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Strontium ferrite nanoparticles synthesized in presence of polyvinylalcohol: Phase composition, microstructural and magnetic properties

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Abstract

Systematic study was devoted to the synthesis of hexagonal strontium ferrite nanoparticles employing polyvinylalcohol as stabilizing agent. Preliminary experiments allowed to select an optimal sol having molar ratio $Sr^{2+}/Fe^{3+} = 12$, weight ratio $PVA/[Sr^{2+} + Fe^{3+}] = 1.4$ and $pH = 2.1$. The obtained sol were transformed to gels by an evaporation of water at 100 °C and drying at 112 °C under vacuum. The subsequent calcination was carried out for 3 h at 400 °C, achieved by heating rate of 17 K/min. The obtained precursor was used for a detail study of influence of annealing conditions (temperature range 600–700 °C, annealing time 10–190 min) on the resulting properties. Semiquantitative X-ray phase analysis approved a gradual increase of the M-phase content and a gradual growth of M-phase crystallites with temperature and time. Magnetic measurements showed a distinct influence of the phase composition, namely ratio of the contents of M-phase and maghemite on the shape of the magnetic loops, while the crystallite sizes have only a slight effect.

Keywords: Strontium ferrite; Nanoparticles; Magnetic properties

1. Introduction

Contemporary studies of magnetic nanoparticles are significantly motivated by their current and potential applications in biology and medicine like cells and biomolecules magnetic separation, drug delivery, contrast agents for magnetic resonance imaging and colloidal mediators for cancer magnetic hyperthermia [1].

The oxide nanoparticles available at the present consist almost exclusively from magnetic cores of magnetite Fe_3O_4 and maghemite γ-Fe_2O_3 covered by a biocompatible polymer corona, such as dextran. These cores are relatively easy to prepare by alkaline coprecipitation but their use is associated with inconveniency, namely it is difficult to adjust their magnetic properties for a specific application.

A suitable approach to solve the outlined task is the use of complex magnetic oxides because their magnetic properties can be suitably tailored by modification of their intrinsic properties depending on their composition and structure. Therefore a search of such materials is advisable.

As an example can serve our recent study of lanthanum manganese perovskite $La_{0.75}Sr_{0.25}MnO_3$ nanoparticles, where heating power (SAR value) promising for hyperthermia applications was found (SAR higher than 350 W/g_{Mn} at 108 kHz) much higher than maghemite SAR values at the same frequency ($SAR = 13\,W/g_{Fe}$) [2]. Furthermore, the Curie temperature in this system can be suitably adjusted with respect to a surrounding medium so that the overheating risk is ruled out [3].

Another promising possibility is the exploitation of a large family of the hexagonal ferrites, so-called hard ferrites, possessing relatively high saturated and remanent magnetizations and exhibiting high magnetocrystalline anisotropy. A high heating effect can thus be expected.

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Their structures, of a polytypic nature, can be conventionally described in terms of an intergrowth of the blocks S, R and T. The S block is a (1 1 1) slice of the common spinel structure, while R and T are blocks of hexagonal symmetry which represent weak links in the magnetic exchange interactions. Among them let us mention as examples the phase M arising from the stacking of the type …SRS*R*… and the phase Y formed by the stacking of the type …$S_1T_1S_2T_2S_3T_3$… . The hexagonal ferrites are complex magnetic systems and offer several kinds of the non-equivalent sites, octahedral, bipyramidal and tetrahedral, that can be occupied by diverse magnetic or non-magnetic cations [4,5]. Their magnetic properties thus can be readily modified by variation of the stacking of the individual blocks and of the composition in a desirable way.

There are a number of proposed and applied methods for the synthesis of hexagonal ferrites as submicron particles, mostly via wet chemistry (e.g. sol–gel methods, hydroxide coprecipitation) completed by a subsequent thermal treatment [6–13].

