

MULTIFERROICS BASED ON EUROPIUM AND IRON OXIDES

^{1,2}Nadezhda Ivanovna Steblevskaya, ^{1,3}Mikhail Azaryevich Medkov, ¹Margarita Vitalyevna Belobeletskaya

¹Institute of Chemistry, Far-East Branch, Russian Academy of Sciences, Vladivostok, Russia

²Far East State Technical Fisher University, Vladivostok, Russia

³Far Eastern Federal University, Vladivostok, Russia

Abstract- Perspectives of obtaining of complex oxide europium, iron, and bismuth nanocomposites as both bulk powders and thin film coatings on various supports by low-temperature pyrolysis of organic extracts based on extraction systems with different polyfunctional ligands were shown. Magnetic properties of nano-scale bismuth and europium ferrites $\text{Bi}_{0,775}\text{Eu}_{0,225}\text{O}_{1,5}$, EuFeO_3 , and $\text{Eu}_3\text{Fe}_5\text{O}_{12}$ were studied. Influence of the size of the particles on the magnetic properties of the multiferroic EuFeO_3 was stated.

Keywords - Europium and iron oxides, nanocomposites, functional materials.

INTRODUCTION

Functional materials based on rare-earth oxides and mixed oxides of rare-earth elements, iron, manganese, bismuth, silicon, zirconium, and other metals are used as adhesive-protective coatings, optic processors, waveguides, luminophors, multiferroics, catalysts, acoustooptic, memory and readout devices[1-3]. In particular, materials with electric dipoles induced by magnetic ordering, such as rare-earth manganites and ferrites, may be one of the best as useful multiferroic[2]. The choice of methods of synthesis of the above-mentioned oxide functional materials as both bulk ceramic samples and thin films influences in the large degree on particles composition, properties, structure, and size as well as technology of their obtaining. Up to present, working out and perfection of concrete techniques of their obtaining are among the important directions of modern investigations in the sphere of synthesis of nanotubular oxides and materials on their basis. On the one hand, it is conditioned by variety of nanomaterial compositions, and properties and, on the other hand, it lets to widen the choice of such substances and to create samples of various nanotubular types with the least expenditures. In this respect, so-called the "soft-chemical" or solution methods: sol-gel, extraction-pyrolytic or deposition from solutions – are perspective as compared to the high-temperature solid-phase synthesis[4-6].

The present report is dedicated to study of possibility to obtain complex oxide europium, iron, and bismuth nanocomposites as both bulk powders and thin film coatings on various supports by low-temperature pyrolysis of organic extracts based on extraction systems with different polyfunctional ligands as well as to investigation of their properties.

MATERIALS AND METHODS

Our experiments on determination of optimum concentrations of extragents in the initial organic phase and compositions of the aqueous phases shows that in order to obtain saturated extracts for their further usage in synthesis of

multiferroics based on mixed europium and iron oxides by the pyrolytic method one can successfully use extraction of metals with neutral, anion-exchange extractants, and β -diketones from chloride solutions. Europium concentration in the aqueous phase equaled $6 \cdot 10^{-3}$ mole/L. Extraction of europium (III) was carried out with mixed benzene solutions of trialkylbenzylammonium chloride (TABACH) and acetylacetone (AA) or benzoic acid (BA), AA and 2,2'-dipyridyl (Dip) or diphenylguanidine (DPhGA) including those in the presence of polyfunctional organic substances: acrylamide (AAm), tris-(hydroxyl-methyl)-aminomethane (THMAM), 1,10-phenanthroline (Phen) – in the aqueous phase. Bismuth (III) was extracted with methylhexylketone (MHK), trialkylbenzylammonium thiocyanate (TABAT) or TABACH and acetylacetone (AA) solutions in benzene. Iron was extracted with benzene solution of n-trioctylamine (TOA). The compositions of the aqueous and organic phases were determined by the atomic absorption and X-ray radiometric as well as the luminescent and IR spectroscopy methods. For identification of the extractable europium complexes the low-temperature luminescence spectra of the extracts were recorded at 77 K at a CDL-1 spectrometer. The IR spectra of the extractable coordination compounds were registered at a Specord IR-75 spectrometer. The organic phase was evaporated and exposed to pyrolysis at the temperature range 400 - 700 °C in a muffle furnace. The X-ray diffraction patterns of the samples of the extracts after pyrolysis were registered at a DRON-2.0 diffractometer in CuK_α – radiation. The X-ray diffraction patterns were recorded at a D8 ADVANCE diffractometer in CuK_α -radiation with the graphite monochromator. The composition of the powders was controlled by the X-ray diffraction analysis using the EVA search program with the PDF-2 powder data bank. The magnetic characters were measured at a SQUID MPMS 7 magnetometer in the range 2-300 K and the normal magnetization curves of the nanocomposites were recorded at an automatic vibromagnetometer: an initial powdered material was placed into a quartz container and

