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Characterization, structural and magnetic properties of the as-prepared Mg-substituted Cu-nanoferrites

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ABSTRACT

The as-prepared $Cu_{1-x}Mg_xFe_2O_4$ nanoferrites, $0 \leqslant x \leqslant 1$, were synthesized using the co-precipitation method. The samples were characterized using the X-ray diffraction, transmission electron microscopy, infrared (IR) and Mössbauer spectroscopy and vibrating sample magnetometer. This study proved that the samples have single-phase cubic spinel structure, nanometric size and superparamagnetic behavior. The nanoparticle and crystallite size (R) showed a dependence on the Mg ion content x. The Mössbauer spectra were analyzed and assigned to two magnetic subpatterns and/or two quadrupole doublets due to Fe ions among the tetrahedral A-sites and octahedral B-sites. Six IR absorption bands were observed and assigned to the corresponding vibration modes. The saturation magnetization showed decrease against x and proved dependence on R. The lattice constant, hopping lengths, strain, site characteristic bands and B-site force constant showed x dependence, whereas oxygen parameter and A-site force constant did not. The site ionic radii and edges, density, porosity, Debye temperature, stiffness constant, hyperfine interaction and magnetic parameters were deduced and discussed as functions of x and the cation distributions were estimated.

1. Introduction

Nanoferrites are very interesting materials and used in many applications of technical, drug and medical fields [1]. The physical properties of nanoferrites depend on their chemical composition, electronic structure of the magnetic ions, preparation conditions and crystal structure of the lattice [2]. Spinel nanoparticles are of much interest in fundamental science for understanding relationship between their physical properties and their crystal chemistry and structure. The nanoparticles have novel and/or improved properties in comparison to the bulk materials which arise from their reduced size. This makes great interest to study different properties of normal and mixed nanoferrite systems. Many techniques are being used to prepare spinel nanomaterials including rapid solidification, sputtering, gas condensation, sol–gel method, crystallization of amorphous phases, electrodeposition, mechanical attrition-ball milling, sonochemical reactions, combustion, hydrothermal route and wet-chemical methods like coprecipitation [1,2]. The chemical co-precipitation method has arisen as a popular process to synthesize spinel nanoparticles because it seems to be the most convenient one for producing good chemical homogeneity and small grain sizes. On the other hand, it is easy to carry out and allows a good governing of the shape and size distribution of the nanoparticle due to mixing the components at a molecular level during synthesis [1,2].

A number of investigations have been done in studying the magnesium and cupper nanoferrites [3–6] were prepared by the co-precipitation method. These studies proved that the samples have single-phase cubic spinel structure. The lattice constant was x dependent and the crystallite and particle size were affected by the additional factor x and lied in the nanometric range. The saturation magnetization, magneton number and other magnetic properties were strongly dependent on x. It is well known that the Cu- and Mg-nanoferrites are partially inverse spinels and their degree of inversion is sensitive to the sample microstructure and preparation method. The Mg ions play a large role in governing the increase of growing planes of nanocrystals, where the nanoparticle size plays very important role in controlling magnetic properties [5]. The as-prepared magnesium nanoparticles present unusual magnetic properties like superparamagnetism, which lead to the suppression of long range magnetic ordering and quenching of magnetic moments [5]. The existence of high concentration of Cu ions leads to increasing the tetragonality of the sample which become more pronounce under higher thermal treatments. Therefore, this investigation is concerned on studying the effect

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of substituting Mg ions instead of Cu ions in the as-prepared $Cu_{1-x}Mg_xFe_2O_4$ nanoferrites ($0 \leqslant x \leqslant 1$) by the co-precipitation method on their structural, magnetic, electrical and other physical properties. The techniques used are X-ray diffraction, Transmission electron microscopy, infrared and Mössbauer spectroscopy and vibrating sample magnetometery.

2. Experimental

2.1. Sample preparation

The samples were prepared by using the wet-chemical co-precipitation method as reported previously [6,7], according to the equation:

$$(1-x)CuCl_2 \cdot 2H_2O + x(MgCl_2 \cdot 6H_2O) + 2FeCl_3 + 8NaOH \rightarrow 8NaCl + 6H_2O + Cu_{1-x}Mg_xFe_2O_4$$

where x = 0, 0.2, 0.4, 0.6, 0.8 and 1. Desired stoichiometric proportion amounts of high purity $FeCl_3$, $CuCl_2{\cdot}2H_2O$ and $MgCl_2{\cdot}6H_2O$ salts were dissolved in 0.1 M aqueous solutions and mixed with the starting materials, in lower temperature, by magnetic stirrer. NaOH solution, put in ice bath, was added to the salt solution drop-wise to control the PH value to reach 13. The solution was heated to 90 °C for 2 h till the precipitation occurs. The precipitations were washed many times in deionized water to remove the unwanted salt residuals, dried at room temperature and ground in an agate mortar to fine powder.

2.2. Measurements

The X-ray diffraction patterns were recorded for all samples using X-ray diffractometer of the type Shimadzu 7000 Maxima and Cu Kα1 radiation with λ = 1.540568 Å. The interplaner distance and lattice constant were obtained using Bragg's law [6–8]. The bulk and theoretical (X-ray) densities, sample porosity, hopping length at the A- and B-sites, oxygen positional parameter and other lattice parameters were calculated as explained early [6–8]. The crystallite size (R) of the samples was determined using the prominent diffraction peak (3 1 1) and Scherer's equation:

$$R = 0.9\lambda/\beta_{1/2}\cos\theta$$

where $\beta_{1/2}$ is the full width at half maximum of the peak (3 1 1). $\beta_{1/2}$ is obtained from the relation $\beta_{1/2} = (B^2 - b^2)^{1/2}$, where B is the measured line width and b the instrumental broadening. The mean ionic radius of the A-and B-sublattices (R_A and R_B) was calculated using the cationic distribution and equations [6–8]:

$$R_A = y r_{Cu} + z r_{Mg} + (1-z-y) r_{Fe}$$

$$R_B = (1-x-y) r_{Cu} + (x-z) r_{Mg} + (1+z+y) r_{Fe}$$

where r is the ionic radius, y is the number of Cu^{+2} ions and z is the number of Mg^{+2} ions at the A-sites.