The hexaferrite particles of the $BaFe_{12}O_{19}$ and analogous $SrFe_{12}O_{19}$ of the mean size bigger than 100 nm are synthesized by annealing of precursors above 700 °C while smaller particles grow up at lower temperatures. The reaction in the latter case is, however, usually incomplete and the produced powders are multiphase, containing γ-Fe_2O_3 and α-Fe_2O_3. Evidently it leads to a coercivity decrease undesirable for some applications like magnetic recording. The problem is, however, less critical for the potential use of this type of materials in medical and biological applications, like magnetic fluid hyperthermia.

Therefore the present study, considered as an initial point, is devoted to the optimization of $SrFe_{12}O_{19}$ nanoparticles synthesis with respect to the phase compositions of the products, size of the nanoparticles and resulting magnetic properties.

2. Synthesis

Synthesis of nanoparticles of hexagonal strontium ferrite was based on a method employing polyvinylalcohol as stabilizing agent, reported previously [14]. The starting chemicals were $Sr(NO_3)_2$ p.a. (Aldrich Germany), $Fe(NO_3)_3 \cdot 9H_2O$ p.a. (Fluka Switzerland), polyvinylalcohol ($M = 30.000-70.000$ g/mol, Sigma USA) and diethylamine 99.5+ (Aldrich USA). The compounds $Sr(NO_3)_2$ and $Fe(NO_3)_3 \cdot 9H_2O$ were chemically analyzed in order to determine the actual contents of the cationic components. Precise quantities of cationic compounds were dissolved separately and mixed together in molar ratios of Fe^{3+}/Sr^{2+} in the range of 11.86–12.02. The mixture of dissolved cations was heated up to 80 °C and mixed together with a solution of polyvinylalcohol in the weight ratio of $PVA/[Sr^{2+} + Fe^{3+}] = 0.755-5.606$. After cooling to room temperature, pH of the solution was adjusted by diethylamine to values in the range of ~1–10.

Table 1
Properties of selected sols

	Molar ratio, Fe/Sr	Mass ratio, PVA/(Sr^{2+} + Fe^{3+})	Adjusted pH
A	12.00	1.4	2.1
B	12.00	2.8	2.3

The obtained sols were then transformed to gels by an evaporation of water at 100 °C and drying at 112 °C under vacuum. The subsequent calcination of the precursors was carried out for 3 h at 400 °C, achieved by heating rate of 17 K/min. Finally the precursors were inserted into a furnace preheated at a given temperature, annealed during a given time and then rapidly quenched down to liquid nitrogen. This approach was used in order to minimize time and temperature uncertainties arising during cooling from the annealing temperature.

Properties of two sols used in the systematic study aimed to an optimization of the conditions of the synthesis are given in Table 1.

3. Characterization

X-ray powder diffraction using Bruker D8 diffractometer (CuKα, SOL-X energy dispersive detector) was employed to determine the phase compositions and crystallite sizes. X-ray diffraction patterns were analyzed with the Rietveld method using the FULLPROF program [15]. The structures of detected phases were collected with the help of ICSD [16]. Thompson–Cox–Hastings pseudo-Voigt profile was used to resolve instrumental, strain and size contributions to peak broadening. Instrumental resolution was determined by measuring strain-free tungsten powder with grain size 9.4 μm.

Particles size and shape were directly observed by TEM (Philips EM 201). The magnetic hysteresis loops were measured by magnetosusceptometer DSM 10 (Manics) at room temperature in the fields up to ±2 T.

4. Results and discussion

Comparison of the M-phase growth carried out by annealing of the calcinated precursors A and B at 600 °C, see Fig. 1, shows a considerable influence of the sol properties. It seems that a major role can be attributed to the influence of composition while the influence of slight pH variations is probably less important. An origin of this effect is comprehensible in a context of the starting ratio $PVA/(Fe^{3+} + Sr^{2+})$, see Table 1. Due to a higher content of ($Fe^{3+} + Sr^{2+}$), nucleation during the germinal stage of the sol–gel conversion in the sol A is favored compared to growth of these nuclei insomuch that a number of arising nuclei is much higher than in the latter case where one can suppose a tendency to the growth of "isolated" grains to a larger size. With respect to a fundamental requirement for