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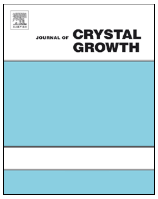

Influence of polyols on the formation of nanocrystalline nickel ferrite inside silica matrices

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ABSTRACT

We have synthesized nickel ferrite/silica nanocomposites, using a modified sol–gel method that combines the sol–gel processing with the thermal decomposition of metal-organic precursors, leading to a homogenous dispersion of ferrite nanoparticles within the silica matrix and a narrow size distribution. We used as starting materials tetraethyl orthosilicate (TEOS) as source of silica, Fe(III) and Ni(II) nitrates as sources of metal cations, and polyols as reducing agent (polyvinyl alcohol, 1,4-butanediol and their mixture). TG/DTA coupled technique evidenced the redox interaction between the polyol and the mixture of metal nitrates during the heating of the gel, with formation of nickel ferrite precursors in the pores of the silica-gels. FT-IR spectroscopy confirmed the formation of metal carboxylates inside the silica-gels and the interaction of the polyols with the Si–OH groups of the polysiloxane network. X-ray diffractometry evidenced that in case of nanocomposites obtained by using a single polyol, nickel ferrite forms as single crystalline phase inside the amorphous silica matrix, while in case of using a mixture of polyols the nickel oxide appears as a secondary phase. TEM microscopy and elemental mapping evidenced the fine nature of the obtained nickel ferrite nanoparticles that are homogenously dispersed within the silica matrix. The obtained nanocomposites exhibit magnetic behavior very close to superparamagnetism slightly depending on the presence and nature of the organic compounds used in synthesis; the magnetization reached at ~5 kOe magnetic field was ~7 emu/g for all composites.

1. Introduction

Magnetic spinel ferrites MFe_2O_4, where M usually represents one or, in mixed ferrites, more than one of the divalent transition metals Mn, Fe, Co, Ni, Cu and Zn, or Mg and Cd, are an important class of magnetic materials. These spinel ferrites have remarkable magnetic properties, physical flexibility, high electrical resistivity, mechanical hardness and chemical stability [1]. Their properties remarkably change when the size of the particles reaches the nanometer range. Due to their unique magnetic properties which can be influenced by their shape, particle size and their composites with other materials, nickel ferrite ($NiFe_2O_4$) nanoparticles have been widely studied [2,3]. Nickel ferrite based nanomaterials have different practical applications in high frequency devices, power transformers, and gas sensors [4]. There are also potential applications of superparamagnetic nickel ferrite nanoparticles in medicine for local hyperthermia and targeted delivery of drugs in the body [5], as well as in some catalytic processes [6]. However, magnetic nanoparticles have a strong tendency to aggregate due to interparticle magnetic interactions and large nanoparticle surface reactivity. In order to avoid unwanted crystallite coarsening and particle aggregation, different routes like dispersion of the particles in various matrices (ion exchange resin [5], polymers [7,8] and silica [9,10]) or surface coating [11] were adopted. Composite materials formed by metallic or oxide particles dispersed in ceramic or vitreous matrices have important applications in areas such as catalysis and electronics [12]. Directional surface design and chemical engineering of nanocomposite layers opens enormous opportunities for creating unique magnetic adsorbents and next-generation drugs. Mesoporous materials formed by template synthesis have attracted increasing attention as potential materials for catalysis, separation and adsorption of molecules [6]. Chemical co-precipitation or microemulsion methods can be used to obtain ferrite nanoparticles well-encapsulated in silica shells and isolated from each other, while the ferrite nanoparticles prepared by sol–gel technique are confined in the silica matrix [13]. Generally, the sol–gel technique is considered as an

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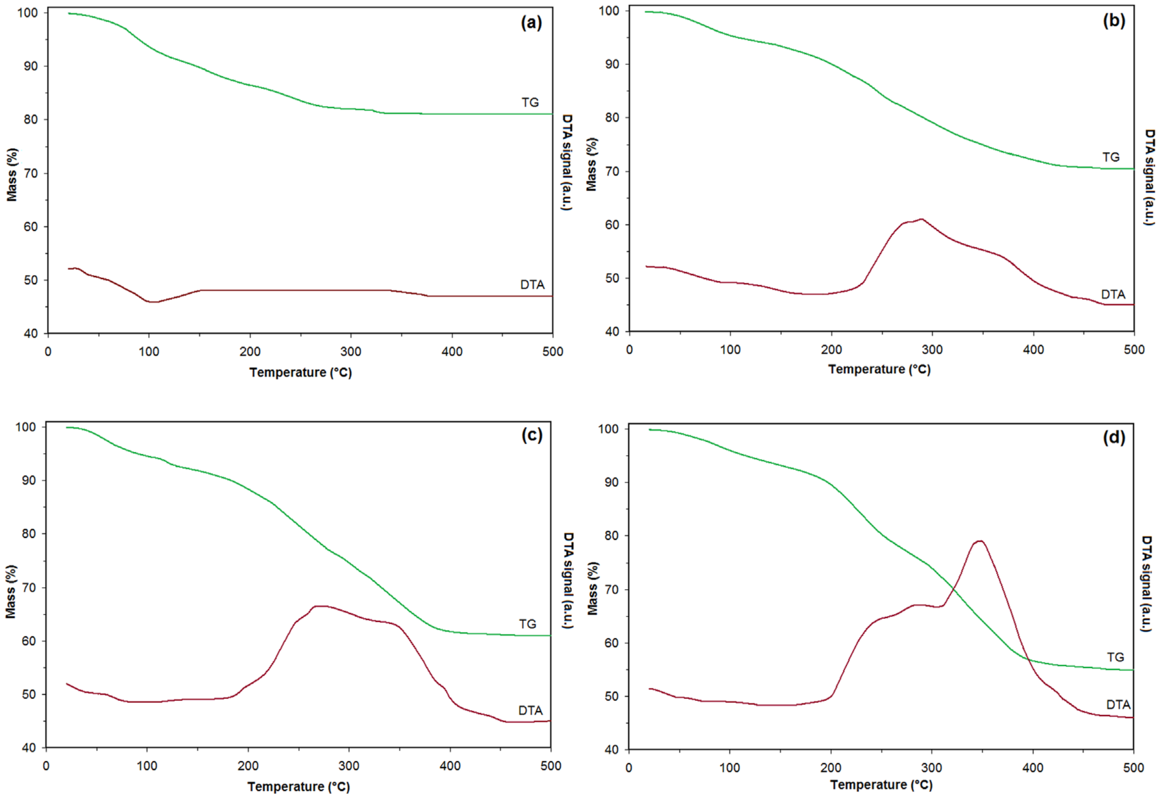

