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Structural, Magnetic, and Optical Properties of Zinc- and Copper-Substituted Nickel Ferrite Nanocrystals

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Abstract Ferrite nanocrystals are an interesting material due to their rich physical properties. Here we add non-magnetic dopants Zn and Cu to nickel ferrite nanocrystals, Ni$_{1-x}$M$_x$Fe$_2$O$_4$ (0 $\leq$ x $\leq$ 1, M = Cu, Zn), and study how relevant properties of the samples are modified accordingly. Basically, these dopings cause a rearrangement of Fe$^{3+}$ ions into the two preexisting octahedral and tetrahedral sites. In fact, this, we show, induces pertinent magnetic properties of the doped samples. In the case of the Cu-doping, the Jahn–Teller effect also emerges, which we identify through the Fourier Transform Infra-Red Spectroscopy of the samples. Moreover, we show an increase in the lattice parameters of the doped samples, as well a superparamagnetic behavior for the doped samples is shown, while the Jahn–Teller effect precludes a similar behavior in the CuFe$_2$O$_4$ nanocrystals. The influences of Zn and Cu substitutions are investigated on the optical properties of nickel ferrite nanocrystals by photoluminescence measurement at room temperature.

Keywords Ferrites · Sol-gel processing · Nanocrystalline magnetic materials · Superparamagnetic · Magnetic anisotropy · Jahn–Teller effect

1 Introduction

Spinel ferrites, with common formula of MFe$_2$O$_4$, have wide technological applications, e.g., in multilayer chip inductor (MLCI), ferrofluids, high-speed digital tape or recording disks, rod antenna, and humidity sensor [1–9]. Ferrite nanocrystals are also of interest in various applications, such as inter-body drug delivery [10–12], bioseparation, and magnetic refrigeration systems [13], in particular due to their specific properties, such as superparamagnetism. In addition, zinc ferrites are used as a catalyst in some chemical processes [14] as well as a photocatalyst [15, 16].

Doping ferrite nanocrystals with various metals, such as chromium, copper, manganese, and zinc are usually used to improve some of their electric or magnetic properties [17–19]. For example, Zn/Ni ferrites have applications as soft magnetic materials with high frequency (due to high electrical resistivity and low eddy-current loss [8]). Along that line, (Cu, Zn)/Ni ferrites offer a further improvement as softer magnetic materials [20].

In this work, we study effects of Zn/Ni and Cu/Ni substitutions on nickel ferrite nanocrystals synthesized through the sol-gel method. Specifically, we characterize structural and magnetic properties of the doped samples at room temperature. We also exhibit the emergence of the Jahn–Teller effect in the case of the CuFe$_2$O$_4$ nanocrystals, and we argue that the modification of the structural properties is in principle due to the occupation of the A sites vs. B sites. In this exhaustive characterization, various techniques are employed such as X-ray diffraction (refined with the Rietveld
method with the MAUD software), Field-Emission Scanning Electron Microscope (FE-SEM), Transmission Electron Microscope (TEM), Fourier Transform Infra-Red (FT-IR) spectroscopy, Vibrating Sample Magnetometer (VSM), and Photoluminescence (PL), and UV-Vis spectrometer at room temperature. We thus compare the effect of dopings not only regarding structural and magnetic properties, but also in the sense of optical properties. In addition, here the Jahn–Teller effect is studied through the investigation of the structural and magnetic properties.

2 Experimental

2.1 Preparation Method

Several chemical methods are used for the synthesis of ferrite nanocrystals [21] that the sol-gel method is widely used in synthesis of ferrite nanocrystals because of its high reaction rate, low preparation temperature, and production of small particles. Hence, in our experiment, magnetic nanocrystalline Ni$_{1-x}$Zn$_{x}$Fe$_2$O$_4$ with $x = 0$, 0.3, 0.5, 0.7, 1 and Ni$_{1-x}$Cu$_x$Fe$_2$O$_4$ with $x = 0$, 0.5, 1 were synthesized by this method. Citric acid C$_6$H$_8$O$_7$, ferric nitrate Fe(NO$_3$)$_3$.9H$_2$O (98 %), nickel nitrate Ni(NO$_3$)$_2$.6H$_2$O (99 %), zinc nitrate Zn(NO$_3$)$_2$.6H$_2$O (99 %) and copper nitrate Cu(NO$_3$)$_2$.3H$_2$O (99 %) were produced by Merck company and were used as raw materials. The stoichiometric amount of nitrates and acid citric were dissolved separately in deionized water to make 0.5 M solutions. The mole ratio of metal nitrates to citric acid was taken as 1:1. We adjusted the pH of our medium to 1 by adding appropriate ratio of metal nitrates to citric acid. Next, the sol was heated continuously at 70 °C, and was then ground into powder. To obtain various Cu$_{1-x}$ and Zn$_{1-x}$ substitutions, we calcined the powder at 300–600 °C for 4 h.

2.2 Characterization

The X-ray diffraction patterns (XRD) of the synthesized nanocrystals were obtained using a Philips® CM30 (250kV) Transmission Electron Microscope. Photoluminescence (PL) measurement was performed by a VARIAN® CARY ECLIPSE spectrometer (using a diode laser with the wavelength of 430 nm). The optical absorption spectra were recorded by a Perkin-Elmer® Lambda35 UV-Vis spectrometer. The magnetic properties of the samples were measured by Meghnatis Daghigh Kavir Co.© Vibrating Sample Magnetometer (VSM) at room temperature. Note that during such measurements the maximum applied magnetic field was 9 kOe.

