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Impact of V substitution on the physical properties of Ni–Zn–Co ferrites: structural, magnetic, dielectric and electrical properties

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Abstract

We have investigated the Vanadium- (V) substituted Ni–Zn–Co ferrites where the samples are prepared using the solid-state reaction technique. The impact of V⁵⁺ substitution on the structural, magnetic, dielectric and electrical properties of Ni–Zn–Co ferrites has been studied. The XRD analysis confirms the formation of a single-phase cubic spinel structure. The lattice constants have been calculated both theoretically and experimentally along with other structural parameters such as bulk density, x-ray density and porosity. The FESEM images are studied for analyzing the surface morphology. FTIR measurement confirms spinel structure formation. The saturation magnetization ($M_s$), coercive field ($H_c$) and Bohr magneton ($\mu_B$) are calculated from the obtained M–H loops. The temperature-dependent permeability is studied to obtain the Curie temperature. The frequency and the composition dependence of permeability are also analyzed. Frequency dependent dielectric behavior and ac resistivity are also investigated. An inverse relationship is observed between the composition dependent dielectric constant and ac resistivity. The obtained results such as the electrical resistivity, dielectric constants and magnetic properties suggest the appropriateness of the studied ferrites in microwave device applications.

Introduction

Ferrites, the influential ceramic materials, are composed by combining, firing and blending a huge portion of Fe₂O₃ (iron (III) oxide) with a small amount of at least one metallic element, for example, manganese, zinc, nickel, barium, cobalt, etc [1]. Ferrites are mainly used in three sectors of electronics: power applications, low-level applications and Electro-Magnetic Interference (EMI) suppression. Therefore, there is always an ever increasing demand to improve their characteristics for utilizing in-home communication appliances, computers, electrical and other technical fields [2]. The interest in such oxides emerges from their versatile applicability from relatively high to microwave frequency region. Among various ferrites, soft ferrites are being used extensively in electronic applications for its high resistive at high frequency such as transformer cores, inductors, antenna rods, microwave devices, computer memory chips, magnetic recording media, etc after their first commercial introduction [3]. Mostly these electrical and magnetic properties depend on the method of preparation, preparative parameters, preparative conditions, particle size, nature of dopants, etc [4]. Hence, many researchers bestowed their time and efforts on various ferrites with various dopants to enhance their electric and magnetic characteristics.

The important electronic properties make the spinel Ni–Zn–Co ferrites prominent [5]. A good combination of its magnetic and electrical properties along with its low-cost aspects makes them potential candidates for
high-frequency applications [6]. These ferrites have high saturation magnetization, high resistivity, high permeability, high Curie temperature [7–10]. It is technologically sound due to its potential use in targeted microwave devices, sensors, magnetic recording applications and drug delivery systems [11–15]. For the aforementioned interests, many researchers have turned their attention to the Ni–Zn–Co ferrites. Mallapur et al have investigated the structural and electrical properties of Ni–Zn–Co spinel ferrite system [16]. Electric properties of nanocrystalline Ni–Zn–Co ferrites have been reported by Ghodake et al [17]. Spectral studies such as room temperature Mossbauer, x-ray and infrared IR spectra of Ni–Zn–Co ferrites have been carried out by Amer et al [18]. Knayzey et al reported on the structural and magnetic properties of Ni–Zn–Co ferrites [19]. Besides, Mohit et al [20], Stergiou et al [21], Ghodake et al [22], Hassan et al [23], Mattel et al [24], Chen et al [25], etc have also investigated the Ni–Zn–Co ferrites. Moreover, reports on the different ions substituted-Ni–Zn–Co ferrites are also available e.g., Ren et al [26] have performed a study on La$^{3+}$ substituted Ni–Zn–Co ferrites. Saini et al [27] researched on In substituted Ni–Zn–Co ferrites. Y and La substituted Ni–Zn–Co ferrites have also been investigated by Stergiou et al [28], Gd and La-doped Ni–Zn–Co ferrites are studied by Zhou et al [29]. Zheng et al have analyzed BaO-doped Ni–Zn–Co magneto-dielectric ferrites [30]. Previously, we have reported on various characteristics of Gd substituted Ni–Zn–Co ferrites [31].

