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Study on the influence of annealing temperature and ferrite content on the structural and magnetic properties of $x(NiFe_2O_4)/(100-x)SiO_2$ nanocomposites

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ABSTRACT

Magnetic nanocomposites of nickel ferrite nanoparticles uniformly dispersed in the silica matrix have been synthesized successfully by a sol–gel process using tetraethylorthosilicate (TEOS) and metallic nitrates as precursors. In addition, the influence of the annealing temperatures, varying from 400 to 900 °C, and $NiFe_2O_4$ contents, $x(NiFe_2O_4)/(100-x)SiO_2$ ($10 \le x \le 60$ wt.%), on the structural and magnetic properties of the nanocomposite samples have been investigated. The studies carried out using XRD, FT-IR, TEM, STA (TG–DTG–DTA) and VSM techniques. The results indicated that the structural and magnetic properties of the samples showed great dependence on the variation of the particle size caused by the annealing temperature and $NiFe_2O_4$ content. The crystallization, saturation magnetization M_s and remenant magnetization M_r increased as the annealing temperature and $NiFe_2O_4$ content increase. But the variation of coercivity H_c was not in accordance with that of M_s and M_r, indicating that H_c is not determined only by the size of $NiFe_2O_4$ nanoparticles. TEM images showed spherical nanoparticles homogeneously dispersed in the silica network and were uniform in both morphology and particle size distribution with sizes of 10–15 nm. The results showed that the well-established silica network provided nucleation locations for $NiFe_2O_4$ nanoparticles to confinement the coarsening and aggregation of nanoparticles. The synthesized nanocomposites with adjustable particle sizes and controllable magnetic properties make the applicability of nickel ferrite even more versatile.

1. Introduction

Magnetic nanocomposites consisting of nanometric spinel ferrites embedded in an insulating matrix such as silica have attracted much attention in recent years due to their new magnetic properties [1] and their applicability in a variety of areas such as magnetic recording media, high-density information storage, ferrofluid technology, bioprocessing, magnetic drug delivery, catalysts, magnetic resonance imaging enhancement, gas sensors and magneto-optical devices [2–9].

Among spinel ferrites, nickel ferrite is one of the most versatile and technologically important ferrite materials because of its magnetic properties, high electrochemical stability, catalytic behavior, abundance in nature, low conductivity and thus lower eddy current losses [10]. In addition, $NiFe_2O_4$ is the most suitable material for device applications in the upper microwave and lower millimeter wave ranges. Apart from its technological importance in the electronic and magnetic industries, $NiFe_2O_4$ has been used as a highly reproducible gas [9,11] and humidity [12] sensor material.

Various synthetic routes have been reported in the literature for the preparation of nanoscale ferrites such as ceramic method [13], sol–gel [14], co-precipitation [15], solvent evaporation [16], hydrothermal [17], combustion [18], microemulsion [19] and citrate methods [20]. In the previous report, spinel cobalt ferrite nanoparticles have been synthesized by the polymeric precursor method [21]. While the nanoparticles obtained usually have a strong tendency to aggregate; this makes it very difficult to exploit their unique physical properties [22]. The preparation of magnetic nanocomposites through the dispersion of ferrite nanoparticles in a suitable matrix represents a route to obtain very fine nanoparticles by reducing particle agglomeration [23] leading to a narrow distribution of the dimensions. Also this technique allows one to stabilize the particles and study their formation reactions.

The interest in the preparation of magnetic nanocomposites has increased in the last years due to the properties presented by these materials, which are dependent on particle sizes, component ratio and distribution in the matrix. Magnetic nanocomposites showed considerable differences in the magnetic properties when compared with their equivalent pure and bulk materials. Different nanoparticles such as Fe [24], Ni [25], Fe_2O_3 [26], and NiZn-ferrite [27] dispersed in the silica matrix with applications in areas such as catalysis, sensors and electronic devices have been studied. Magnetic nanocomposites of nickel ferrite nanoparticles dispersed in

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the silica matrix have been studied [28–35] revealing behavior different from that of bulk systems and as a model for the study of small particles.