Transmission electron microscope of the kind JEOL.JEM-100SX was used for taking the TEM images. The infrared spectra were recorded by using Bruker Tensor 27 FT-IR spectrometer in the range 200–2000 cm^{-1}. The force constant F_C was calculated using the relation [6,9,10]:

$$F_C = 4\pi^2 C^2 v^2 \mu$$

where C is the light velocity, v is the sublattice frequency and μ is the reduced mass of Fe and O ions (2.061×10^{-23} gm). A constant acceleration computerized Mössbauer spectrometer and 25 mCi ^{57}Fe radioactive source diffused in rhodium matrix were used. Metallic iron foil was used for calibration. The taken Mössbauer spectra at room temperature were fitted using the least squares fit computer program. The magnetic hysteresis loops were recorded at room temperature by using vibrating sample magnetometer, LDJ Electronic Inc. Troy MI. A maximum applied field up to 20 kG was used for reaching the saturation magnetization of the samples.

3. Results and discussion

3.1. X-ray diffraction (XRD) analysis

The XRD patterns recorded for the as–prepared $Cu_{1-x}Mg_xFe_2O_4$ nanoferrites, x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1, are depicted in Fig. 1. The observed diffraction peaks prove single-phase cubic spinel structure of these nanoparticles. Increasing the broadness of diffraction peaks as Mg ion content x increases points to decreasing the particle size and increasing the fine nature of nanoparticles. For deducing the peak position and interplaner distance a fitting computer program was used which indexed to the published JCPDS cards. The obtained values of lattice constant a lie in the range of 8.341–8.437 Å which agree well with the literature values [3–5]. Fig. 2 shows the variation of a against x. It is shown that a decreases with x which is ascribed to the substitution of smaller ionic radius Mg^{2+} (0.72 Å) for Cu^{2+} (0.78 Å). The calculated values of crystallite size (R) range 3.03–23.49 nm which agree with the reported in the literature [11,12]. The relation between R and x is seen in Fig. 3. It is seen that R decreases sharply with x which may be due to the substitution process and migration of the cations between the crystal sublattices. The decrease in R proves that the addition of the Mg ions into the crystal lattice leads to a sharp reduction of the crystallite size and increasing tendency of the materials to be amorphous.

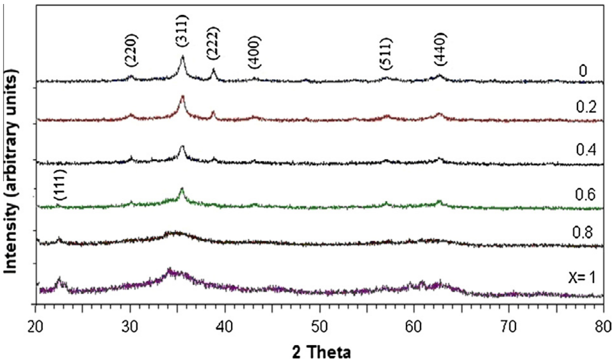

Fig. 1. XRD patterns of the as-prepared $Cu_{1-x}Mg_xFe_2O_4$ nanoferrites.

The calculated values of the lattice parameters [6,8]; L_A and L_B are the hopping lengths, u the oxygen positional parameter, d_{AO} and d_{BO} the tetrahedral and octahedral bond lengths, d_{AE} the tetrahedral edge and d_{BE} and d_{BEU} the octahedral shared and unshared edges, respectively, are listed in Table 1. It is obvious that L_A and L_B reflect the same behavior of a [9–11]. The trend of R_A, d_{AO}, d_{AE}, d_{BO}, d_{BE} and d_{BEU} values increases against x, whereas that of R_B values decreases. These variations of the lattice parameters may be assigned to the substitution process and motion of cations between the crystal sublattices by substitution process. The values of u lie around 0.398 and are higher than the standard value (0.375). That points to a trigonal distortion of the B-site oxygen coordination, which may result from the oxygen dissociation through the samples during their preparation.

Fig. 4 displays variation of the theoretical (X-ray) density (D_x), bulk density (D) and porosity (P) against x. It is displayed that D_x and D decrease against x, while P slowly decreases for $x \leqslant 0.6$ and increases sharply thereafter. The decrease in D_x and D may be due to the substitution of lighter atomic weight Mg ions (24.305) for Cu ions (63.54). The decrease in P may be assigned

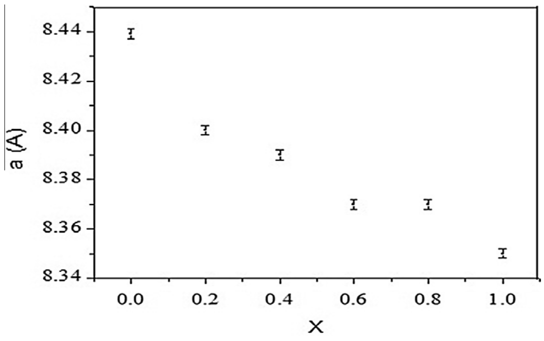

Fig. 2. Variation of lattice constant a against Mg ion content x.