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exposed to influence of constant magnetic field in the range to 900 Oe. The nano-scale coatings on amorphous silicon dioxide and quartz were obtained by repeated applying of the saturated extracts with following drying and pyrolysis of the precursors at 700 °C. Saturation of the samples of amorphous silica was carried out by shaking with the saturated extracts and following distillation off the solvent. The SEM images and morphology of the nanocomposite samples were studied using a Hitachi S 5500 high-resolution scanning electron microscope and NT-MDT atomic-force microscope.

RESULTS AND DISCUSSIONS

In the case of ferrites the samples of EuFeO_3 and $\text{Eu}_3\text{Fe}_5\text{O}_{12}$ (individual according to the X-ray diffraction analysis) with the particles 5 - 20 nm in size were obtained by pyrolysis of the mixture of europium saturated extracts of a known concentration with saturated iron extracts the molar ratios $\text{Eu:Fe} = 1:1$ and $\text{Eu:Fe} = 3:5$, respectively. The extraction-pyrolytic method was also used for obtaining of complex oxide nanocomposites of europium and bismuth, terbium and bismuth as well as iron and bismuth which were identified by the X-ray diffraction method as $\text{Bi}_{0.775}\text{Eu}_{0.225}\text{O}_{1.5}$, BiTbO_3 , and BiFeO_3 , respectively (Table).

The advantages of the extraction-pyrolytic method are the most full displayed in preparation of nano-scale films and coatings of various functional materials. The coatings of the multiferroic EuFeO_3 on quartz glass and amorphous silicon dioxide were also obtained (Table).

Table Composition and Conditions of Complex Oxide Composites Obtaining

extraction system	t °C	phase composition
($\text{BiCl}_3 + \text{MHK} + \text{AA}$) + ($\text{EuCl}_3 + \text{MHK} + \text{AA}$)	700	BiEuO_3
($\text{BiCl}_3 + \text{TABACH} + \text{AA}$) + ($\text{EuCl}_3 + \text{BA} + \text{THMAM}$ or AAm)	700	$\text{Bi}_{0.775}\text{Eu}_{0.225}\text{O}_{1.5}$
($\text{EuCl}_3 + \text{TABACH} + \text{AA}$) + ($\text{FeCl}_3 + \text{TOA}$)	700	$\text{Eu}_3\text{Fe}_5\text{O}_{12}$
EuCl_3 or $\text{Eu}(\text{NO}_3)_3 + (\text{AA} + \text{Dip}) + (\text{FeCl}_3 + \text{TOA})$	600	EuFeO_3
EuCl_3 or $\text{Eu}(\text{NO}_3)_3 + (\text{AA} + \text{Dip}) + (\text{FeCl}_3 + \text{TOA})$	600	$\text{Eu}_3\text{Fe}_5\text{O}_{12}$
($\text{EuCl}_3 + \text{TABACH} + \text{AA}$) + ($\text{FeCl}_3 + \text{TOA}$)	700	EuFeO_3
($\text{EuCl}_3 + \text{BA} + \text{THMAM}$ or AAm) + ($\text{FeCl}_3 + \text{TOA}$)	700	EuFeO_3
($\text{BiCl}_3 + \text{TABACH} + \text{AA}$) + ($\text{FeCl}_3 + \text{TOA}$)	700	BiFeO_3
$\text{BiCl}_3 + \text{TbCl}_3 + \text{TABACH} + \text{MHK} + \text{AA}$	700	BiTbO_3
EuCl_3 or $\text{Eu}(\text{NO}_3)_3 + (\text{AA} + \text{Dip}) + (\text{FeCl}_3 + \text{TOA})$	600	$\text{EuFeO}_3/\text{SiO}_2$