Among various synthetic routes, the sol–gel process offers some advantages in making inorganic composite materials containing highly dispersed magnetic particles. The process facilitates a good and homogeneous dispersion of the particles into the inorganic matrix. The porous nature of the sol–gel derived amorphous silica matrix is an excellent host for supporting different types of guest nanoparticles which provides nucleation sites for magnetic nanoparticles and minimizes the aggregation imposing an upper limit to the size of the particles. This method makes possible the introduction of various concentrations of different components in a matrix with molecular homogeneity, which can be vitreous or crystalline, either porous or densified.

In this paper, the influence of annealing temperature and $NiFe_2O_4$ content on the structural and magnetic properties of $x(NiFe_2O_4)/(100-x)SiO_2$ (x = 10, 20, 30, 40, 50, 60 wt.%) nanocomposites prepared by sol–gel method has been reported aiming at tuning the magnetic properties of $NiFe_2O_4$ nanoparticles dispersed in a silica matrix and greatly expanding the range of applications by adjusting the annealing temperature and $NiFe_2O_4$ content. Also, the alcogel precursors with different weight percents of components have been investigated. Therefore, special attention is given to the correlation between the structural and magnetic properties of $NiFe_2O_4$ nanoparticles embedded in a silica matrix, for different annealing temperatures and component ratios.

2. Experimental

All the chemicals were of analytical grade and used without any further purification. Nanocomposites of nickel ferrite dispersed in a silica matrix were prepared by sol–gel process using tetraethylorthosilicate (TEOS) as a precursor of silica and metallic nitrates as precursors of the ferrite. The TEOS:EtOH:H_2O and Fe:Ni molar ratios were controlled at 1:4:8 and 2:1, respectively. The weight ratios of the nanocomposites were $x(NiFe_2O_4)/(100-x)SiO_2$ (x = 10, 20, 30, 40, 50, 60 wt.%). The sols were prepared by dissolving $Fe(NO_3)_3{\cdot}9H_2O$ and $Ni(NO_3)_2{\cdot}6H_2O$ in deionized water, followed by the addition of the alcoholic solution of TEOS. After vigorous stirring for 1 h, the sols were allowed to gel at room temperature for 4 days in partially closed glass vessels. The obtained alcogels G1–G6 matching to x = 10–60 wt.%, respectively were put into an oven for further drying at 110 °C for 24 h to obtain xerogels. The xerogels were annealed at different temperatures varying from 400 to 900 °C for 2 h with a heating rate of 10 °C/min in ambient atmosphere.

X-ray diffraction (XRD) patterns were collected using a Philips PNA-analytical diffractometer with Cu Kα radiation. FT-IR spectra (500–4000 cm^{-1}) were recorded on a PerkinElmer Spectrum One spectrophotometer with KBr pellets. Thermal analyses (TG–DTG–DTA) including the thermogravimetery (TG), derivative thermogravimetery (DTG) and differential thermal analysis (DTA) were carried out using a PerkinElmer simultaneous thermal analyzer (STA Pyris Diamond Model) with the heating rate of 5 °C/min in flowing air. TEM images were recorded on a Philips CM 200 FEG transmission electron microscope. Selected area electron diffraction (SAED) patterns were obtained on the TEM to ascertain the crystallinity. Magnetic measurements were carried out at room temperature using a vibrating sample magnetometer (VSM).

3. Results and discussion

3.1. X-ray diffraction (XRD) analysis

The XRD patterns of the 30 wt.% $NiFe_2O_4/SiO_2$ samples annealed at different temperatures varying from 400 to 900 °C were shown in Fig. 1 to investigate the influence of the annealing temperature on the structure. The weak diffraction peaks assigned to $NiFe_2O_4$ appeared at 400 °C suggesting that the particles of $NiFe_2O_4$ had been nucleated in the silica matrix.

