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Influence of annealing treatment on magnetic properties of Fe_2O_3/SiO_2 and formation of ε-Fe_2O_3 phase

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ABSTRACT

Magnetic properties of Fe_2O_3/SiO_2 samples were studied after being produced by sol-gel synthesis and formation of ε-Fe_2O_3 polymorph. Samples were thermally treated, using different annealing temperatures and annealing times. The size and morphological characteristics of the iron oxide nanoparticles were examined using a TEM microscope. We used the "ellipticity of shapes", which is a measure of how much the shape of a nanoparticle differs from a perfect ellipse, in order to quantitatively describe morphological properties of nanoparticles. Coercivity measurements were used to identify and monitor the formation of the epsilon-iron oxide phase during the thermal treatments (annealing). Coercivity values were in the range from 1.2 to 15.4 kOe, which is in accordance with previous experience regarding the existence of ε-Fe_2O_3. We have determined the optimal formation conditions for the ε-Fe_2O_3 polymorph (t=1050 °C for 7 h, H_C=15.4 kOe), as well as the narrow temperature interval (1050–1060 °C) in which the polymorph abruptly vanished (H_C=2300 Oe), on the basis of results of the magnetic properties. The threshold temperature for the ε-Fe_2O_3 phase transformation was measured as 1060 °C. We found that different annealing temperatures and annealing times significantly affected magnetic properties of the examined samples.

1. Introduction

In recent years, various kinds of magnetic nanomaterials [1–6], their composites [7–10], and materials with nanostructures [11–21] have been paid much concentration pertaining to their superior properties. Among them, ferric oxide (ε-Fe_2O_3) is a subject of comprehensive scientific research due to the variety of its potential applications [22–25] and complex physical properties [26–39].

This iron oxide polymorph is a promising material for applications in electronic and storage technologies, such as spintronics [40–45], development of multiple-state-memory [46], or magnetizable printing [47]. It possesses unique magnetic properties, which are subject of various interpretations with no clear consensus about their origins [48–50]. This iron oxide polymorph exhibits very high coercivity (~2 T) [51–53], that is affected by a number of parameters: annealing conditions, magnetocrystalline anisotropy, weight content of epsilon-iron oxide phase in the Fe_2O_3/SiO_2 nanocomposite, as well as particle size, and size distribution [54,55]. The synthesis of pure ε-Fe_2O_3 phase is therefore challenging. The difficulty of preparing pure epsilon-iron oxide phase by the sol-gel synthesis method is related to the particle agglomeration [56]. The products of such a synthesis are usually a mixture of ε-Fe_2O_3 and other iron oxide phases (usually in the α-Fe_2O_3 and γ-Fe_2O_3 phases) and in the form of Fe_2O_3/SiO_2 nanocomposite. The formation and transformation of the ε-Fe_2O_3 phase are determined by two annealing conditions: annealing temperature and annealing time. Annealing of ε-Fe_2O_3 at temperatures around 1200 °C usually results in the ε-Fe_2O_3→α-Fe_2O_3 phase transformation [57], although there are also reports [58] in the literature of the ε-Fe_2O_3→β-Fe_2O_3 transformation. Formation of the epsilon-iron oxide phase may occur in a very wide temperature range, viz. between 300 °C and 1200 °C, that depends on the method of synthesis [59–62].

Until now, the ε-Fe_2O_3 phase was synthesized by variety methods, such as: a) impregnation of mesoporous silica by iron salt [63,64]; b) the oxidative hydrolysis of potassium ferricyanide [61]; c) thermal decomposition of the clay mineral nontronite and subsequent isolation of the ferric oxide by leaching the silicate phases [54]; d) direct one-

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cycle plasma dynamic synthesis [65]; e) plasma-enhanced chemical vapor deposition with microwave torch discharge [66], vapor-phase synthesis in combination with CVD/sputtering approach [67]; f) deposition of ε-Fe_2O_3 by dip-coating on Si (100) wafers [68], and others. Most commonly the ε-Fe_2O_3 phase is prepared by way of an acid or base catalyzed sol-gel synthesis, with a subsequent thermal treatment of the sample [69]. Alteration of the annealing temperature and duration time initiates the formation of ε-Fe_2O_3 phase. Tronc et al. [70] prepared the epsilon-iron oxide phase via a coprecipitation of the Fe^{2+} and Fe^{3+} ions in a reaction with triethoxysilane. Annealing was carried out by heating the sample at temperatures between 1000 °C and 1400 °C for 30 min. Brazda et al. [71] obtained the ε-Fe_2O_3 by a sol-gel method using a coordination complex EDTA as a single precursor of both the iron oxide nanoparticles and the SiO_2 matrix. They annealed samples at 1000 °C for 1 h. Korte et al. [72] prepared the ε-Fe_2O_3 by a custom-built cold-wall CVD apparatus, starting from $Fe(hfa)_2TMEDA$, at deposition temperature of 400 °C and duration time of 60 min. Lancok et al. [73] prepared a Fe_2O_3/SiO_2 nanocomposite, containing ε-Fe_2O_3 phase by the sol-gel route, annealing the sample at 1000 °C for 4 h. Morber et al. [74] obtained the epsilon-iron oxide phase on an alumina substrate, starting from Fe_3O_4 as a precursor, by a pulsed laser deposition. Thereafter, samples were heated in the furnace at 700–1000 °C, for an annealing time of 35 min to 1h. Yakushin et al. [75] prepared the ε-Fe_2O_3 phase by a pores-filling impregnation synthesis, using a $FeSO_4$ solution and a KSKG silica gel. Samples were annealed at temperatures ranging from 400 °C to 900 °C for the duration of 1–4 h. Hutlova et al. [76] prepared epsilon-iron oxide phase as a vacuum preheated sample with formamide by a synthesis process consisted of $Y_3Fe_5O_{12}$ as the initial precursor. Then the sample was treated for 8 h in a furnace at 1000 °C [76]. Kurmoo at al. [77] prepared the epsilon-iron oxide from $Fe(NO_3)_3$*$9H_2O$ and $Y(NO_3)_3$*$6H_2O$ precursors. They formed the ε-Fe_2O_3 phase by annealing the samples in the temperature interval between 800 °C and 1100 °C, with the largest content of epsilon-iron oxide being obtained after annealing for 10 h at 1000 °C. Sawada et al. [78] synthesized ε-Fe_2O_3 particles by thermal precipitation in RF-sputter-deposited SiO_2 film. The as-deposited films were annealed at 900 °C or 1000 °C from 38 min to 48 h. Popovici et al. [79] reported synthesis of ε-Fe_2O_3 phase, using non hydrated $Fe(NO_3)_3$ as a precursor of iron ions. So-obtained samples were annealed at different temperatures, ranging from 300 °C to 1100 °C, with 3 h of annealing time added for every 100 °C. In our previous work [80] we observed the formation of epsilon-iron oxide particles formation at 740 °C. We concluded that the epsilon-iron oxide phase occurred due to α-Fe_2O_3 phase transformation during the sol-gel synthesis. Zboril et al. [81] obtained ε-Fe_2O_3 phase by oxidation of iron sulfate in the air, annealing the γ-Fe_2O_3 particles at 460 °C for 20 h. Sakurai et al. [82] formed the ε-Fe_2O_3 single-phase via combination of sol-gel and microemulsion methods, by heating the sample at 900 °C for 4 h. Jin et al. [48] prepared the ε-Fe_2O_3 phase by a combination of sol-gel synthesis, and the reverse micelle method. They reported that epsilon-iron oxide phase formed in the temperature region of 980–1030 °C.