It was shown by the magnetic investigation that $\text{Bi}_{0.775}\text{Eu}_{0.225}\text{O}_{1.5}$ is paramagnetic. The nano-scale multiferrous BiFeO_3 is a material with a high value of electric and magnetic ordering[7].

Europium ferrites $\text{Eu}_3\text{Fe}_5\text{O}_{12}$ and EuFeO_3 are ferromagnetic semiconductive materials of the oxide group [2]. The normal magnetization curves of $\text{Eu}_3\text{Fe}_5\text{O}_{12}$ and EuFeO_3 are presented in Figure 1. The dependences of the

total (I_s) and residual (I_{rs}) magnetization of the nano-scale $\text{Eu}_3\text{Fe}_5\text{O}_{12}$ and EuFeO_3 prepared by the extraction-pyrolytic method indicate to displaying of magnetic properties depending on the composition. The first compound is characterized by the practically linear dependence of the total magnetization on the magnitude of the constant magnetic field but behaviour of the residual magnetization indicates to displaying of ferromagnetic properties. Such a behaviour of the full and residual magnetization is typical for nanocrystal ferromagnetic structures and amorphous magnetic materials.

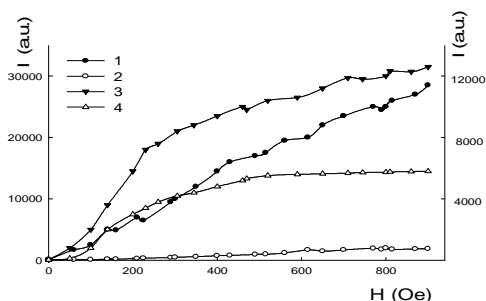


Fig. 1 Magnetization of $\text{Eu}_3\text{Fe}_5\text{O}_{12}$ (1,2) and EuFeO_3 (3,4) in the constant magnetic field to $H=900$ Oe at the room temperature; 1,3 – total magnetization; 2,4 – residual magnetization; 1 a.u. = $1,2 \cdot 10^{-9}$ A/m².

A hard-magnetic compound EuFeO_3 displaying pronounced ferromagnetic properties with a rather high value of coercive force (Figure 1, curves 3, 4) was prepared by the extraction-pyrolytic method. Its samples have the blocking temperature comparable or exceeding 300 K, i.e. they display ferromagnetic properties at the room temperature. The size of its particles varies in the range 10-20 nm. The maximum value of coercive force at the room temperature (300 K) achieves 2068 Oe and that of full magnetization ~ 0.35 emu/g. It indicates to possibility to use the extraction-pyrolytic method for obtaining of perspective potential magnetic materials.

The magnetic properties of the two europium ferrite EuFeO_3 samples prepared by different ways: 1) joint hydrolysis of salts (europium and iron chlorides) with following calcination at 700 °C and dispersing in ethyl alcohol and 2) the extraction-pyrolytic method – were studied. According to the atomic-force microscopy (ASM) method the size of the particles prepared by the first way equals $\sim 3 \mu\text{m}$ (№ 1) and that of the second one – 10-20 nm (№ 2).