3 Results and Discussion

3.1 Structural Studies

The X-ray diffraction patterns of the synthesized ferrite nanocrystals have been shown in Figs. 1 and 2. The existence of the (220), (311), (400), (422), (511), and (440) major lattice planes in the XRD patterns confirms the formation of spinel cubic structure with the Fd$ar{3}$m space group, which is consistent with the powder diffraction file of JCPDS (10-0325 for trevorite (NiFe$_2$O$_4$), 08-0234 for nickel zinc iron oxide (Ni/Zn ferrite), 22-1012 for franklinite (ZnFe$_2$O$_4$), and 25-0283 for cuprospinel (CuFe$_2$O$_4$). Also the presence of the (111), (222), (331), (533), (622), (444), (642), and (731) minor lattice planes in the XRD patterns agrees well with the powder diffraction of spinel cubic JCPDS file. All samples are considered to be single-phase spinel structure. In addition, as Fig. 2 shows, the XRD patterns of the Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$ and CuFe$_2$O$_4$ nanocrystals confirm that almost all Cu atoms have been placed in the cubic spinel structure. However, note that in some previous studies, there are reports of excess phases, e.g., the CuO phase [22] or tetrahedral CuFe$_2$O$_4$ phase [23]. Specifically, it has been reported in Ref. [22] that both cubic spinel structure and CuO phase were observed in the Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$ nanocrystals (with pH 3–4) when the calcination process lasted for 3 h at 600 °C, while only the single cubic spinel structure was formed when the calcination temperature was up to 1000 °C. In the case of our experiment, the Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$ nanocrystals (with pH = 1) were calcined at 375 °C for 4 h, and crystallized in the single cubic spinel structure with almost no excess phases.

The average crystallite sizes $D$ are calculated from the characteristics of the (311) XRD-peaks through Scherrer’s formula in the range of 1.4–19.6 nm (Tables 1 and 2). Note that, similar to the case of Zn/Ni ferrites prepared by the combustion-reaction method [24], here an increase in the Zn content does in fact increase the particle size. The existence of broad peaks in the XRD pattern of our synthesized nickel ferrite nanocrystals can be attributed to the small crystallite size of them (see the inset of Fig. 1).
The X-ray diffraction data of the synthesized ferrite nanocrystals has been refined by using the MAUD software and Rietveld’s method for the structural analysis, cation distribution and lattice parameter calculations. The obtained lattice parameters for the nanocrystals are listed in Tables 1 and 2. It is seen that the lattice parameters increase for larger Zn and Cu contents. This increase can be attributed to larger ionic radii of Cu$^{2+}$ (0.72 Å) and Zn$^{2+}$ (0.82 Å) relative to Ni$^{2+}$ (0.69 Å); this is consistent with Refs. [22, 25]. In addition, because the ionic radius of Zn$^{2+}$ is larger than the ionic radius of Cu$^{2+}$, the Zn$^{2+}$ substitution leads to larger expansion of the lattice; thus the lattice parameter increases more in comparison to the Cu$^{2+}$ substitution in the synthesized nanocrystals. Also, the shift of the (311) XRD-peak to small diffraction angle with the increase in the Zn and Cu contents may be attributed to this point that the sample with higher Zn and Cu contents has a larger lattice parameter [26]. These shifts are larger for the Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ nanocrystals because of larger ionic radius of Zn$^{2+}$ in comparison to Cu$^{2+}$.

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**Table 1** Crystalline size, lattice parameter, saturation magnetization, and coercivity of Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ nanocrystals

| Zn content (x) | Composition | Cation distribution | Crystalline size (nm) | Lattice parameter (Å) | Saturation magnetization (emu/g) | Coercivity (Oe) |
|---------------|-------------|---------------------|-----------------------|-----------------------|-------------------------------|----------------|
| 0             | NiFe$_2$O$_4$ | ($F_{4}^{3+}O_{4}^{2-})_{tet}[Ni^{2+}_{1.0},Fe^{3+}_{1.0}]_{oct}$ | 1.4                   | 8.340                 | 6.4                           | 0.6         |
| 0.3           | Ni$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ | ($Zn^{2+}_{0.7},Fe^{3+}_{0.3})_{tet}[Ni^{2+}_{1.0},Fe^{3+}_{1.0}]_{oct}$ | 6.2 ± 0.1             | 8.370                 | 25.6                          | 0.7         |
| 0.5           | Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ | ($Fe^{3+}_{0.5},Fe^{3+}_{0.5})_{tet}[Ni^{2+}_{1.0},Fe^{3+}_{1.0}]_{oct}$ | 9.8 ± 0.1             | 8.389                 | 34.8                          | 0.9         |
| 0.7           | Ni$_{0.3}$Zn$_{0.7}$Fe$_2$O$_4$ | ($Zn^{2+}_{0.3},Fe^{3+}_{0.7})_{tet}[Ni^{2+}_{1.0},Fe^{3+}_{1.0}]_{oct}$ | 13.5 ± 0.2            | 8.400                 | 28.4                          | 1.0         |
| 1             | ZnFe$_2$O$_4$ | ($Fe^{3+}_{1.0})_{tet}[Fe^{3+}_{1.0},Fe^{3+}_{1.0}]_{oct}$ | 19.6 ± 0.4            | 8.430                 | 1.7                           | 3.3         |

