Structural analysis of Cu substituted Ni\Zn in Ni-Zn Ferrite

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\textbf{ABSTRACT}
Ni-Zn ferrites are soft ferrites basically popular for high frequency devices. They have low coercivity, low permeability and higher resistivity. These properties have their own benefits on one hand but on the other hand, we can make them more efficient by doping suitable element in order for tuning their properties for other applications. It this work, highly conducting Cu is used for substituting Ni in Ni-Zn ferrites and prepared Ni\textsubscript{0.5-x}Cu\textsubscript{x}Zn\textsubscript{0.5}Fe\textsubscript{2}O\textsubscript{4} (x = 0, 0.05, 0.1, 0.15 and 0.2) samples using the sol-gel auto-combustion process. We have studied their resulting structural parameter using X-ray Powder Diffraction (XRD) and Fourier Transform Infrared (FTIR) Spectroscopy method and compared with that of Cu substituted Zn Ni-Zn ferrites. Their structures are found to be single phase cubic spinel similar to that of Cu substituted Zn. The lattice constant increases with Cu concentration opposite to that at Zn substitution. Likewise, the size of the crystallites were not in monotonic change with the doping concentration in both cases due to internal strain and cation distribution. The difference in the pattern of XRD and FTIR of our samples indicate their different but significant properties. The changes in the structure shows the effect of Cu doping and indicates the possible interesting changes in their electric, electronic and magnetic properties.

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1. Introduction

Ferrites have general structure A\textsuperscript{2+}Fe\textsuperscript{3+}O\textsubscript{4} which are the structure under spinel with general formula AB\textsubscript{2}X\textsubscript{4}. Here, A and B are various divalent and trivalent metal cations and, X is O, S, Se etc. ‘A’ cation covers 1/8\textsuperscript{th} of the tetrahedral holes and ‘B’ covers ½ of the octahedral holes. They are easy to synthesize and have simple structure for analysis. The spinel nanoferites are useful in the fields like microwave devices, ultra-high-density magnetic encoding, coating, etc. [1-3]. They have crystallographic structure which can bring feasible change in their microstructure and electromagnetic characteristics. The study of the shape and material properties of different composition of Ni-Cu-Zn ferrite system is increasing these days [4-7]. Magnetic nanoparticles (NPs) of Cu\textsuperscript{2+} added Nickel-Zinc magnetic oxides are commonly utilized in magnetic component like rotary DY
core, transformer and magnetic inductive core etc. In the present study, it is planned to formulate NPs of Cu substituted Ni in Ni-ZN ferrites containing iron oxide as their main components using sol-gel method and compare their structure with Cu substituted Zn in Ni-ZN ferrites [8]. Their investigation on Cu substituted Zn shows that Cu substituted Zn in Ni-ZN ferrites is appropriate for Multilayer Chip Inductor (MLCI) as magnetic material. The structural investigation of our compositions is carried out by utilizing X-ray diffraction (XRD) and Fourier Transform Infrared (FTIR) spectroscopy.

2. Materials and Method

Copper substituted Ni-Zn NPs are prepared by sol-gel auto-combustion method as the precursors under considerations react readily with water and can form colloidal solution. Moreover, the process is easy, simple, cheap and densification takes place comparatively at lower temperature giving chemically homogeneous sample. The starting materials are A grade 99.99% pure Nickel nitrate, Copper nitrate, Zinc nitrate, Iron nitrate and Citric acid monohydrate with molecular formula (Ni(NO$_3$)$_2$·6H$_2$O), Cu (NO$_3$)$_2$·H$_2$O, (Zn (NO$_3$)$_2$·6H$_2$O), (Fe(NO$_3$)$_3$·9H$_2$O) and (Cu$_2$H$_2$O$_2$·H$_2$O) respectively supplied by Himedia and Merk India. The ferrites Ni$_{0.5-x}$Cu$_x$Zn$_{0.5}$Fe$_2$O$_4$ samples with x = 0.0, 0.05, 0.1, 0.15 and 0.2 are prepared. The mixture of these metal nitrates and citric acid were mixed in molar ratio 1:1 and were dissolved in the distilled water to get clear solution. The solution was made neutral by adding liquid ammonia and then stirred in magnetic stirrer maintained at 100°C for 4 hr. They were then decanted and dried at normal temperature for 40 hrs. The flakes thus obtained were combusted and converted into a powder. The powder was sintered in a muffle furnace at 800 °C for 4 h at 5%/min and was used for testing several properties. We have used Rigaku X-ray diffractometer (Rigaku Miniflex II) incorporated with Cu-Kα radiation of wavelength 1.5406 Å and FTIR (IR Prestige21, Shimadzu, Japan) for their structural property in Analytical Research Laboratory, AU.

