rightarrow {}^4T_{2g}(^4D)$ (Fe^{3+}, O_h)
3	-	8	$^1A_{1g}$ $(I) \rightarrow {}^1T_{1g}(I)$ (Co^{3+}, O_h)
4	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (Co^{2+}, O_h) or $p(O^{2-}) \rightarrow t_{2g}(Co^{2+})$	9	$^6A_{1g}(^6S) \rightarrow {}^4T_{2g}(^4D)$ (Fe^{3+}, O_h)
5	$^1A_{1g}(I) \rightarrow {}^1T_{2g}(I)$ (Co^{3+}, O_h)	10	$^6A_{1g}(^6$ $S) \rightarrow {}^4T_1(^4D)$ (Fe^{3+}, O_h)

smaller, this can be explained by the fact that we cannot accurately take into account which part of the sample is the mass of magnetic nanoparticles. At the same time, the question remains why the composite has a coercive force of 60 Oe, apparently due to an increase in the size of the initial FeCo nanoparticles, or a strong interparticle interaction of magnetic and non-magnetic particles. The temperature dependences of magnetization Fig. 3, *b* also show a rather strange increase in the blocking temperature of nanoparticles from 210 K to 250 K, respectively for FeCo and $BaTiO_3$/FeCo.

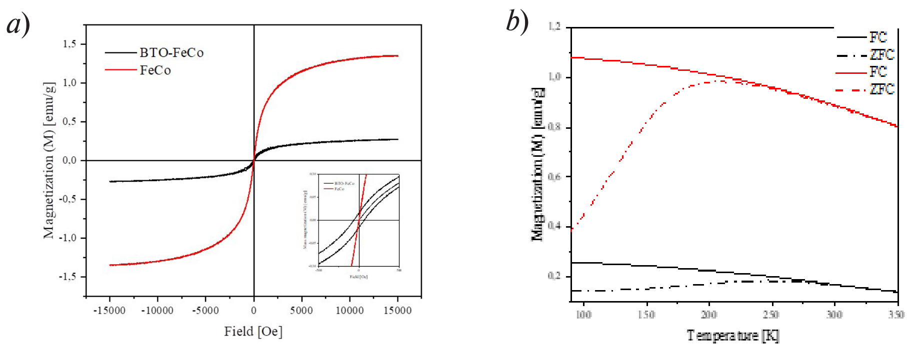

Fig. 3. Magnetic hysteresis loops of $BaTiO_3$/FeCo nanostructure and FeCo nanoalloy at 300K (*a*) and temperature dependences of magnetization for $BaTiO_3$/FeCo (black) and FeCo (red) in the field 2 kOe (*b*)

Conclusion

Ferroelectromagnetics composites $BaTiO_3$/FeCo were obtained and a preliminary study of their magnetic and magneto-optical properties was carried out. It has been demonstrated that dilution of the initial FeCo magnetic nanoparticles with perovskite-like ferroelectric BTO nanoparticles leads to strong interparticle interaction and, apparently, to a violation of the surface layer of magnetic nanoparticles, which significantly affects their properties. In any case, the resulting composite requires further investigation.

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