**Table 2** Crystalline size, lattice parameter, saturation magnetization, and coercivity of Ni$_{1-x}$Cu$_x$Fe$_2$O$_4$ nanocrystals

| Cu content (x) | Composition | Cation distribution | Crystalline size (nm) | Lattice parameter (Å) | Saturation magnetization (emu/g) | Coercivity (Oe) |
|---------------|-------------|---------------------|-----------------------|-----------------------|-------------------------------|----------------|
| 0             | NiFe$_2$O$_4$ | ($F_{4}^{3+}O_{4}^{2-})_{tet}[Ni^{2+}_{1.0},Fe^{3+}_{1.0}]_{oct}$ | 1.4                   | 8.340                 | 6.4                           | 0.6         |
| 0.5           | Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$ | ($Cu^{2+}_{0.5},Fe^{3+}_{0.5})_{tet}[Ni^{2+}_{1.0},Fe^{3+}_{1.0}]_{oct}$ | 4.6 ± 0.1             | 8.355                 | 16.2                          | 2.3         |
| 1             | CuFe$_2$O$_4$ | ($Fe^{3+}_{1.0})_{tet}[Cu^{2+}_{1.0},Fe^{3+}_{1.0}]_{oct}$ | 5.8 ± 0.1             | 8.370                 | 14.9                          | 168.2        |

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**Fig. 1** XRD patterns of synthesized Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ nanocrystals: (a) NiFe$_2$O$_4$, (b) Ni$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$, (e) Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$, (d) Ni$_{0.3}$Zn$_{0.7}$Fe$_2$O$_4$, (e) ZnFe$_2$O$_4$ (± Bragg reflection positions)

**Fig. 2** XRD patterns of synthesized Ni$_{1-x}$Cu$_x$Fe$_2$O$_4$ nanocrystals: (a) NiFe$_2$O$_4$, (b) Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$, (c) CuFe$_2$O$_4$ (± Bragg reflection positions)
To ensure that spinel structure for the synthesized nanocrystals has been formed, as well to investigate how the ferromagnetic ions (Fe$^{3+}$, Ni$^{2+}$) and non-magnetic transition metal ions (Cu$^{2+}$, Zn$^{2+}$) occupy tetrahedral and octahedral sites, we refined the XRD data by employing the MAUD software. Table 3 shows the before- and after-refinement values, indicating relatively high accuracy in synthesizing the nanocrystals without formation of extra phases.

Based on the XRD data refinement, the formation of single-phase spinel cubic structure with Fd3m space group has been confirmed in all samples. Additionally, the MAUD results indicate that the synthesized nickel ferrite (NiFe$_2$O$_4$) and copper ferrite (CuFe$_2$O$_4$) nanocrystals have inverse spinel structure that can be represented by the formula [Fe$^{3+}$]$_{tet}$[A$^{2+}$, Fe$^{3+}$]$_{oct}$O$_2$$^2$$^-$ (A = Ni, Cu), where the “tet” and “oct” indices represent the tetrahedral and octahedral sites, respectively. Likewise, the MAUD results specify that the synthesized zinc ferrite (ZnFe$_2$O$_4$) nanocrystals have a normal spinel structure that can be displayed by the formula [Zn$^{2+}$]$_{tet}$[Fe$^{3+}$]$_{oct}$O$_2$$^2$$^-$ . Also these results indicate that the synthesized Zn/Ni ferrite (0 < x < 1) and Cu/Ni ferrite (Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$) nanocrystals have a mixed spinel structure where the M$^{2+}$ (M = Zn, Cu) cations are substituted for the Fe$^{3+}$ ions in the tetrahedral sites, and these Fe$^{3+}$ ions move to the octahedral sites, as shown by the gray color in Table 3. In other words, in these nanocrystals the M$^{2+}$ (M = Zn, Cu) ions occupy the tetrahedral sites with the Fe$^{3+}$ ions, while the rest of the Fe$^{3+}$ ions fill the octahedral sites with the Ni$^{2+}$ ions. Thus, these samples can be represented by the formula [M$_x^{2+}$, Fe$_{1-x}^{3+}$]$_{tet}$[Ni$_{1-y}$, Fe$_{1+y}$]$_{oct}$O$_2$$^2$$^-$ . All of these results for the structural analysis and cation distribution calculations for synthesized Zn/Ni ferrites are in agreement with the structure and cation distribution for bulk spinel ferrites of Refs. [26, 27]. Table 3 represents the occupancy of the Zn$^{2+}$ and Cu$^{2+}$ (for the Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$ nanocrystals) contents in the tetrahedral sites, formation of the inverse spinel structure for nickel and copper ferrites, formation of normal spinel structure for zinc ferrites, and formation of mixed spinel structure for the other nanocrystals. Also the cation distributions of the prepared nanocrystals are summarized in Tables 1 and 2, and Fig. 3 represents the XRD patterns for the ZnFe$_2$O$_4$ nanocrystals.

The pattern fitness can be checked for XRD data. There are several parameters for the calculation of pattern fitness. The goodness of fit ($S$) is described by $S = R_{wp}/R_{exp}$, where $R_{wp}$ is the weighted residual error and $R_{exp}$ is the expected error. Refinement has been continued until a convergence was reached for a value of $S$ close to 1, which confirms the goodness of refinement. These parameters are listed in Table 4.

For Cu-doped samples, we have also tested a mixed scenario that puts the copper into both sublattices (for example the cation distribution for CuFe$_2$O$_4$ nanocrystals can be displayed by the formula [Cu$_{2+}^{2+}$, Fe$_{1-y}^{3+}$]$_{tet}$[Cu$_{1-y}^{1+}$, Fe$_{1+y}^{1+}$]$_{oct}$, where $0 < y < 1$ with step 0.1) and thus refined the distribution of the copper in the tetrahedral and octahedral sites and also the distribution and the positions of the other ions by using the MAUD software. With refinement of the XRD data for our Cu-doped samples, the MAUD software showed that, for $0 < y < 1$, it is unable to solve the refinement with the supplied initial parameters, because the correlation matrix from the Choleski decomposition has negative diagonal. Thus we found that for our synthesized Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$ nanocrystals, all copper ions go into the tetrahedral sites so that the cation distribution for this sample can be displayed by the formula [Cu$_{2+}^{2+}$, Fe$_{1-y}^{3+}$]$_{tet}$[Ni$_{1-y}$, Fe$_{1+y}$]$_{oct}$ . Also for our synthesized CuFe$_2$O$_4$ nanocrystals, all copper ions go into the octahedral sites thus the cation distribution can be displayed by the formula [Fe$_{1-y}^{3+}$]$_{tet}$[Cu$_{1+y}$, Fe$_{1+y}$]$_{oct}$ . Note that the FT-IR results are consistent with the MAUD analysis for the cation distribution. In addition, this cation distribution for Cu-doped samples explains well their magnetic properties.

