Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Journal of Magnetism and Magnetic Materials 290–291 (2005) 106–109
Journal of magnetism and magnetic materials
www.elsevier.com/locate/jmmm

Preparation of strontium hexaferrite nanowires in the mesoporous silica matrix (MCM-41)

A.A. Eliseev[a,*], D.F. Gorozhankin[a], D.D. Zaitsev[a], A.V. Lukashin[a], A.V. Knotko[a], Yu.D. Tretyakov[a], P. Görnert[b]

[a]*Department of the Materials Sciences, Moscow State University, Leninskie Gory 1-3, 119992, Moscow, Russian Federation*
[b]*INNOVENT e.V., Prüssingstrasse 27 B, D-07745 Jena, Germany*

Available online 8 December 2004

Abstract

We report a novel method of synthesis of ordered magnetic strontium hexaferrite nanowires in the mesoporous silica matrix by incorporation of metal complexes into the freshly prepared mesoporous silica–surfactant composite. The shape and size of obtained nanowires are consistent with the dimensions of the porous framework. The obtained nanocomposites are characterized by high blocking temperatures up to 160 K. Mesoporous silica serves as nanoreactor for the formation of nanowires.

PACS: 75.50.K; 81.05.Y

Keywords: Mesoporous silica; Magnetic nanocomposites; One-dimensional systems; Superparamagnetism; Ferrite

1. Introduction

One of the most important issues in physics and materials science today is the preparation of ordered nanostructure arrays with controlled properties and dimensions. The most challenging nanosystems are nanowires owing to the highest anisotropy parameters in them, which could certainly increase the functional properties of nanomaterials [1]. For example, highly anisotropic magnetic nanowires possess ferromagnetic properties at room temperature even at diameters of 2 nm. Recently iron and iron oxide nanowires with characteristic widths of 1–2 nm and different length/diameter ratios were synthesized in the mesoporous silica matrix [2]. However, magnetic characteristics of these composites still need to be improved for their further use in magnetic storage media with ultrahigh areal density.

One of the promising magnetic materials that possess high enough coercivity and saturation magnetization is strontium hexaferrite. These properties as well as an extremely high magnetic anisotropy of hexaferrites also suggest its possible use for the preparation of ordered arrays of nanowires in the mesoporous silica matrix. The synthesis of strontium hexaferrite phase usually requires rather high temperatures (above 1000 °C). However, the mesoporous structure of MCM-41 shrinks at temperatures above 800 °C [3]. Therefore for the preparation of $SrFe_{12}O_{19}$ in the mesoporous silica matrix one should achieve the formation of hexaferrite phase at low temperature. According to the literature, low-temperature formation of $SrFe_{12}O_{19}$ was realized by decomposition

*Corresponding author. Chemistry Department, Division of Inorganic Chemistry, Moscow State University, Leninskie Gory 1-3, 119992 Moscow, Russian Federation. Tel.: +7 095 939 59 31; fax: +7 095 939 09 98.
E-mail address: eliseev@inorg.chem.msu.ru (A.A. Eliseev).

0304-8853/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jmmm.2004.11.223

of iron and strontium citrates at 650 °C [4] and even at 250 °C [5].

Thus, in the present work the variant of the citric method reported by Garcia et al. was used for the formation of strontium hexaferrite nanoparticles within the porous system of MCM-41 mesoporous silica phase [5]. Intercalation of citrates into the MCM-41 matrix was carried out by simple soaking of the unannealed silica/template composite in a water solution of the citrate complexes. During the impregnation process, one should expect intercalation of negatively charged anionic complexes into the porous structure of silica sieves, which appears due to excess charge of the template cations compensated only by silanol $Si–O^-$ groups. Actually, intercalation of the anions could be proved by a simple experiment: deionized water does not wet dry mesoporous silica/template composite while the solution containing any of anions or anionic complexes except OH^- is quickly absorbed by this matrix.