3. Result and Discussion

X-Ray Diffraction

The XRD plots of different Ni$_{0.5-x}$Cu$_x$Zn$_{0.5}$Fe$_2$O$_4$ (x = 0.0, 0.05, 0.1, 0.15 and 0.2) samples are shown in figure 1 showing single phase cubic spinel structure according to the JCPDS card No.48- 0489 standard under Fd-3m group. The lattice constant ‘a’ is determined with the following relation [9]:

\[ a = d_{hkl} \sqrt{h^2 + k^2 + l^2} \]  \hspace{1cm} (1)

where, \( d_{hkl} \) is interplaner spacing for given hkl planes and is calculated by Bragg’s law.

The plot of intensity against the diffracting angle (2θ) for different concentration of Cu, x = 0.0, 0.05, 0.1, 0.15 and 0.2 in Ni$_{0.5-x}$Cu$_x$Zn$_{0.5}$Fe$_2$O$_4$ ferrite (NPs) are shown in figure 1. The sharp peaks in the pattern shows the crystalline nature of the sample. The highest intensity (311) peak indicates the appropriate orientation in order to find the average crystallite size of all samples [10]. The peaks are almost similar with that of Cu substituted Zn as shown in figure 2. The maximum intensity with corresponding diffracting angle in each concentration is as shown in figure 3. The overall effect is the decrease in the maximum intensity and shifting of maxima towards lower angle side with the increment in the concentration of copper. This is due the change in ionic radii and size of crystallite.

The Debye-Scherer’s formula gives the average size of the crystallite size [11].

\[ D_{311} = \frac{\lambda \beta \cos \theta}{2 \sin \theta} \]  \hspace{1cm} (2)

where, \( D_{311} \), \( \lambda \), \( \beta \) and \( \theta \) are volume-averaged crystallite size, wavelength of X-ray (1.5406 Å), full width at half maximum of (311) peak and diffraction angle respectively.
The crystallite size, lattice parameters and cell volume of the composition \( \text{Ni}_{0.5-x}\text{Cu}_x\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 \) \((x = 0.0, 0.05, 0.1, 0.15 \text{ and } 0.2)\) are listed in Table 1. The crystallite size ranges from 29.01 to 42.68 nm in random order. There are mainly three factors responsible in these random changes: 1. synthesis condition (almost constant in our case) 2. Stress created on adsorption (ion substitution process expands lattice parameter thereby generating inter stress and distortion in the lattice structure and hence affects the crystal growth rate and crystallite size) and 3. Energy difference between metal-oxygen bond (lower energy) and Fe-oxygen bonds (higher energy).

Initially at lower concentration, the increase in lattice parameter due to the \( \text{Cu}^{2+} \) entrance creates internal stress, decreases the growth rate of crystal and hence reduce the crystallite size \([12]\). As the concentration increases further, lower energy requirement for their bonding with oxygen accelerate the growth process thereby increasing the crystallite size. After sufficient bonding, the cations now begins to move from one denser site to another site sometimes with distortion of bond thereby decreasing the growth process. Simultaneously, the lattice compression takes place due to the partial oxidation of \( \text{Ni}^{2+} \) to \( \text{Ni}^{3+} \), \( \text{Cu}^{2+} \) to \( \text{Cu}^{3+} \) \([13-15]\). The crystallite size and lattice parameter variation with concentration is as shown in figure 4 and figure 5 for \( \text{Cu} \) substituted \( \text{Ni} \) and \( \text{Cu} \) substituted \( \text{Zn} \) respectively.

The lattice parameter increases with the \( \text{Cu}^{2+} \) ions concentration. This is due to the larger ionic radius of \( \text{Cu}^{2+} \) ions \((0.73\text{Å})\) \([16]\) as compared \( \text{Ni}^{2+} \) \((0.69\text{Å})\) \([17]\) thereby expanding the unit cell or increasing lattice constant \([18]\). The reverse pattern is obtained in case of \( \text{Cu} \) substituted \( \text{Zn} \) as \( \text{Zn}^{2+}(0.74\ \text{Å}) \) has more ionic radius than that of \( \text{Cu}^{2+}(0.73\text{Å}) \). In some cases, the lattice constant do not show the usual response if \( \text{Cu} \) replace \( \text{Zn} \) in the octahedral site \([19]\). The variation of lattice constant is more significant in smaller size of NPs.
From Scherer’s formula, the diffraction peak width (\(\beta\)) is inversely proportional to the size of the crystallite. The increase in the lattice parameter expand the volume of unit cell accordingly. Decreasing in crystallite size enhances sintering which in turn decreases the lattice defects and involved strain but facilitate the coalition of the crystals resulting the increase in particle size.

The ambiguity created in the structural parameters like crystallite size variation with concentration, can be resolved by the FTIR spectroscopy. It gives the exact information about cation distribution or the functional group and the force creating vibration in the crystal by which absorption and diffraction takes place.