3.2 FT-IR Study

The FT-IR spectra of the synthesized nanocrystals, shown in Figs. 4a and 4b, confirm the formation of the spinel structures suggested by the MAUD analysis. The band around 3415 cm$^{-1}$ is due to the O–H stretching vibration of the free or absorbed water. This indicates existence of hydroxyl groups in our synthesized ferrites, which is apparently seen in earlier experiments too [28, 29]. The bands at 1620 and 1100 cm$^{-1}$ are attributed to the C=O and C–O stretching vibration of the citric acid, respectively and the band around 1380 cm$^{-1}$ is related to the NO-stretching vibration due to nitrate group [30, 31]. These bands disappear when Cu and Zn contents (and thus calcination temperature) increased.
| Composition | Structural parameters before refinement | Structural parameters after refinement |
|-------------|----------------------------------------|--------------------------------------|
| NiFe₂O₄    | NiFe²⁺(oct) 0 0 0 0 0 0 1 6.25 0.625 0.625 0.625 0.625 0.5 1 0.3825 0.3825 0.3825 1 | NiFe²⁺(oct) 1.5 x 10⁻⁷ ≈ 0 1.8 x 10⁻⁷ ≈ 0 2.3 x 10⁻⁷ ≈ 0 1.0002 |
| NiFe₂O₄    | NiFe²⁺(oct) 0 0 0 0 0 0 1 6.25 0.625 0.625 0.625 0.625 0.5 1 0.3825 0.3825 0.3825 1 | NiFe²⁺(oct) 0.6251 0.6254 0.62536 0.62513 0.62544 0.62513 0.5002 |
| Ni₂Zn₁Fe₂O₄| NiFe²⁺(oct) 0 0 0 0 0 0 1 6.25 0.625 0.625 0.625 0.625 0.5 1 0.3825 0.3825 0.3825 1 | NiFe²⁺(oct) 0.6248848 0.6249957 0.6250193 0.624851 0.625003 0.624773 0.3501 |
| Ni₂Zn₁Fe₂O₄| NiFe²⁺(oct) 0 0 0 0 0 0 1 6.25 0.625 0.625 0.625 0.625 0.5 1 0.3825 0.3825 0.3825 1 | NiFe²⁺(oct) 0.624531 0.625434 0.625003 0.624531 0.625434 0.625003 0.2499 |
| Ni₂Zn₁Fe₂O₄| NiFe²⁺(oct) 0 0 0 0 0 0 1 6.25 0.625 0.625 0.625 0.625 0.5 1 0.3825 0.3825 0.3825 1 | NiFe²⁺(oct) 0.625004 0.625001 0.625051 0.624859 0.625003 0.624859 0.1503 |
| Ni₂Zn₁Fe₂O₄| NiFe²⁺(oct) 0 0 0 0 0 0 1 6.25 0.625 0.625 0.625 0.625 0.5 1 0.3825 0.3825 0.3825 1 | NiFe²⁺(oct) 0.624888 0.625001 0.625051 0.624859 0.625003 0.624859 0.1503 |
| Ni₂Zn₁Fe₂O₄| NiFe²⁺(oct) 0 0 0 0 0 0 1 6.25 0.625 0.625 0.625 0.625 0.5 1 0.3825 0.3825 0.3825 1 | NiFe²⁺(oct) 0.625004 0.625001 0.625051 0.624859 0.625003 0.624859 0.1503 |
| Ni₂Zn₁Fe₂O₄| NiFe²⁺(oct) 0 0 0 0 0 0 1 6.25 0.625 0.625 0.625 0.625 0.5 1 0.3825 0.3825 0.3825 1 | NiFe²⁺(oct) 0.624888 0.625001 0.625051 0.624859 0.625003 0.624859 0.1503 |
| Ni₂Zn₁Fe₂O₄| NiFe²⁺(oct) 0 0 0 0 0 0 1 6.25 0.625 0.625 0.625 0.625 0.5 1 0.3825 0.3825 0.3825 1 | NiFe²⁺(oct) 0.625004 0.625001 0.625051 0.624859 0.625003 0.624859 0.1503 |
| Ni₂Zn₁Fe₂O₄| NiFe²⁺(oct) 0 0 0 0 0 0 1 6.25 0.625 0.625 0.625 0.625 0.5 1 0.3825 0.3825 0.3825 1 | NiFe²⁺(oct) 0.624888 0.625001 0.625051 0.624859 0.625003 0.624859 0.1503 |
| CuFe₂O₄    | CuFe²⁺(oct) 0 0 0 0 0 0 1 6.25 0.625 0.625 0.625 0.625 0.5 1 0.3825 0.3825 0.3825 1 | CuFe²⁺(oct) 1.6 x 10⁻⁷ ≈ 0 4.2 x 10⁻⁷ ≈ 0 1.8 x 10⁻⁷ ≈ 0 1.0002 |
| CuFe₂O₄    | CuFe²⁺(oct) 0 0 0 0 0 0 1 6.25 0.625 0.625 0.625 0.625 0.5 1 0.3825 0.3825 0.3825 1 | CuFe²⁺(oct) 0.6251 0.6254 0.62536 0.62513 0.62544 0.62513 0.5002 |
| CuFe₂O₄    | CuFe²⁺(oct) 0 0 0 0 0 0 1 6.25 0.625 0.625 0.625 0.625 0.5 1 0.3825 0.3825 0.3825 1 | CuFe²⁺(oct) 0.625004 0.625001 0.625051 0.624859 0.625003 0.624859 0.1503 |
| CuFe₂O₄    | CuFe²⁺(oct) 0 0 0 0 0 0 1 6.25 0.625 0.625 0.625 0.625 0.5 1 0.3825 0.3825 0.3825 1 | CuFe²⁺(oct) 0.624888 0.625001 0.625051 0.624859 0.625003 0.624859 0.1503 |
Table 4  The parameters for the calculation of pattern fitness for Ni$_{1-x}$M$_x$Fe$_2$O$_4$ nanocrystals