Fig. 1. TG and DTA curves for the gels thermally treated at 150 °C: (a) NiFeSi; (b) NiFeBDSi; (c) NiFePVSi; (d) NiFeBDPVSi.

easy method to fabricate ferrite nanoparticles in a silica matrix, permitting an easy control of experimental conditions, simple operation and batch production, insuring homogenous dispersion and a good control of stoichiometry [14].

The sol–gel derived amorphous silica matrix is an excellent host for supporting different types of guest nanoparticles. The porous nature of the amorphous silica provides nucleation sites for nanoparticles and minimizes the aggregation phenomena imposing an upper limit to the size of the particles [12]. Tetraalkoxysilanes (tetramethoxysilane – TMOS, and tetraethyl orthosilicate – TEOS) are the most common precursors of silica matrices. Their hydrolysis in aqueous solutions and further polycondensation reactions cause formation of sol particles of which the cross-linking leads to the self-organization into a porous three-dimensional network in the bulk [15]. Nickel ferrite/silica nanocomposites have been obtained starting from different tetraethoxysilane without [16], or with modifiers as formamide [17], citric acid [11] and PVA [18]. Our previous studies have shown that polyols are efficient modifiers for the silica matrix, leading to obtaining homogenous magnetic ferrite/silica nanocomposites [19]. The polyols generate hybrid gels by chemical bonding of C–OH groups through condensation with the Si–OH groups from the siloxane network, affecting the final silica matrix structure and morphology [19]. Furthermore, due to their interaction with the metal nitrates, when M(II) and M(III) carboxylates form as precursors of ferrite nanoparticles, the polyols also have an influence on the formation of ferrite nanoparticles.

The present work reports on the influence of different polyols (polyvinyl alcohol – PVA and 1,4-butanediol – BD) on the formation of nickel ferrite nanocrystals embedded in the silica matrix. A complete structural and morphological characterization of the obtained nanocomposites was performed and the results are also presented.

2. Experimental

2.1. Materials and methods

Tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$, 99.5%), 1,4-butanediol (BD, $C_4H_{10}O_2$, 99.5%), polyvinyl alcohol (PVA, $[CH_2CH(OH)]_n$, with an average molecular weight of 60,000 g/mol and hydrolysis degree of 98%), nonahydrate iron (III) nitrate ($Fe(NO_3)_3 \cdot 9H_2O$, $>99\%$), hexahydrate nickel(II) nitrate ($Ni(NO_3)_2 \cdot 6H_2O$, $>99\%$) and absolute ethanol were supplied by Merck and used without further purification.

The sols (i) TEOS–PVA–$Ni(NO_3)_2$–$Fe(NO_3)_3$ (sample NiFePVSi), (ii) TEOS–BD–$Ni(NO_3)_2$–$Fe(NO_3)_3$ (sample NiFeBDSi), and (iii) TEOS–PVA–BD–$Ni(NO_3)_2$–$Fe(NO_3)_3$ (sample NiFePVBDSi) were synthesized using the molar ratios TEOS:PVA$=$1:1, TEOS:BD$=$1:1 and TEOS:PVA:PD$=$1:1:1, respectively. The molar ratio TEOS:$Ni(NO_3)_2$:$Fe(NO_3)_3$ corresponds to a final content of 30% $NiFe_2O_4$ in SiO_2. In order to evidence the influence of the polyols, the sol TEOS–$Ni(NO_3)_2$–$Fe(NO_3)_3$ (sample NiFeSi) was prepared in the same conditions but without using a polyol.

In a typical synthesis, the necessary amount of TEOS was prehydrolyzed by adding double distilled water in a molar ratio TEOS:$H_2O$$=$1:4, under magnetic stirring and addition of ethanol until the solution becomes clear. Separately, the necessary amounts of metal nitrates were dissolved in the necessary volume of polyol (in case of PVA, in 4% PVA aqueous solution); the obtained solution was added very slowly, under intense magnetic stirring and heating at 50 °C, until a clear solution was obtained. In the case of PVA, because to the high content of H_2O, supplementary quantities of ethanol were slowly and carefully added in drops after PVA addition, until the solution became clear.

The four sols were left for gelation at room temperature. The obtained gels were dried at 50 °C, and further subjected to a controlled thermal treatment: (1) heating at 150 °C (when ferrite precursors form inside the gels); (2) thermal decomposition at

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