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Nanostructural, magnetic and electrical properties of Ag doped Mn-ferrite nanoparticles

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ABSTRACT

Nano-crystalline $MnFe_{2-x}Ag_xO_4$ ($x = 0$, 0.1, 0.2, 0.3 and 0.6) samples with average grain size of 4–7 nm were synthesized by a simple method based on decomposition of metal nitrates in presence of citric acid. The samples were characterized by different structural, magnetic and electrical measurements. Rietveld refinement of X-ray diffraction data confirmed cubic spinel structure of the samples. Results show that Ag doping decreases the crystallite size, magnetization and coercivity of nanoparticles. By increasing the Ag content in the samples the saturation magnetization shows interesting temperature dependent behavior. It was realized that magnetization of smaller particles show higher sensitivity to temperature variations than larger particles. DC electrical resistivity measurements in the temperature range of 300–650 K show that the resistivity first increases and then decreases by increasing the Ag content in the samples. Curie temperature (T_c) and polaron activation energy in ferromagnetic and paramagnetic regions were estimated by using resistivity curves.

1. Introduction

Spinel ferrites are very important magnetic materials because of their potential applications in storage media, ferro-fluids, microwave devises and recently in medicine [1–4]. Also due to the very low electrical conductivity and high saturation magnetization, ferrites are good candidates for magnetic devices and magnetic cores. Ferrites nanoparticles have been subjects of intensive study because of their novel properties in comparison with corresponding bulk ferrites. Generally, it is accepted that nano-sized magnetic materials show different properties compared with bulk materials [5,6]. In the core–shell model, it is assumed that there is a core with a regular atomic arrangement which form the crystalline structure. On the other hand the shell of a nanoparticle consists of the structural deficiencies and broken bands. Crystalline deficiencies lead to amorphous atomic arrangement and formation of grain boundaries. Grain boundaries play a significant role in different properties of ferrites. The electrical transport in most of materials is affected by the grain boundaries [7]. For aggregated nanoparticles in which the particles are in direct contact, the surface of nanoparticles plays grain boundary role between neighbor particles. Therefore any variation in surface structure can change the electrical properties of nanoparticles.

Mn-ferrite ($MnFe_2O_4$) is a well-known spinel ferrite which has very interesting features such as simple preparation methods, high saturation magnetization value (M_s ~ 83 emu/g at 300 K), high chemical stability and low Curie temperature (T_c ~ 580 K) among spinel ferrites [8]. In most cases, cation distribution in the stoichiometric Mn-ferrite is demonstrated as: $(Mn^{2+}_{0.8}Fe^{3+}_{0.2})_A(Mn^{2+}_{0.2}Fe^{3+}_{1.8})_B$ where A and B denote the tetrahedral and octahedral sites in spinel structure, respectively. However Kang et al. [9] showed that it can be described by a mixed valence state as: $(Mn^{2+}_{0.8}Fe^{3+}_{0.2})_A(Mn^{2+}_{0.2}Fe^{3+}_{1.6}Fe^{2+}_{0.2})_B$. This representation of cation distribution could well justify the observed electrical transport in this material. Based on the Verwey model, the observed electrical conductivity in spinel ferrites is described by electron transition between Fe^{2+} and Fe^{3+} in lattice structure [10]. In the other words the simultaneous presence of Fe^{2+} and Fe^{3+} ions is responsible for electrical conductivity in ferrites.

There are various studies on the effect of Al, Mn, Ni, Co, In, Cr, V, etc. substitution in A or B sites of spinel ferrites [11–15]. These substitutions change the cation distribution and lead to noticeable effects on magnetic, electrical and structural properties of ferrite samples.

In this study the effect of Ag doping on structural, magnetic and DC electrical properties of $MnFe_{2-x}Ag_xO_4$ ($x = 0$, 0.1, 0.2, 0.3 and 0.6) nanoparticles has been reported. This study includes of X-ray

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diffraction, Fourier transform infrared spectra, Field emission scanning electron and Transmission electron microscopes images, Energy-dispersive X-ray spectra, Vibrating sample magnetometer and Direct current electrical measurements.

2. Experimental details

The $MnFe_{2-x}Ag_xO_4$ (where $x = 0$, 0.1, 0.2, 0.3 and 0.6) nanoparticles were prepared with a simple synthesis method, as described elsewhere [16]. In this method, manganese nitrate ($Mn(NO_3)_2.4H_2O$, Merk, 99%), iron nitrate ($Fe(NO_3)_3.9H_2O$, Merk, 99%), silver nitrate ($Ag(NO_3)$, Merk, 99.8%) and citric acid ($C_6H_6O_7$, Merk, 99.5%) were mixed by an equal molar ratio of total metal nitrates to citric acid. The powders were ball milled in a planetary ball mill for 1 h. The ball milled powders were annealed in the ambient air at 350 °C for 1 h. The samples were named Ag0, Ag1, Ag2, Ag3 and Ag6 for Ag level from 0.0 to 0.6 respectively. X-ray diffraction (XRD) patterns of the samples were taken on a Philips X'Pert Pro MPD X-ray diffractometer with Cu-Kα radiation ($\lambda = 0.154$ nm). Fourier transform infrared (FTIR) spectra of samples were recorded using a JASCO 680 plus spectrometer within the range of 400–4000 cm^{-1}. Nanostructural, morphology and elemental composition of the samples were studied using a Hitachi Model S-4160 field emission scanning electron microscope (FESEM) equipped with energy-dispersive X-ray (EDX) spectroscopy and a transmission electron microscope (Philips CM120 TEM). Magnetization curves versus magnetic field were measured at different temperatures using a vibrating sample magnetometer (VSM). In order to investigate the electrical properties of the samples, DC resistivity measurements were carried out in the temperature range of 300–650 K by using the conventional four-probe method.