| Composition   | $R_w$  | $R_p$  | $R_{exp}$ | $S$ |
|---------------|--------|--------|-----------|-----|
| NiFe$_2$O$_4$ | 0.118  | 0.110  | 0.095     | 1.24|
| Ni$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ | 0.131  | 0.103  | 0.103     | 1.27|
| Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ | 0.113  | 0.108  | 0.098     | 1.15|
| Ni$_{0.3}$Zn$_{0.7}$Fe$_2$O$_4$ | 0.114  | 0.108  | 0.101     | 1.13|
| ZnFe$_2$O$_4$ | 0.117  | 0.102  | 0.097     | 1.20|
| Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$ | 0.104  | 0.083  | 0.084     | 1.22|
| CuFe$_2$O$_4$ | 0.089  | 0.069  | 0.073     | 1.21|

In the range of 800–400 cm$^{-1}$, two main absorption bands were observed in the range of 604–542 cm$^{-1}$ and 463–416 cm$^{-1}$. These bands are attributed to the vibration of the tetrahedral and octahedral metal-oxygen (M–O) bonds in the lattices of the synthesized nanocrystals, respectively. These FT-IR frequency bands for various Zn and Cu contents have been listed in Tables 5 and 6. It is understood from these tables that the value of $\nu_1$ and $\nu_2$ are found to decrease and increase, respectively, with the increase in the Zn and Cu contents except for the CuFe$_2$O$_4$ sample.

These results can be explained as follows: The addition of Zn$^{2+}$ and Cu$^{2+}$ (from $x = 0$ to $x = 0.5$ for Ni/Cu ferrites) ions in the tetrahedral sites with larger radius and greater atomic weight, makes the Fe$^{3+}$ ions migrate to the octahedral sites, and consequently decreases the tetrahedral vibration frequency. Similarly, migration of the Fe$^{3+}$ ions to the octahedral site increases the octahedral vibration frequency. For the CuFe$_2$O$_4$ nanocrystals, the increase of the tetrahedral vibration frequency and the decrease of the octahedral vibration frequency may be due to the presence of half of the Fe$^{3+}$ ions in the A sites and presence of the Cu$^{2+}$ ions with larger radius and greater atomic weight in the B sites. There is a weak splitting around octahedral vibration frequency ($\nu_2$) of the CuFe$_2$O$_4$ nanocrystals that can be attributed to the existence of Cu$^{2+}$ ions, a Jahn–Teller ion [32, 33], in the octahedral sites, and causes some lattice distortion. This distortion normally takes the form of stretching the bonds to the ligand lying along the $z$ axis, but sometimes happens as a shortening of these bonds as well. This affects the octahedral Cu–O vibration frequency in the CuFe$_2$O$_4$ nanocrystals. Note that all of these results are also consistent with the MAUD analysis for the cation distribution.

3.3 Morphological Study

The FE-SEM images of the CuFe$_2$O$_4$, Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ and ZnFe$_2$O$_4$ nanocrystals have been shown in Figs. 5a, 5b, 5c. The average grain size of the CuFe$_2$O$_4$, Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ and ZnFe$_2$O$_4$ nanocrystals are 15, 20, and 30 nm, respectively. Note that the average grain size of the samples obtained from SEM images is larger than the nanocrystals’ size.
Table 5 FT-IR absorption band frequencies and optical parameter of Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ nanocrystals

| Zn content ($x$) | Composition     | FT-IR frequency bands (cm$^{-1}$) | Indirect band gap (eV) | Direct band gap (eV) |
|------------------|----------------|-----------------------------------|------------------------|----------------------|
|                  |                | A-site (tet) $\nu_1$ | B-site (oct) $\nu_2$  |                        |                      |
| 0                | NiFe$_2$O$_4$  | 604.33                      | 425.66                  | 1.85                 | 2.55                 |
| 0.3              | Ni$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ | 590.21                      | 426.11                  | 1.87                 | 2.56                 |
| 0.5              | Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ | 578.28                      | 426.60                  | 1.87                 | 2.56                 |
| 0.7              | Ni$_{0.3}$Zn$_{0.7}$Fe$_2$O$_4$ | 571.55                      | 426.63                  | 1.88                 | 2.56                 |
| 1                | ZnFe$_2$O$_4$  | 542.37                      | 463.14                  | 1.90                 | 2.56                 |