In this work, the formation and stability of the ε-Fe_2O_3 phase were studied in the temperature range between 900 °C and 1060°C. Monitoring of the phase transformation was carried out by magnetic measurements using a SQUID magnetometer. These measurements showed a maximal value of H_C~1.54 T for the sample annealed at 1050 °C for 7 h. A sharp decrease of coercivity (ΔHc=1.17 T) was observed after annealing at 1060 °C for 3 h, and after annealing at 1050 °C for 25 h, thus demonstrating the instability of ε-Fe_2O_3 phase.

2. Experimental

2.1. Sample preparation

The samples were prepared by a sol-gel process [79]. Catalyst solution contained Fe^{3+} ions in an aqueous solution (in the molar ratio $Fe(NO_3)_3$×$9H_2O$:H_2O of 0.013:1). Synthesis was self-catalyzed by the nitric acid, which appeared in the system as a product of the hydrolysis reaction of an iron nitrate precursor. An alcoxide solution was prepared separately (TEOS:H_2O:C_2H_5OH was mixed in molar proportion 1:12:12). The solution was added to the catalyst solution and stirred for 5 h at room temperature. Gelation of alcogel took place for 36 days in a partially closed beaker. Thereafter, alcogel was dried at 80 °C for 19 h. Different parts of the alcogel, taken from the same batch, were subjected to thermal treatments in the air atmosphere. The prepared samples consisted of 15% of Fe_2O_3 in Fe_2O_3/SiO_2 structure.

2.2. Characterization methods

Thermo-gravimetric analysis (TG) was performed using a thermal analyzer TA-SDT 2090 in the temperature range: 25–1100 °C. In order to measure the TG and DTA curves within a standard procedure, the dried sample that had not been subjected to any thermal treatment, was placed in the TGA furnace and heated up to 1100 °C at a rate of 20 °C/min in the air atmosphere. The isothermal TG curve was also recorded during the heating of the dried sample at 1050 °C. The sample was kept at 1050 °C for 90 min while the TG curve was measured.

The structure of the synthesized sample was analyzed by a Rigaku RINT-TTRIII diffractometer using Ni-filtered CuKα monochromatic radiation (λ=1.5418 Å). The diffraction pattern was recorded at room temperature over a 2Θ range: 10–70°, with the exposure time 30 s/step.

The size and morphology of the synthesized sample were observed by transmission electron microscopy (TEM, JEOL 2010 F).

Magnetic measurements were carried out by Quantum Design MPMS XL-5 SQUID magnetometer. The magnetization versus temperature curves were obtained by applying the zero-field-cooled (ZFC) and the field-cooled (FC) protocols. The ZFC protocol included cooling of the sample from 300 K to 2 K in a zero magnetic field. Thereafter, the ZFC magnetization was measured during the reheating of sample within the same temperature interval, and in an applied field of 100 Oe. In the FC protocol, the sample was cooled in an applied magnetic field (H=100 Oe) and the magnetization was measured during the reheating in the same magnetic field. Hysteresis loops were measured at 200 K in the field range $-5\ T < H < +5\ T$. Changes of the coercivity were monitored after annealing treatment of the samples at different temperatures and for different annealing times.

3. Results and discussion

3.1. Thermal analysis measurements

The thermo-gravimetric analysis was performed with an aim of investigating the temperature range for the formation of the ε-Fe_2O_3 phase. The sample was heated from the room temperature to 1100 °C. The recorded TG and DTA curves are depicted in Fig. 1. Analysis of the TG curve indicates a sharp decrease, of about 65%, in the weight as the temperature is increased to 210 °C. To distinguish whether the mass losses were accompanied by endothermic or exothermic processes, we recorded a DTA curve (Fig. 1a)). DTA minima at 93 °C and 150 °C are ascribed to the elimination of chemically or physically adsorbed H_2O