3. Results and discussion

Fig. 1 shows rietveld refinement of XRD data of the samples. Red hollow spheres show experimental data and the black solid lines are calculated values by using rietveld method. As it can be seen from Fig. 1 there is a good agreement between experimental and calculated data which confirms formation of crystalline spinel phase in the samples. Also there is no trace of secondary phases in XRD patterns of Ag0–Ag3 samples. The metallic silver phase is seen in the XRD pattern of the sample Ag6 which is also clear in rietveld pattern of this sample. Different reports confirm the presence of metallic silver or hematite impurity as secondary phase for high doping level of Ag in spinel ferrites structure [17,18]. Because of the larger atomic radius of Ag^{1+} (1.26 Å) compared to Fe^{3+} (0.64 Å) and Mn^{2+} (0.83 Å) ions, substitution of Ag in Fe or Mn sites could causes crystalline deficiencies in the spinel structure and form the metallic Ag in the shell of nanoparticles in which the particle has no regular arrangement of atoms.

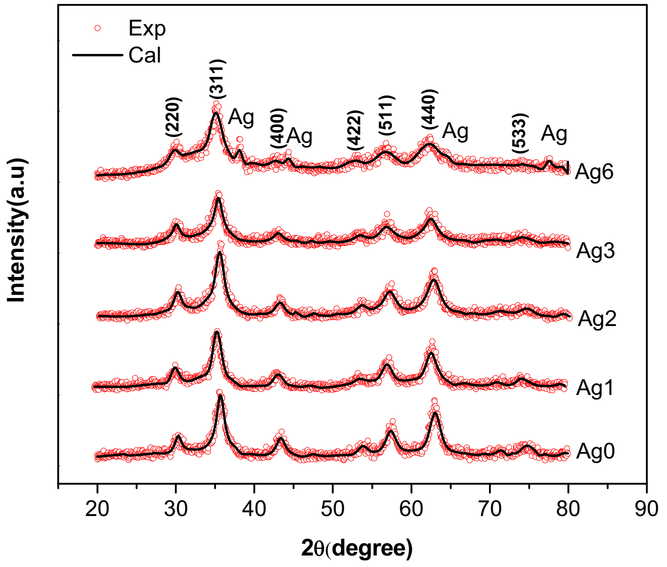

Fig. 1. Rietveld refinement of X-ray diffraction data. Red spheres are experimental and the solid lines are calculated value. XRD pattern and shift in peaks position were reported in ref.[16]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Average crystallite size (D) of the samples was calculated according to the Debye-Scherrer equation [16,19]. It can be seen from Fig. 2 that the estimated D value decreases with increasing the Ag doping level. This result can be attributed to low tendency of Ag for entering into spinel structure. In fact, it seems that Ag^{1+} ions create crystalline deficiencies in the shell of nanoparticles and then prevent the growth of crystallite size.

In order to further study of the structural properties of samples, lattice constant (a), X-ray density (ρ_x) and porosity (P) of samples were calculated using the following formulas [16,20]:

$$\frac{1}{d^2}=\frac{h^2+k^2+l^2}{a^2} \tag{1}$$

$$\rho_x=\frac{8M}{N_A a^3} \tag{2}$$

$$P\left(\%\right)=\frac{\rho_x-\rho_m}{\rho_x} \tag{3}$$

Where M is molecular weight of sample, N_A is the Avogadro's constant and ρ_m is mass density of samples. The obtained results are shown in Table 1. By increasing the Ag content, the spacing between the planes (d) in the atomic lattice increases and consequently leads to increase in lattice constant value (Fig. 2). Also because of larger atomic weight of Ag (107.87) than that of Fe (55.85) increase of M and ρ_x by increasing the Ag content is an acceptable result. However, as it can be seen from Table 1 the porosity of samples increases with increasing the Ag doping level. This result can be justified by size mismatch between Ag^{1+} (1.26 Å) and Fe^{3+} (0.64 Å) ions which can creates structural deficiencies in the doped samples.

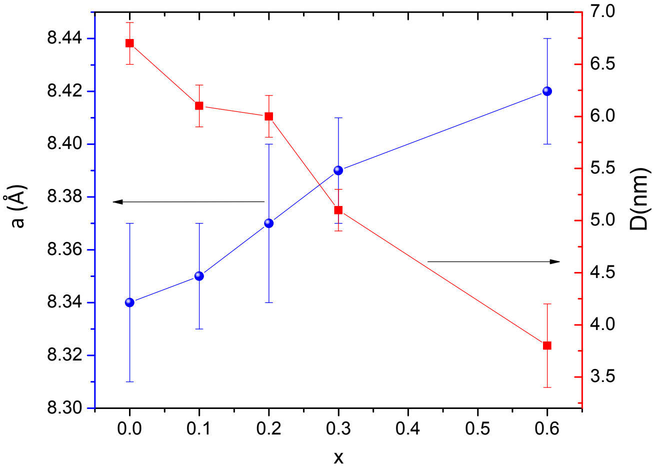

Fig. 2. Crystallite size (D) and lattice parameter (a) versus Ag doping level (x).