Table 6 FT-IR absorption band frequencies and optical parameter of Ni$_{1-x}$Cu$_x$Fe$_2$O$_4$ nanocrystals

| Cu content ($x$) | Composition     | FT-IR frequency bands (cm$^{-1}$) | Indirect band gap (eV) | Direct band gap (eV) |
|------------------|----------------|-----------------------------------|------------------------|----------------------|
|                  |                | A-site (tet) $\nu_1$ | B-site (oct) $\nu_2$  | $\nu'_2$           |                        |                      |
| 0                | NiFe$_2$O$_4$  | 604.33                      | 425.66                  | –                    | 1.85                 | 2.55                 |
| 0.5              | Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$ | 574.69                      | 428.13                  | –                    | 1.87                 | 2.55                 |
| 1                | CuFe$_2$O$_4$  | 585.86                      | 422.22                  | 416.61               | 1.87                 | 2.55                 |

Fig. 5a FE-SEM image of synthesized CuFe$_2$O$_4$ nanocrystals

as calculated using the XRD measurements, which simply indicates that each grain is formed by aggregation of a number of nanocrystals. The TEM micrographs of the ZnFe$_2$O$_4$ nanocrystals have been shown in Fig. 6. The TEM micrographs show that there is strong agglomeration between the ZnFe$_2$O$_4$ nanocrystals. The cohesion of grains is due to the magnetic attraction and the average grain size of this sample is smaller than 100 nm.

3.4 Magnetic Study

The magnetic properties of the synthesized nanocrystals are analyzed using a Magnetometer (VSM) at room temper-
ature from the $M-H$ curves as 6.4 and 1.7 emu/g, respectively (Tables 1 and 2). These values are less than the corresponding values for bulk nickel and zinc ferrites (50 and 5 emu/g, respectively) [34, 35]. This observation can be attributed to the presence of small nanoparticles having core-shell morphology, containing a spin-glass-like surface layer and ferrimagnetically lined-up core spins. As a result, the surface layer spins exhibit canting and disorder due to broken superexchange bonds in contrast to the inner spins. This in turn leads to a smaller $M_s$ in these nanocrystals. We note that the effect of such surface/boundary spins becomes more dominant for smaller ferrite nanoparticles with larger surface/volume ratio. In addition, such effects are especially important in the case of ferrites due to the presence of superexchange interactions. Having said all this, one can conclude that the $M_s$ of the synthesized NiFe$_2$O$_4$ nanocrystals (with 1.4 nm crystallite size) be much smaller than the value for the bulk.

According to Néel’s ferrimagnetic theory, in the spinel structure the cations on different sublattices (tetrahedral and octahedral sites) have oppositely aligned magnetic moments [29, 36]. Hence, the magnetic moment per formula unit ($n_B$) in the $\mu_B$ units is

$$n_B = M_{\text{oct}} - M_{\text{tet}}$$

(1)
where $M_{\text{oct}}$ and $M_{\text{tet}}$ are the magnetic moments of the octahedral and tetrahedral sites, respectively. The magnetic behavior of our synthesized nanocrystals measured by VSM can be attributed to the competition of ferromagnetic ions such as Fe$^{3+}$, Ni$^{2+}$ and the Cu$^{2+}$ and Zn$^{2+}$ ions as nonmagnetic transition metal ions in the occupancy of the tetrahedral and octahedral sites. This can be explained by the obtained cation distribution from the MAUD analysis of XRD patterns (summarized in Tables 1 and 2), and Néel’s theory with the knowledge of ionic magnetic moment of 0, 1, 2, and $5\mu_B$ for Zn$^{2+}$, Cu$^{2+}$, Ni$^{2+}$ and Fe$^{3+}$ ions, respectively.

Our principal objective in replacing Cu ions was not to compare its effect in contrast to the Zn ions effect in the sense of different doping values. We basically aimed to show that Cu ions, in contrast to Zn ions (although both are nonmagnetic) can exhibit the Jahn–Teller effect, and in turn hinders superparamagnetism. To see this phenomenon, it sufficed to prepare Cu-doped samples with $x = 0, 0.5, 1$. However, after showing this, it was natural to compare the Zn-doped and Cu-doped samples in the sense of magnetization ($M_s$) and coercivity ($H_c$).

It is evident from Tables 1 and 2 that the saturation magnetization of the synthesized nanocrystals has been enhanced with the increase in Zn and Cu contents up to $x = 0.5$. This is consistent with the obtained cation distribution the MAUD analysis of the XRD patterns and FTIR analysis. The occupancy of Zn$^{2+}$ and Cu$^{2+}$ substituted ions in the tetrahedral sites causes transfer of Fe$^{3+}$ ions from there to the octahedral sites. This increases the concentration of Fe$^{3+}$ ions in octahedral sites and so increases the magnetization in the octahedral sublattice. This in turn enhances the magnetization of the nanocrystals. These results agree well with the bulk sample in that the maximum $M_s$ is found in the Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ for Zn/Ni bulk ferrites. Tables 1 and 2 indicate that the increase in $M_s$ for Zn/Ni ferrite is more than Cu/Ni ferrite nanocrystals. This can be explained by the total spin moment of the tetrahedral site and octahedral site interactions. Due to placement of Zn$^{2+}$ and Cu$^{2+}$ ions in the tetrahedral sites, the magnetization of the B sublattice is expected to be identical for Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ and Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$ nanocrystals, while for the A sublattice it increases with substitution of higher magnetic moment of Cu$^{2+}$ ($1\mu_B$) in comparison to Zn$^{2+}$ ($0\mu_B$). Consequently, because of the antiferromagnetic coupling, the result is a decrease in the net overall magnetic moment (Eq. (1)) of the Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$ relative to the Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ nanocrystals. In addition, higher calcination temperature for the Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ (450 °C) in contrast to the Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$ (375 °C) nanocrystals implies larger grain size and higher crystalline quality in the ferrites, thereby leads to higher $M_s$ value.