The dependency of the physical properties of ferrites on the distribution of cations over tetrahedral (A) and octahedral (B) sites opens the way for modifying their properties by introducing different ions into these two sites [32–34]. Reports on the addition or substitution of vanadium into various ferrite systems are available [35, 36]. Korkmaz et al [37] noted a decline of saturation magnetization due to V substitution in the NiFe$_2$O$_4$ (x ≤ 0.3) nanoparticles system. Magnetic properties of V substituted Li-Zn-Ti ferrites have been investigated by Maisnam et al [38]. They reported a decrease in Curie temperature ($T_C$) and saturation magnetization with an increase in V contents. Slimani et al [39] have investigated how magnetic and optical properties of NiFe$_2$O$_4$ (0.0 ≤ x ≤ 0.3) NPs are influenced by varying calcination temperature. Heiba et al [40] studied the V substituted Co ferrites. M. Kaiser also reported the effect of V substitution on the magnetic and dielectric properties of Ni–Zn–Cu ferrites [41]. The presence of V with their low melting temperature causes the formation of the liquid phase and thus accelerates the grain growth process at low sintering temperature [42, 43]. Therefore, alteration of physical properties by the incorporation of a small amount of V into Ni–Zn–Co is also expected. Large eddy current is the one drawback of Ni–Zn–Co ferrites which decelerates its device applications. Researchers reported an increase in resistivity with the substitution of V which in turns can reduce the leakage current [42]. Hence, substitution of V is expected to reduce the leakage current of Ni–Zn–Co ferrites. Moreover, according to our knowledge from literature survey, no study has yet been reported on V doped Ni–Zn–Co ferrites. Therefore, the objective of the current study is to investigate the influence of V substitution on the electrical and magnetic properties of Ni–Zn–Co ferrites.

**Experimental details**

Ferrites can be synthesized by co-precipitation [44], microwave combustion method [45], sol-gel auto combustion route [46], double sintering ceramic technique and so on. In this study, we followed solid state reaction method to prepare V$^{5+}$ substituted Ni–Zn–Co ferrite [Ni$_{1-x}$Zn$_x$Co$_{0.1}$Fe$_{2}$V$_x$O$_4$ (0 ≤ x ≤ 0.12)] as this route is eco-friendly and economic. Moreover, the prepared samples show high density, low porosity, great longevity and impressive hardness. The shape and size are easily adjustable for industrial manufacturing. The following operations are performed to prepare the desired samples and the details can be found elsewhere [31]. However, the sample preparation procedure is shown in figure 1.

X-ray diffraction (XRD) using Philips X’pert PRO x-ray diffractometer (PW3040) with Cu-K$_x$ radiation (λ = 1.5405 Å), Field Effect Scanning Electron Micrographs (FESEM) (JEOL JSM-7600F), Fourier transform infrared spectroscopy (FTIR) (PerkinElmer FT-IR Spectrometer) were studied for the synthesized samples. A Wayne Kerr precision impedance analyzer (6500B) [Frequency range: 1 kHz–120 MHz, drive voltage of 0.5 V] was also used to study the dielectric and permeability properties. The magnetic properties were obtained by a Physical Properties Measurement System (PPMS), Quantum Design Dyna Cool at ambient conditions.

**Results and discussion**

**Structural properties**

Figure 2 illustrates the x-ray diffraction (XRD) patterns of Ni$_{1-x}$Zn$_x$Co$_{0.1}$Fe$_{2}V_x$O$_4$ (0 ≤ x ≤ 0.12) ferrites sintered at 1100 °C. The diffraction peaks at different planes (111), (220), (311), (222), (400), (422), (511) and (440) confirms the cubic spinel structures (JCPDS # 08-0234) of the synthesized samples [47]. The diffraction peaks become broaden with the increased concentration of V which indicates the decrease of grain size (table 1) with the increase of V contents. It is occurred because of the smaller ionic radii of the V$^{5+}$ ions than the ionic radii of the Fe$^{3+}$ ions.
Figure 1. The sample preparation procedure of Ni$_{0.7}$Zn$_{0.2}$Co$_{0.1}$Fe$_{2-x}$V$_x$O$_4$ ($0 \leq x \leq 0.12$) ferrites.

