Effect of Al\(^{3+}\) Substitution on Structural and Magnetic Properties of NiZnCo Nano Ferrites

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Abstract: Sol-gel method incorporating auto combustion is used to prepare Al\(^{3+}\) substituted Ni\(_{0.4}\)Zn\(_{0.35}\)Co\(_{0.25}\)Fe\(_2\)\(_x\)Al\(_x\)O\(_4\) with concentration (\(x = 0.0, 0.10, 0.20\)) samples. XRD shows their Cubic spinel structure with lattice constant increasing and crystallite sizes decreasing from 32.15 nm to 22.89 nm with Al\(^{3+}\). The spinel structure is confirmed with the help of FT-IR. They have isotropic nature with the single ferrimagnetic domain as given by VSM. The product is widely used.

Keywords: Al\(^{3+}\) substituted NiZnCo ferrite; XRD; SEM; FT-IR; magnetic properties.

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1. Introduction

These spinel nanomaterials or ferrites with cations in their tetrahedral and octahedral sites are used as soft magnetic materials in everyday life [1]. Changing their internal with doping can make them applicable in more advanced devices. Most of them have M\(^{2+}\)Fe\(^{3+}\)O\(_4\)\(^2-\) the type of structure [2]. M is the cation of transitional metal on their tetrahedral site and Fe\(^{3+}\) on the octahedral site [3]. NiZnCo ferrite is highly stable at higher frequency magnetic materials due to their remarkable properties, and therefore they have been widely studied [4]. This soft magnetic ferrite’s high resistivity and low power loss made them be used in multilayered chip inductors, microwave absorption materials, information storage systems, transformer core, computer circuitry, and electronic communication [5]. Mallapur et al. and Knyazev et al. have investigated the structural, magnetic, and electrical properties of the spinel ferrite system of NiZnCo [6, 7].

Moreover, reports on the different ions substituted NiZnCo ferrites are also available in review reports [8, 9]. Recent approaches like microemulsion, co-precipitation, ceramic, hydrothermal, sol-gel methods, etc., help synthesize the material of our interest. The easy and faster sol-gel method is used for ultrafine particles at room temperature [10-12].

After a review of the literature, the Al\(^{3+}\) substituted NiZnCo (Ni\(_{0.4}\)Zn\(_{0.35}\)Co\(_{0.25}\)Fe\(_2\)\(_x\)Al\(_x\)O\(_4\) (\(x = 0.0, 0.1, \text{ and } 0.2\)) ferrite is not synthesized and studied yet. So, we have tried to synthesize it and study its different properties.
2. Materials and Methods

The sol-gel auto-combustion method is used for the synthesis of Al\textsuperscript{3+} substituted NiZnCo nanoparticles. 99.99\% pure nitrates (of Nickel, Zinc, Cobalt, Aluminum, Iron) and citric acid are mixed in appropriate ratio (1:1) to prepare Ni\textsubscript{0.4}Zn\textsubscript{0.35}Co\textsubscript{0.25}Fe\textsubscript{2-x}Al\textsubscript{x}O\textsubscript{4} (x = 0.0, 0.1, 0.2) samples. They were mixed with distilled water and made neutral with the help of liquid ammonia. The solution was then stirred at 100 °C for 4 h, decanted, and dried at room temperature for 40 h. The resultant was then powdered and again sintered at 800 °C for 4 h at 5°/min. After hydraulic pressing, polishing with gold, the disc-shaped electrodes are prepared and sintering again at 800 °C. PVA can be used as a binder.

We used Rigaku X-ray diffractometer (RigakuMiniflex II) incorporated with CuKα radiation of wavelength (1.5406 Å) for the structural property, TESCAN, MIRA II LMH SEM with attached Inca Oxford EDX for the detection of functional group, FT-IR analysis for the textural and compositional images, EZ VSM model for the magnetic at room temperature. The two-probe DC resistivity method was used for checking its conductivity.

3. Results and Discussion

3.1. X-ray diffraction analysis.

The XRD plots of different Ni\textsubscript{0.4}Zn\textsubscript{0.35}Co\textsubscript{0.25}Fe\textsubscript{2-x}Al\textsubscript{x}O\textsubscript{4} (x = 0.0, 0.1, and 0.2) samples are shown in Figure 1. The samples structure is found to be a cubic spinel structure according to the JCPDS card No.08-0234 [13].

