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Role of copper on structural, magnetic and dielectric properties of nickel ferrite nano particles

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ABSTRACT

Copper doped nickel ferrites $Ni_{(1-x)}Cu_xFe_2O_4$ (where $x=0.2$, 0.4, 0.6) nanoparticles are prepared by co-precipitation method and sintered at 600 °C. The XRD study confirms the formation of single-phase cubic spinel Ni–Cu ferrites. The particle size increases with Cu substitution. FT-IR spectra confirm the absorption bands around 554–547 cm^{-1} for the tetrahedral sites and around 448–450 cm^{-1} for the octahedral sites. The inclusion of copper shifts the tetrahedral band to lower values. The saturation magnetization (M_s) and remanent magnetization (M_r) decrease with increase in copper concentration and the coercivity (H_c) is found to increase for all the compositions sintered at 600 °C. The dielectric constant decreases drastically for all the compositions and reaches a constant value. These nanoparticles can be tested for humidity sensing applications.

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1. Introduction

Spinel ferrites and substituted ferrites are found to be very attractive and versatile magnetic materials. Nickel ferrite is the most suitable one in which the magnetic and transport properties are affected by the substituents [1]. The substitution can be divided into the following types: direct replacement of Fe^{3+} on tetrahedral (A) or octahedral (B) sublattice by the substituent ion, with consequential redistribution of Fe^{3+} ions among A− or B− sublattices which lead to the change of ferrimagnetic spin structure. The amount of replaced iron is dictated by the valency of the substituent ions. The extent of iron redistribution depends on the specific nature of the substituting ion.

Diamagnetic substitutions in super and mixed ferrites have received a great deal of attention over the past few years. The substitutions of various magnetic and nonmagnetic ions at different sublattices in ferrite materials have provided interesting magnetic structures and electrical properties. Novel magnetic behavior is observed for the nanosized magnetic particles when compared to that of the bulk.

Many investigators have carried out research work on nickel ferrite containing various cations such as Zn [2–7]. The substitution of Cu brings about a structural phase transition accompanied by a reduction in the crystal symmetry due to cooperative Jahn–Teller effect [8,9], which ultimately results in some interesting electrical and magnetic properties. Hence in the present study, an attempt has been made to study the structural, magnetic and dielectric properties of copper doped nickel ferrite nanoparticles prepared by co-precipitation method.

2. Materials and methods

Copper doped nickel ferrites $Ni_{(1-x)}Cu_xFe_2O_4$ (where $x=0.2$, 0.4, 0.6) are prepared by co-precipitation method. The desired composition is obtained by using stoichiometric amounts of nickel chloride [$Nicl_2 \cdot 6H_2O$], cupric chloride [$CuCl_2 \cdot 2H_2O$] and anhydrous ferric chloride [$FeCl_3$] dissolved in distilled water. The neutralization is carried out with sodium hydroxide solution and pH is maintained at 8. The precipitate is thoroughly washed with distilled water, dried and sintered at 600 °C. These samples are subjected to FT-IR spectral analysis, X-ray diffraction, SEM, EDX, TEM, SAED, VSM and dielectric studies and the results are discussed below.

3. Results and discussion

3.1. FT-IR spectral analysis

FT-IR absorption spectra of nickel–copper ferrites of different

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compositions $Ni_{(1-x)}Cu_xFe_2O_4$ ($x=0.2$, 0.4, 0.6) sintered at 600 °C and recorded in the range 4000–400 cm^{-1} is shown in Fig. 1. It is observed from the spectra that there is a long shoulder around 554–547 cm^{-1} for the tetrahedral site band and also the depth increases as the concentration of copper increases. This may be attributed to the presence of lower ionic states in that site i.e. diffusion of Ni^{2+} [10] and Cu^{2+} by the replacement of Fe^{3+}in the A-site. The octahedral site band appears around 450 cm^{-1}. The spectra also shows a small subsidiary band around 435 cm^{-1} as observed for the pure nickel ferrite. The inclusion of copper shifts the band υ_1 to lower values and small shoulders are observed around 693 $cm^{-1}$and 671 cm^{-1} as reported for pure nickel ferrite. The absorption bands around 3500 cm^{-1} and1600 $cm^{-1}$are assigned to the stretching (υ) vibrations of the free or absorbed water on the surface of nickel–copper ferrite nanoparticles.

3.2. Structural analysis

X-ray diffraction patterns of nickel–copper mixed ferrites of different compositions $Ni_{(1-x)}Cu_xFe_2O_4$ ($x=0.2$, 0.4, 0.6) synthesized at pH equal to 8 and sintered at 600 °C is shown in Fig. 2. The experimentally observed d spacing values and relative intensities of the diffraction peaks are compared and indexed using JCPDS Card no (74-2081) and (34-0425) for nickel and copper ferrites. It is observed from Fig. 2 that the diffraction peaks are sharper and narrower thereby indicating the crystalline nature of the samples. An impurity peak of hematite (α-Fe_2O_3) is observed for the sample $Ni_{0.4}Cu_{0.6}Fe_2O_4$ sintered at 600 °C. The formation of α-Fe_2O_3 has been attributed to preferential loss of one or more of divalent cations during the washing and drying stages [11,12]. The percentage of α-Fe_2O_3 is known to be dependent on pH and the temperature of the solution at the precipitation stage.