**FTIR spectroscopy**

The frequency or wave number of the vibration depends on lattice parameter, lattice spacing, masses of cations and cation oxygen bonding. There are two absorption bands \(\nu_1\) and \(\nu_2\) around 400 cm\(^{-1}\) to 600 cm\(^{-1}\) due to two tetrahedral and octahedral sites with A-O-A and B-O-B bond vibration respectively as shown in figure 6 for Cu substituted Ni and figure 7 for Cu substituted Zn respectively. The substitution of Cu shifted the absorption bands of both tetrahedral and octahedral

**Fig. 4:** Variation of lattice constant and crystallite size of Ni\(_{0.5-x}\)Cu\(_{x}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) (\(x = 0.0, 0.05, 0.1, 0.15\) and 0.2) ferrites NPs.

**Fig. 5:** Variation of lattice parameters with composition of Ni\(_{0.5-x}\)Zn\(_{0.5}\)Cu\(_{x}\)Fe\(_2\)O\(_4\) sample (\(x = 0.0, 0.05, 0.1, 0.15\) and 0.2) ferrites NPs (data [8]).

**Fig. 6:** IR spectra of of Ni\(_{0.5-x}\)Cu\(_{x}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) (\(x = 0.0, 0.05, 0.1, 0.15\) and 0.2) ferrite NPs.

**Fig. 7:** IR spectra of of Ni\(_{0.5-x}\)Cu\(_{x}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) (\(x = 0.0, 0.05, 0.1, 0.15\) and 0.2) ferrite NPs [8].
sites slightly towards high frequency region as mentioned in Table 2. As the bond length increases, the frequency decreases as usual. The IR spectra analysis shows the Cu$^{2+}$ ions in the octahedral site as in figure 6. The spectra of Cu substituted Zn is similar but the absorption is more indicating high atomic weight element in the composition. The study of force constants gives the complete information of cation distribution.

Table 1: Lattice parameters of Ni$_{0.5-x}$Cu$_x$Zn$_{0.5}$Fe$_2$O$_4$ (x = 0.0, 0.05, 0.1, 0.15 and 0.2) ferrites NPs.

| Concentration (x) | Compounds              | Tetrahedral absorption bands $\nu_1$(cm$^{-1}$) | Octahedral absorption bands $\nu_2$(cm$^{-1}$) |
|-------------------|------------------------|-----------------------------------------------|-----------------------------------------------|
| 0.0               | Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ | 402.1                                        | 580.4                                         |
| 0.05              | Ni$_{0.45}$Cu$_{0.05}$Zn$_{0.5}$Fe$_2$O$_4$ | 403.2                                        | 583.2                                         |
| 0.1               | Ni$_{0.4}$Cu$_{0.1}$Zn$_{0.5}$Fe$_2$O$_4$ | 405.6                                        | 586.0                                         |
| 0.15              | Ni$_{0.35}$Cu$_{0.15}$Zn$_{0.5}$Fe$_2$O$_4$ | 408.2                                        | 590.2                                         |
| 0.2               | Ni$_{0.3}$Cu$_{0.2}$Zn$_{0.5}$Fe$_2$O$_4$  | 406.1                                        | 599.3                                         |

Table 2: Tetrahedral and Octahedral absorption bands of Ni$_{0.5-x}$Cu$_x$Zn$_{0.5}$Fe$_2$O$_4$ ferrite NPs.

| Concentration (x) | a (Å) | Cell Volume= $a^3$ (for cubic) (Å$^3$) | Crystallite size (nm) | Space Group |
|-------------------|-------|----------------------------------------|-----------------------|-------------|
| 0.0               | 8.3894 | 590.4562                               | 42.68                 | Fd-3m       |
| 0.05              | 8.4119 | 595.2349                               | 29.01                 | Fd-3m       |
| 0.1               | 8.4441 | 602.0943                               | 38.83                 | Fd-3m       |
| 0.15              | 8.4729 | 608.2724                               | 42.08                 | Fd-3m       |
| 0.2               | 8.4878 | 611.4938                               | 40.45                 | Fd-3m       |

4. Conclusions

Diffraction peaks in the XRD pattern show the sample as single phase cubic spinel and the overall effect of the diffraction pattern shows that the maximum intensity peak is moving towards the lower angle side with the concentration of Cu due to the reduction in ionic radii similar to that of Cu substituted Zn. The random pattern of crystallite size is due to the non-uniform lattice strain caused by cation distribution during doping. The lattice parameter increases with the Cu$^{2+}$ ions concentration due to the larger ionic radius of Cu$^{2+}$ (0.73Å) as compared to Ni$^{2+}$ (0.69 Å) thereby increasing lattice constant. FTIR supports the XRD results with slight shifting in higher frequency side due to Cu doping.

Finally, the structural properties of Ni-Zn soft ferrites after doping with Copper substituting with Ni and Zn respectively shows opposite trend for lattice parameter and random crystallite size, and different absorption intensity but with similar single phase cubic spinel structure. The differences in structure between the compositions indicates interesting electric and magnetic properties for further study.

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