It is observed from Tables 1 and 2 that with the increase in the Zn and Cu contents from $x = 0.5$ to $x = 1$, $M_s$ shows a decrease. This reduction is remarkable for the Zn/Ni substitution. The decrease of $M_s$ for the Ni$_{0.5}$Zn$_{0.7}$Fe$_2$O$_4$ nanocrystals is referred to as spin canting in the surface layer of nanoparticles. When the Zn content increases to $x = 0.7$, the occupation of Zn$^{2+}$ ions in the tetrahedral sites decreases the number of spins occupation in the A sites, thus the A–B superexchange interactions are weakened and the spins of the octahedral sites cannot hold collinearity to the small tetrahedral spins. Therefore, the $M_s$ value decreases.

Based on the MAUD analysis and the VSM measurements in Fig. 7a, the small $M_s$ of ZnFe$_2$O$_4$ can be attributed to the absence of the Ni$^{2+}$ ions as ferromagnetic ions and the occupancy of Zn$^{2+}$ ions with zero magnetic moment in all tetrahedral sites, i.e., replacing the complete Fe$^{3+}$ ions in the octahedral sites. Consequently, the interactions between Fe$^{3+}$ ions in the octahedral sites are too weak to be important (the B–B interaction is weak in ferrites), hence the magnetization of ZnFe$_2$O$_4$ nanocrystals is small. Also, with the increase in the Cu content from $x = 0.5$ to $x = 1$, a small reduction is observed in the saturation magnetization. To explain this behavior, we can argue that based on the MAUD analysis, the Cu$^{2+}$ ions move from the tetrahedral to octahedral sites, which have smaller magnetic moment in contrast with the Ni$^{2+}$ ions as mentioned above, and the half of Fe$^{3+}$ ions fill the A sites, so reduce the superexchange interactions between octahedral and tetrahedral sites, which cause the decrease in the $M_s$ value. But since the Jahn–Teller effect occurs, this decrease is small. The existence of the Cu$^{2+}$ ion as a Jahn–Teller ion in the octahedral sites of the CuFe$_2$O$_4$ nanocrystals causes a lattice distortion, which has the effect of removing the electronic and orbital degeneracies of Cu$^{2+}$ cations. It is anticipated that this effect in turn creates large strains in the copper ferrite lattice, and as a result modified magnetic properties. Hence, this causes a reduction in saturation magnetization from $x = 0.5$ to $x = 1$ to be smaller. Note that the Jahn–Teller theorem does not predict the direction of the distortion; it only marks the existence of unstable lattice geometry [33].

Since the coercivity ($H_c$) of a magnetic material is a measure of its magneto-crystalline anisotropy, the small nanoparticles, which have close to zero coercivity and no remanence become single domain with little anisotropy energy. This is a characteristic of superparamagnetic nanocrystals. The coercivity ($H_c$) of the synthesized nanocrystals has been obtained from Figs. 7a and 7b, and is listed in Tables 1 and 2. Note that the $H_c$ values of all prepared nanocrystals are close to zero, except CuFe$_2$O$_4$ nanocrystals (Tables 1 and 2). Thus these nanocrystals show superparamagnetic behavior at room temperature. Such properties make these materials favorable for wide engineering applications such as drug delivery [37], bioseparation [38] and magnetic refrigeration systems [39].
The $H_c$ of the samples increases with the Zn/Ni and Cu/Ni substitutions. This increase is small for Zn/Ni ferrite nanocrystals, while it is significant for Cu/Ni ferrite nanocrystals. This increase can be attributed to higher magneto-crystalline anisotropy of Cu$^{2+}$ in comparison to Ni$^{2+}$ and Zn$^{2+}$ ions (hence the Jahn–Teller effect). Although the CuFe$_2$O$_4$ nanocrystals have average crystallite size smaller than 10 nm, they have large coercivity, as a result of complete substitution of the Cu$^{2+}$ to the Ni$^{2+}$ ions in the octahedral sites and the occurrence of the Jahn–Teller effect. The existence of Cu$^{2+}$ as a Jahn–Teller ion in the octahedral sites of the CuFe$_2$O$_4$ nanocrystals causes the lattice distortion which is anticipated to create large strains in the copper ferrite lattice. This increases the anisotropy and coercivity of this sample, which agrees well with the FT-IR analysis of the CuFe$_2$O$_4$ nanocrystals (see Table 6). Likewise, this effect shows its small influence on the coercivity in Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$ as a result of that the Cu$^{2+}$ ions fill the tetrahedral sites. Thus the Jahn–Teller effect is much less noticeable in tetrahedral complexes.

3.5 Optical Properties

Photoluminescence spectroscopy is measured at room temperature to detect the optical properties of all synthesized nanocrystals for various substitutions of the Zn$^{2+}$ and Cu$^{2+}$ ions (Figs. 8a and 8b). Five clear emission bands have been observed in the entire PL spectra for these nanocrystals. The emission bands, around 541.94 and 518.93 and 460.89 nm are constant with the increase in the Zn and Cu content, and are attributed to the $3d^5 \rightarrow 3d^34s$ transitions of Fe$^{3+}$ ions. We remark that in Ref. [40] similar transitions at 530 and 470 nm have been reported for ZnFe$_2$O$_4$ thin films.