The lattice constant ‘a’ is determined with the following relation [14].

\[
a = d\sqrt{h^2 + k^2 + l^2}
\]

(1)

where \(d_{hkl}\) is the interplanar spacing of hkl planes and is calculated by Bragg’s law. Here, the highest is obtained in (311). This gives the orientation that provides the exact crystallite size value to identify the crystal and given by Debye Scherer’s [15].

\[
D_{311} = \frac{0.9\lambda}{\beta\cos\theta}
\]

(2)

where \(\lambda\), \(\beta\), and \(\theta\) are the wavelength of X-ray, full width at half maximum of (311) peak and angle of diffraction, respectively.

The sizes of the crystallite and lattice constants of the samples are listed in Table 1. As the Al\textsuperscript{3+} ions content is increased, the crystallite size (from 32.15 nm to 22.89 nm for x = 0.0 to 0.2 respectively) while the lattice parameter increases due to the greater ionic radius of Fe\textsuperscript{3+} ions (0.67 Å) [16] as compared to Al\textsuperscript{3+} (0.51 Å) [17], thereby expanding the unit cell [31], as shown in Figure 3. The sample value for x=0.0 is found in the range 8.343 Å - 8.323 Å, according to the previous literature [18]. On the other hand, if Al\textsuperscript{3+} ions replace the Fe\textsuperscript{3+} ions with a larger radius with smaller radii, the unit cell shrinks, preserving the previous shape.

Apart from Scherer’s formula, as in Eqn (2), the sintering reduces the defects in the lattice, thereby producing strain and increasing the coalition hence the particle size.

| Composition (x) | Lattice constant (Å) | Crystallite size (nm) | Space group |
|---------------|----------------------|----------------------|-------------|
| 0.0           | 8.343                | 32.15                | Fd-3m       |
| 0.1           | 8.331                | 26.48                | Fd-3m       |
| 0.2           | 8.323                | 22.89                | Fd-3m       |

Table 1. Lattice constant and crystallite size of Ni\textsubscript{0.4}Zn\textsubscript{0.35}Co\textsubscript{0.25}Fe\textsubscript{2-x}Al\textsubscript{x}O\textsubscript{4} nano ferrite samples.
Figure 1. XRD spectra of Ni$_{0.4}$Zn$_{0.35}$Co$_{0.25}$Fe$_{2-x}$Al$_x$O$_4$ nano ferrite samples.

3.2. Field-Effect Scanning Electron Microscope (FESEM) studies.

Figure 3 are the FESEM images of Ni$_{0.4}$Zn$_{0.35}$Co$_{0.25}$Fe$_{2-x}$Al$_x$O$_4$ ($x = 0.0, 0.1,$ and $0.2$) gives the average grain sizes in the range 70-90 nm which are more or less equal [19]. Similarly, other parameters like grain size, pores, inclusions, grain boundaries, particle size, homogeneity, defects, etc., can be identified [20]. The spin-wave produced in the lattice is controlled for low porosity, which is significant for microwave devices. Similarly, the mobility of the domain and hence the permeability is increased with the larger grain size. The grain boundaries offer resistance for eddy current.

Figure 2. (a) to (c): FESEM image of Ni$_{0.4}$Zn$_{0.35}$Co$_{0.25}$Fe$_{2-x}$Al$_x$O$_4$ nanoferrite samples.
3.3. FTIR studies.

It gives the functional groups in the sample with the help of its absorption spectra lying in the range 400-1200 \( \text{cm}^{-1} \) of our sample's \( \text{Ni}_{0.4}\text{Zn}_{0.35}\text{Co}_{0.25}\text{Fe}_{2-x}\text{Al}_x\text{O}_4 \) (\( x = 0.0, 0.1, \) and \( 0.2) \), indicating spinel ferrite as shown in Figure 4. The two absorption bands at wavenumbers 580.4 to 598.84 \( \text{cm}^{-1} \) and 402.1 to 405.35 \( \text{cm}^{-1} \) are listed in Table 2 are the two respective characteristics bands of each spinel ferrite. The various bond length between \( \text{Fe}^{3+} \) and \( \text{O}^{2-} \) for the sample with different concentrations give rise in the deviation in the peak position of \( v_1 \) and \( v_2 \) towards the high-frequency region [21].