The crystallite size of each composition determined by the Debye-Scherrer relation and the lattice parameter calculated from the (311) diffraction peak are listed in Table 1. The crystallite size increases with increase in copper concentration. It can also be observed from table that the increase in the lattice parameter with increasing Cu content is attributed to the greater ionic radius of

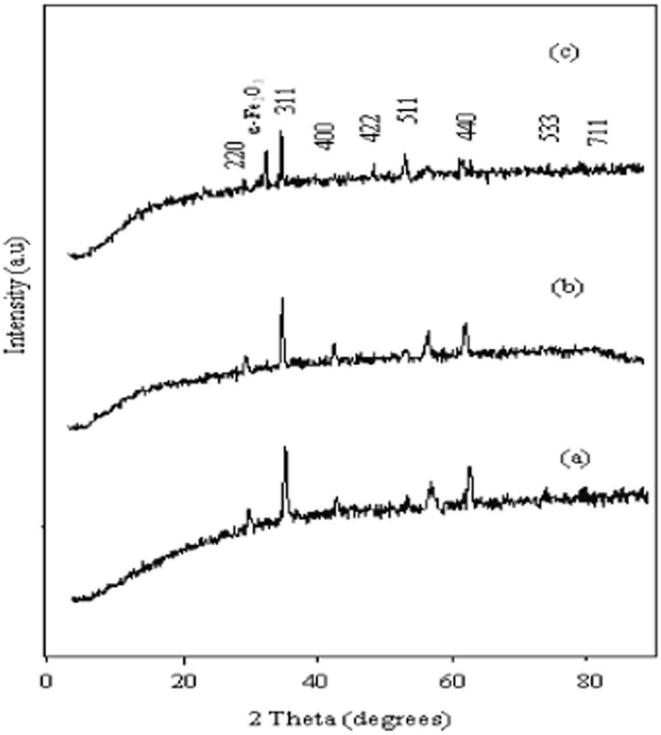

Fig. 2. XRD pattern of $Ni_{(1-x)}Cu_xFe_2O_4$ (a) $x=0.2$ (b) $x=0.4$ (c) $x=0.6$ nanoparticles sintered at 600 °C.

Table 1
Structural parameters of $Ni_{(1-x)}Cu_xFe_2O_4$ ($x=0.2$, 0.4, 0.6) nanoparticles sintered at 600 °C.

Composition	Lattice parameter (a) Å	Crystallite size (D) nm
$Ni_{0.8}Cu_{0.2}Fe_2O_4$	8.298	6
$Ni_{0.6}Cu_{0.4}Fe_2O_4$	8.306	10
$Ni_{0.4}Cu_{0.6}Fe_2O_4$	8.342	12

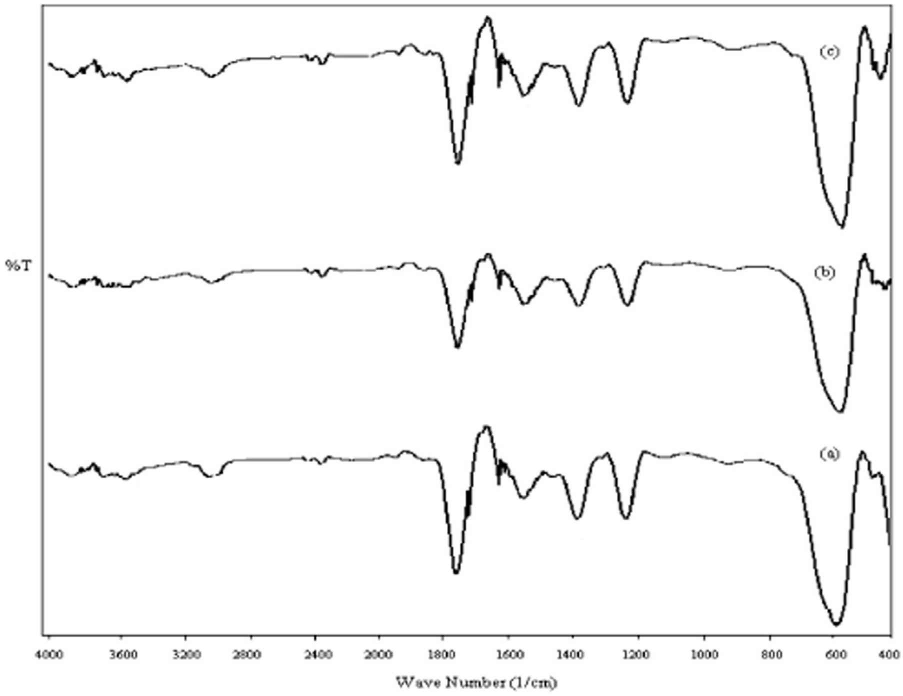

Fig. 1. FT-IR spectra of $Ni_{(1-x)}Cu_xFe_2O_4$ (a) $x=0.2$ (b) $x=0.4$ (c) $x=0.6$ nanoparticles sintered at 600 °C.

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