In addition, the intensity of the emission bands at 541.94 and 518.93 nm vary with the increase in the Zn/Ni substitution. The dependence of these transition intensities of Fe$^{3+}$ ions on the Zn content ($x$) is depicted in Fig. 9. It is evident that these intensities increase with the increase in the Zn content except for $x = 0.5$. This may be explained as follows: (i) Based on the MAUD analysis, with the increase in the Zn$^{2+}$ concentration and leaving of the Ni$^{2+}$ cations in the structure, Zn$^{2+}$ ions occupy the tetrahedral sites and transfer the Fe$^{3+}$ to the octahedral sites. (ii) These changes cause a decrease in the structural isotropy of the synthesized nanocrystals except for the Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ nanocrystals. (iii) The nanocrystals have biggest saturation magnetization among the synthesized nanocrystals and have a structural isotropy in the tetrahedral sites. (iv) The occupation of half of the tetrahedral sites by the Zn$^{2+}$ ions and the rest by the Fe$^{3+}$ ions causes the decrease in transitions of the Fe$^{3+}$ ions in the tetrahedral sites.
UV-Vis spectra of Ni\(_{1-x}\)Zn\(_x\)Fe\(_2\)O\(_4\) nanocrystals at room temperature: (a) NiFe\(_2\)O\(_4\), (b) Ni\(_{0.7}\)Zn\(_{0.3}\)Fe\(_2\)O\(_4\), (c) Ni\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\), (d) Ni\(_{0.3}\)Zn\(_{0.7}\)Fe\(_2\)O\(_4\), (e) ZnFe\(_2\)O\(_4\).

The broad emission bands around 660 and 484 nm are attributed to the indirect and direct band gaps for our synthesized nanocrystals, respectively. The values of the indirect and direct band gaps are listed for various substitutions of the Zn and Cu content in Tables 5 and 6. In particular, there are two minor peaks detected by the spectrometer around 660 nm and 484 nm, presenting, respectively, the indirect and direct band gaps \(E = h\nu/\lambda\). Admittedly the accuracy of this estimation is not high. The minor peaks around 660 nm for Ni\(_{1-x}\)Cu\(_x\)Fe\(_2\)O\(_4\) nanocrystals are displayed next to Fig. 8b. However, to confirm our results, we also performed a UV-Vis experiment for all samples. Figure 10 shows the optical absorption spectra for our Ni\(_{1-x}\)Zn\(_x\)Fe\(_2\)O\(_4\) nanocrystals in the UV region. The optical band gap \(E_g\) can be determined by the equation
\[
\alpha E_p = A(E_p - E_g)^q \quad [41],
\]
where \(E_p\) is the photon energy, \(A\) is a constant that depends on the transition probability, and \(q\) depends on the nature of the transition and is theoretically equal to 2 and 1/2 for allowed indirect and direct electronic transition, respectively. The connection of the linear fits of \((\alpha E_p)^{1/q}\) versus \(E_p\) plots for \(q = 1/2\) and 2 (shown in Fig. 11) on the \(E_p\)-axis determines the direct and indirect band gaps, respectively. The obtained indirect and direct band gaps from the UV-Vis spectra are consistent with these results from the PL measurements.

Note that the value of the indirect band gap increases with the increase in the Zn content, while it is almost constant with the Cu content. The values of the direct band gap are constant for various substitutions of Zn and Cu content. The value of the indirect band gap is affected by various factors such as crystallite size, structural parameter, and presence of impurities. The increase in the indirect band gap for our synthesized Ni\(_{1-x}\)Zn\(_x\)Fe\(_2\)O\(_4\) nanocrystals may be attributed to the more increase in the structural parameter (lattice constant) with the increase in the Zn concentration in comparison to the Cu content (Tables 1 and 2).

The obtained indirect band gap values for our synthesized Zn/Ni nanocrystals (1.85–1.90 eV) are higher than the determinants values for the Zn/Ni ferrite nanocomposites (1.50–1.66 eV) in Ref. [42], which is due to presence of impurities. Note that the obtained values of the indirect and direct band gaps for our prepared ZnFe\(_2\)O\(_4\) nanocrystals are higher than estimated values of the direct and indirect band gaps for zinc ferrite nanowires [43], which are 2.23 and 1.73 eV, respectively, and are similar to the ZnFe\(_2\)O\(_4\) films [44].
4 Conclusion

We have investigated experimentally how properties of spinel nickel ferrites are affected because of doping by Cu and Zn. We have prepared these samples through the sol-gel method, and performed various structural, magnetic, and optical measurements on them. The crystallite size of synthesized nanocrystals was calculated using Scherer’s formula in the range of 1.4–19.6 nm. The X-ray diffraction measurements, refined with Rietveld’s method, have indicated formation of a single-phase cubic spinel with the space group Fd3m, and cation distributions. In particular, the analysis of X-ray diffraction has shown that the structural and magnetic properties are induced by competition of ferromagnetic ions Ni$^{2+}$ and Fe$^{3+}$ and non-magnetic ions Zn$^{2+}$ and Cu$^{2+}$ ions in occupation of the tetrahedral and octahedral sites. Moreover, it has been shown that, as in the bulk case, Zn$^{2+}$ cations have preferred to substitute for Fe$^{3+}$ ions in the tetrahedral sites. Magnetic measurements through VSM indicated an increase in the saturation magnetization ($M_s$) with the Zn/Ni and Cu/Ni content up to $x = 0.5$ and a decrease for $x > 0.5$. We have argued that this is due to an increase in the concentration of the Fe$^{3+}$ ions in the octahedral sites. This increase in $M_s$ is the highest for the case of Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ nanocrystals. All samples showed superparamagnetism behavior except CuFe$_2$O$_4$ nanocrystals.

We have also observed two broad emission bands in the PL spectra. These bands correspond to the presence of the indirect and direct band gaps for synthesized nanocrystals. Remarkably, the indirect band gap of Zn/Ni ferrite nanocrystals has shown an increase with the zinc content.

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