2. Experimental details

2.1. Preparation of the citrates solution

The solution containing 12 Fe^{3+}:1 Sr^{2+}:20 $C_6H_8O_7$:3 C_6H_5COOH:60 $(CH_2OH)_2$:1200 H_2O was prepared as described in Ref. [4]. A suitable amount of $Fe(NO_3)_3 \cdot 9H_2O$ was dissolved in distilled water and precipitated by 25% ammonia solution. The precipitate was repeatedly washed in order to remove NO_3^- anions. Iron hydroxide was dissolved in citric acid at 60 °C. Taking into account possible losses during precipitation, the iron content in this solution was determined by titration of iron with EDTA solution. Next, a calculated amount of $SrCO_3$ was added. After completion of the reaction, benzoic acid and ethylene glycol were also added and the mixture was stirred until the formation of homogeneous solution.

2.2. Synthesis of $SrFe_{12}O_{19}/SiO_2$ nanocomposites

A mesoporous silica sieve was prepared by the template method described elsewhere [6]. The method is based on polycondensation of a silica source (tetraethylorthosilicate (TEOS), 98%, Aldrich) in the aqueous template solution (cetyltrimethylammonium bromide, CTAB, 99.9%, Aldrich) with basic catalyst ($pH \approx 12$, NH_3). The molar ratio of components was 1 TEOS:0.152 CTAB:2.8 NH_3:141.2 H_2O. The precipitate was filtered out, washed by deionized water to $pH = 7$ and dried at 363 K for 12 h. At this stage, the SiO_2/template composite was formed.

The composite was impregnated with the citrate solution at 45 °C for 24 h under continuous stirring. Then it was filtered and carefully washed with deionized water (until the filtrate becomes uncolored) in order to get rid of iron and strontium precursors absorbed on the SiO_2 surface. The obtained yellow precipitate was dried at 80 °C and subsequently annealed in oxygen flow at temperatures of 250–400, 550, 800, 1000 °C for 3 h.

The samples were characterized by chemical analysis, capillary absorption of nitrogen at 77 K (COULTER™ SA 3100™), X-ray powder diffraction (DRON 3M; CuK_α radiation $\lambda_{ave} = 1.54184$; 2θ range 5°–70°, scan step 0.03°), transmission electron microscopy (TEM), electron diffraction (ED) (JEM-2000FXII, JEOL) and magnetic measurements (S600 SQUID magnetometer, Cryogenics and Faraday balance magnetometer).

3. Results and discussion

The template removal after oxidation was verified by the method of capillary absorption of nitrogen at 77 K and carbon analysis. According to the high BET surface

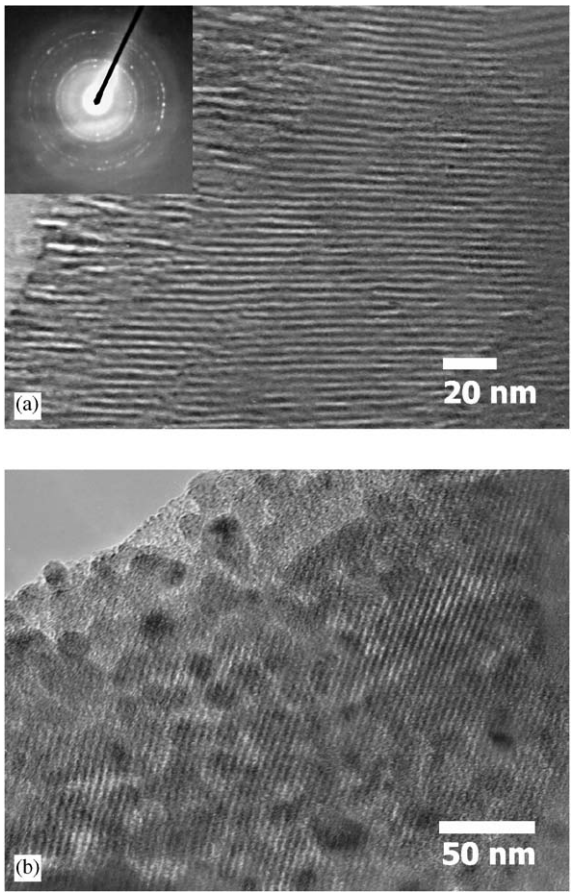

Fig. 1. TEM and diffraction pattern for nanocomposite prepared at 300 °C (a) and 550 °C (b).