Figure 2. (a) X-ray diffraction patterns (b) maximum peak broaden and (c) Lattice constant ($a$) dependence of V-content of Ni$_{0.7}$Zn$_{0.2}$Co$_{0.1}$Fe$_{2-x}$V$_x$O$_4$ ($0 \leq x \leq 0.12$) ferrites.
Table 1. Cation distribution (tetrahedral A-site and octahedral B-site), Ionic radii (r_A for A-site and r_B for B-site), Lattice constant (a_th for theoretical and a_exp for experimental value), X-ray density (ρ_x), Bulk density (ρ_b), Crystallite size, grain size, Lattice strain and Porosity (P) of Ni_{0.7}Zn_{0.2}Co_{0.1}Fe_{2-x}V_xO_4 (0 \leq x \leq 0.12) ferrites.

| V content (x) | Cation distribution | Ionic radii | Lattice constant | Bond Length (Å) | Hoping Length (Å) |
|---------------|---------------------|-------------|-----------------|-----------------|------------------|
|               | A-site | B-site | r_A (Å) | r_B (Å) | a_th (Å) | a_exp (Å) | X-ray density (g/cm³) | Bulk density (g/cm³) | Crystallite Size (nm) | Lattice Strain x 10⁻³ | Grain Size D (μm) | Porosity P (%) | A-site | B-site | A-site | B-site |
| 0.00          | [Ni]_{1.0}^{++} [Fe]_{2.0}^{3+} [Zn]_{0.2}^{2+} [Co]_{0.1}^{2+} [O]_{4}^{2-} | 0.664 | 0.666 | 8.349 | 8.362 | 5.35 | 5.05 | 50.62 | 2.3 | 6.87 | 5.71 | 1.810 | 2.091 | 3.621 | 2.956 |
| 0.02          | [Ni]_{0.98}^{++} [Fe]_{2.02}^{3+} [Zn]_{0.2}^{2+} [Co]_{0.1}^{2+} [O]_{4}^{2-} | 0.664 | 0.665 | 8.348 | 8.361 | 5.51 | 4.26 | 56.11 | 2.1 | 4.43 | 22.68 | 1.810 | 2.090 | 3.620 | 2.956 |
| 0.05          | [Ni]_{0.95}^{++} [Fe]_{2.05}^{3+} [Zn]_{0.2}^{2+} [Co]_{0.1}^{2+} [O]_{4}^{2-} | 0.664 | 0.664 | 8.346 | 8.354 | 5.49 | 4.19 | 40.91 | 2.9 | 3.73 | 23.68 | 1.808 | 2.089 | 3.617 | 2.954 |
| 0.07          | [Ni]_{0.92}^{++} [Fe]_{2.08}^{3+} [Zn]_{0.2}^{2+} [Co]_{0.1}^{2+} [O]_{4}^{2-} | 0.664 | 0.664 | 8.345 | 8.353 | 5.48 | 4.11 | 52.92 | 2.1 | 5.70 | 25.0 | 1.808 | 2.088 | 3.617 | 2.953 |
| 0.10          | [Ni]_{0.88}^{++} [Fe]_{2.12}^{3+} [Zn]_{0.2}^{2+} [Co]_{0.1}^{2+} [O]_{4}^{2-} | 0.664 | 0.663 | 8.343 | 8.350 | 5.46 | 4.08 | 43.31 | 2.7 | 2.58 | 25.27 | 1.807 | 2.087 | 3.616 | 2.952 |
| 0.12          | [Ni]_{0.85}^{++} [Fe]_{2.15}^{3+} [Zn]_{0.2}^{2+} [Co]_{0.1}^{2+} [O]_{4}^{2-} | 0.664 | 0.662 | 8.341 | 8.361 | 5.48 | 4.43 | 62.63 | 1.9 | 3.98 | 19.16 | 1.810 | 2.090 | 3.620 | 2.956 |
The experimental lattice constant \(a\) of all the samples were calculated using the formula [48]:

\[
a_{\text{exp}} = a_{\text{hkl}} \sqrt{h^2 + k^2 + l^2}
\]

where, \(h, k\) and \(l\) are the Miller indices of the crystal planes. The calculated values are given in table 1. The obtained value of \(a_{\text{exp}}\) for \(x = 0.00\) is 8.362 Å and the previously reported value is 8.3719 Å [26]. Our obtained value is lower than the reported value, might be due to different synthesis condition. The lattice constant \(a\) variation with V content is shown in figure 2(c). At first, \(a_{\text{exp}}\) decreases with the increase of V contents and then increases for \(x = 0.12\). The trend in the lattice constant variation is observed to have a good agreement with an earlier report of V-substituted Ni–Zn ferrites [49]. The decrease of the lattice constant is owing to the differences of ionic radii (Shannon 6-coordination numbers) of V\(^{5+}\) ions (0.59 Å) and Fe\(^{3+}\) ions (0.645 Å) [50, 51].