![Figure 3. Wavenumber of Ni_{0.4}Zn_{0.35}Co_{0.25}Fe_{2-x}Al_xO_4 nano ferrite sample.](image)

| Cu content (x) | \( v_1 (\text{cm}^{-1}) \) | \( v_2 (\text{cm}^{-1}) \) |
|---------------|-----------------|-----------------|
| 0.0           | 580.40          | 402.10          |
| 0.1           | 585.92          | 404.46          |
| 0.2           | 598.84          | 405.35          |

3.4. Magnetic properties.

Ferrites have a large value of spontaneous magnetization due to their antimagnetic moment of different magnitude. The exchange integral, depending on interatomic distance, is negative for ferrite [36]. This interaction changing indirectly through oxygen ions limits the easy flow of electrons. So, ferrites have high resistivity [22].

The metal ion concentration in tetra and octahedral site affect the saturation permeability, coercivity, susceptibility, curie temperature, etc., of ferrites and the ferrites’ structure affect its hysteresis loop shapes, resistivity, ac conductivity, and dielectric constant. So, these properties are more sensitive to the system. These properties can be changed by adding external magnetic or non-magnetic metal ions [23].

The hysteresis curves of our respective \( \text{Ni}_{0.4}\text{Zn}_{0.35}\text{Co}_{0.25}\text{Fe}_{2-x}\text{Al}_x\text{O}_4 \) (\( x = 0.0, 0.1, \) and \( 0.2) \) samples are as shown in Figure 6. Figure 7 shows the values of coercivity (\( H_c \)), saturation magnetization (\( M_s \)), etc., that are important for their magnetic properties. The values of \( M_s \) and \( H_c \) are listed in Table 3.
From Table 3, Ms values are decreased in decreasing Al\textsuperscript{3+} concentration. On adding copper ions to the Nickel-Zinc-Cobalt mixture, they exchange a few magnetic ions, Fe\textsuperscript{3+} and Ni\textsuperscript{2+} in B-site (same in a site) increases AB interaction that interferes with the antiparallel spin B site due to increased. Weiss's theory reports that the A-B and B-A interactions are higher than the A-A and B-B interactions [24].

![Figure 4](https://doi.org/10.33263/BRIAC125.60936099)

**Figure 4.** Hysteresis loops of Ni\textsubscript{0.4}Zn\textsubscript{0.35}Co\textsubscript{0.25}Fe\textsubscript{2-x}Al\textsubscript{x}O\textsubscript{4} nano ferrite sample at room temperature.

| Concentration (x) | Ms (emu/g) | Hc (Oe) |
|------------------|-----------|---------|
| 0.0              | 14.1      | 325     |
| 0.1              | 44.5      | 264     |
| 0.2              | 25.4      | 959     |

**Table 3.** Ms and Hc of Ni\textsubscript{0.4}Zn\textsubscript{0.35}Co\textsubscript{0.25}Fe\textsubscript{2-x}Al\textsubscript{x}O\textsubscript{4} nano ferrite sample.

4. Conclusions

Sol-gel auto-combustion method is used to prepare Ni\textsubscript{0.4}Zn\textsubscript{0.35}Co\textsubscript{0.25}Fe\textsubscript{2-x}Al\textsubscript{x}O\textsubscript{4} (x = 0.0, 0.1, and 0.2) ferrite NPs. XRD shows the single-phase cubic spinel ferrite structure. The lattice parameter decreases, and the crystallite size increases with the Al concentration due to the greater ionic radius of Fe\textsuperscript{3+} ions (0.67 Å) than Al\textsuperscript{3+} (0.51 Å). FESEM reveals microstructural growth along with heat action. The FTIR verifies functional groups needed for ferrite structure and supports the XRD result. The magnetic measurements show that magnetization reduces and coercivity enhances.

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Conflicts of Interest

We declare that this article has no conflict of interest.

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