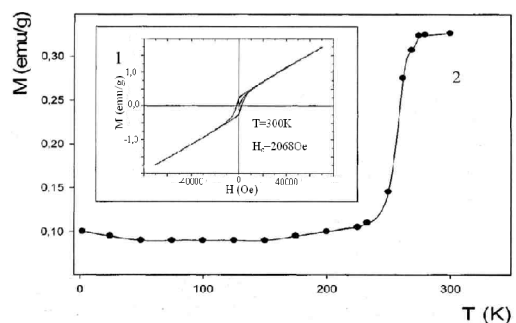


Fig. 2 Dependence of specific magnetization on the magnetic field intensity at 300K (1) and on the temperature at 3000 Oe (2) for EuFeO_3 , № 2.

The hysteresis curves at 2 and 300 K and dependences of specific magnetization on the temperature for the both samples are given in Figure 2-3 and 4, respectively.

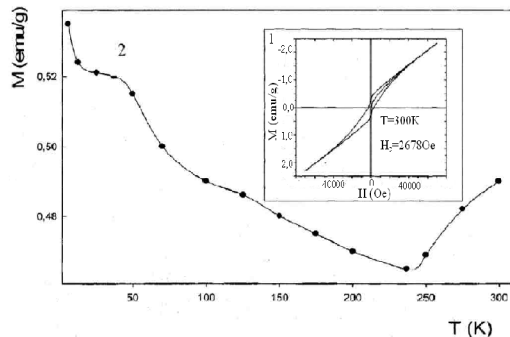


Fig. 3 Dependence of specific magnetization on the magnetic field intensity at 300 K (1) and on the temperature at 3000 Oe (2) for EuFeO_3 № 1.

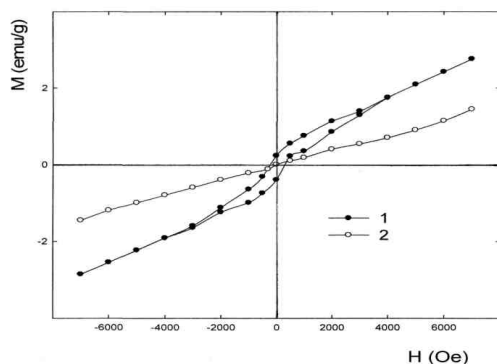


Fig. 4 Dependence of specific magnetization on the magnetic field intensity at 2 K for EuFeO_3 № 1 (1) and № 2 (2).

The presence of the hysteresis loop and high coercive force values (Figure 3, 1) let to attribute EuFeO_3 sample № 1 to the hard-magnetic materials ($H > 126$ Oe). The temperature dependence of magnetization (Figure 3, curve 2) lets to suggest that EuFeO_3 № 1 is a complex magnetic structure. Such magnetic structures are antiferromagnetic in the temperature range between T_N and T_1 ($0 < T_1 < T_N$) and became ferromagnetic below T_1 . This suggestion is confirmed by the hysteresis loop for the compound № 1, at 2 K (Figure 4, curve 1).

Narrowing of the hysteresis loop in its central part as well as its certain displacement indicate to competition between antiferromagnetic and ferromagnetic interactions. The sample of EuFeO_3 № 2 prepared by the extraction-pyrolytic method, like the sample EuFeO_3 № 1 at 300 K may be attributed to the hard-magnetic materials (Figure 2). However, in the compound № 2, the temperature decrease results in the rather sharp decrease of coercive force magnetization (Figure 2, curve 2). Such temperature behaviour of magnetization may indicate that below 230 K the compound is slightly ferromagnetic. Thus, in this case, one can observe influence of the size of the particle on the magnetic properties of EuFeO_3 . It should be noted that there is a critical size of a

single domain of magnetic compounds as well as a critical super paramagnetic size varying from 10 nm to 100 nm depending on a substance composition[8].

CONCLUSIONS

Possibility of synthesis of nano-scale mixed europium, iron, and bismuth oxides as both bulk powders and thin film coatings on various supports by the low-temperature extraction-pyrolytic method was shown. The nano-scale complex oxide europium and bismuth composites as well as europium and bismuth ferrites having magnetic properties were obtained. Influence of the size of the particle on the magnetic properties of the ferrite EuFeO_3 was stated.

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