Our results showed that with increasing the annealing temperature, the intensity of peaks increases and the diffraction peaks become sharper and narrower. This indicates the enhancement of the crystallinity which originated from the increment of the crystalline volume ratio due to the size enlargement of the nuclei

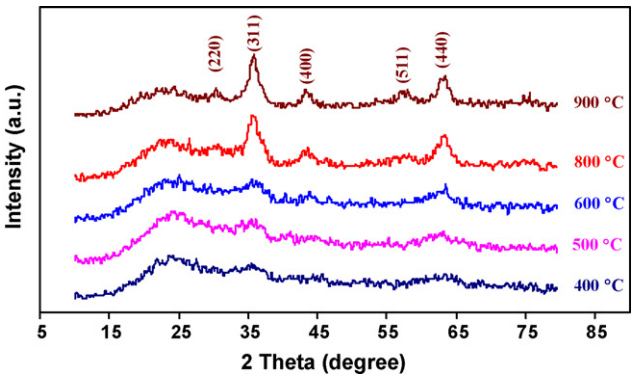

Fig. 1. XRD patterns of the 30 wt.% $NiFe_2O_4/SiO_2$ samples annealed at different temperatures varying from 400 to 900 °C.

[36]. The full-width at half maximum (FWHM) of the diffraction peaks decreases with increasing annealing temperature discloses that the average crystallite size is becoming bigger correspondingly. The very broad peak at 2θ of around 23° in XRD patterns of all samples was attributed to the characteristic diffraction peak of the amorphous SiO_2 matrix. All of the diffraction peaks confirmed the formation of the pure single-phase nickel ferrite with the face-centered cubic spinel phase and $Fd3m$ (2 2 7) space group. No diffraction peaks of impurities were observed in the patterns. It showed that Ni-ferrites synthesized successfully under current mild experimental conditions.

To study the influence of the $NiFe_2O_4$ content on the structure, the XRD analyses were done on the $x(NiFe_2O_4)/(100-x)SiO_2$ (x = 10, 20, 30, 40, 50, 60 wt.%) nanocomposites annealed at 800 °C as shown in Fig. 2. As the $NiFe_2O_4$ content increases from 10 to 60 wt.%, the characteristic diffraction peaks of $NiFe_2O_4$ gradually grow and become stronger in intensity but narrower in FWHM, which indicates that the crystallite size of $NiFe_2O_4$ increases with increasing the $NiFe_2O_4$ content. When the $NiFe_2O_4$ content is up to 40 wt.%, the evidence of the amorphous silica almost disappears. The position of all peaks coincided with the characteristics peaks of the standard $NiFe_2O_4$ phase.

The increase of the annealing temperature and the Ni-ferrite content results in sharper peaks with the increased intensity and higher crystallization without changes in the obtained phases. The influence of the annealing temperature and Ni-ferrite content on the crystallite sizes of the nanocomposite samples were shown in Tables 1 and 2, respectively.

The crystallite size of all samples prepared at different annealing temperatures and Ni-ferrite contents estimated from XRD peak

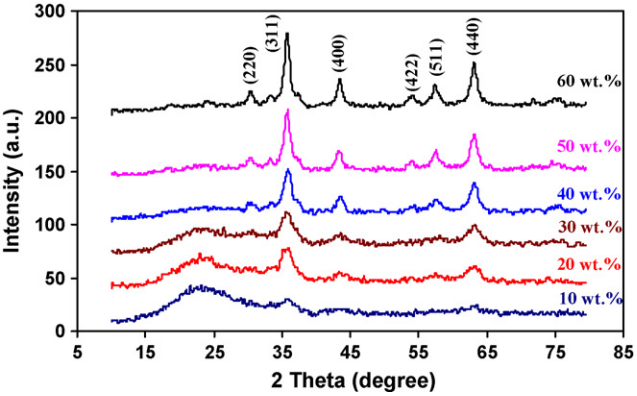

Fig. 2. XRD patterns of the $x(NiFe_2O_4)/(100-x)SiO_2$ (x = 10, 20, 30, 40, 50, 60 wt.%) nanocomposites annealed at 800 °C.