The theoretical lattice constant of studied samples Ni\(_{0.7}\)Zn\(_{0.2}\)Co\(_{0.1}\)Fe\(_{2-x}\)V\(_x\)O\(_4\) (0 ≤ \(x\) ≤ 0.12) has also been calculated to compare with the experimental one. The lattice constant can be calculated theoretically using the following equation [2]:

\[
a_{\text{th}} = \frac{8}{3\sqrt{3}} \left[ (r_A + R_0) + \sqrt{3} (r_B + R_0) \right]
\]

where, \(R_0\), \(r_A\), \(r_B\) are the ionic radii of oxygen (1.32 Å) [52], \(A\)- and \(B\)-sites, respectively. The \(r_A\) and \(r_B\) can be calculated by the following equations [53, 54]:

\[
r_A = C_{\text{NiZn}} r(\text{Zn}^{2+}) + C_{\text{NiFe}} r(\text{Fe}^{3+})
\]

and

\[
r_B = \frac{1}{2} \left[ C_{\text{NiNi}} r(\text{Ni}^{2+}) + C_{\text{BCo}} r(\text{Co}^{2+}) + C_{\text{BFe}} r(\text{Fe}^{3+}) + C_{\text{BV}} r(\text{V}^{5+}) \right].
\]

The calculated x-ray density, bulk density, porosity, crystallite size and strain of Ni\(_{0.7}\)Zn\(_{0.2}\)Co\(_{0.1}\)Fe\(_{2-x}\)V\(_x\)O\(_4\) (0 ≤ \(x\) ≤ 0.12) samples are represented in table 1. The equations used can be found elsewhere [31]. A decreasing trend of x-ray density and the bulk density with increasing V-content till \(x = 0.12\) is noted while an inverse relation is followed by the porosity. This trend can be explained based on the atomic mass of V\(^{5+}\) (50.94 amu) and Fe\(^{3+}\) (55.84 amu). V ions of lower atomic mass decreased the density of ferrites while being substituted in place of Fe ions. Whereas, for \(x = 0.12\) the increase in density was observed due to the increase of lattice constant. Moreover, the bulk density, \(\rho_B\) is found to be lower than the \(\rho_x\), because the pores are considered in the calculations of bulk density which are absent in the x-ray density calculations [55]. The obtained crystallite size varies depending on the strain shown in table 1.

Figure 3 demonstrates FESEM images from where the changes in the microstructures owing to the V substitution can be observed. In addition, the average grain size (shown in table 1) for the compositions has been estimated by the linear intercepting method and a decreasing trend with V contents is also observed except at
x = 0.12 which is similar to the variation of density and porosity with V contents. The changes in the average grains size, density and porosity can be understood from the FESEM images. The change in average grains size is also related to the difference between ionic radii of V$^{5+}$ (0.59 Å) ions and Fe$^{3+}$ ions (0.645 Å) [50, 51]. As can be seen from table 1, smaller V ions decreased the lattice parameter of the crystallites. Hence, grain size reduced with the increasing V content as crystallites cluster together to form grains during the sintering process.

**FTIR analysis**

FTIR Spectroscopy is an important technique to study the completion of the solid-state reaction and inspect the presence of deformation in the spinel ferrites due to substitution of ions [55, 56]. In the case of ferrites, there are two characteristic peaks in the FTIR spectra. The first peak at low frequency is associated with M-O (Metal-Oxide) stretching vibrations at B-sites while the peak at higher frequency side results from M–O stretching vibrations at A-sites [57]. Figure 4 displays the FTIR spectra of V substituted Ni–Zn–Co ferrite compositions in which the peaks are observed at expected positions and confirm the completion of solid-state reaction [58]. It has two major absorption bands in the range of 365 to 800 cm$^{-1}$.

The band’s position for the studied compositions is tabulated in table 2. The bands at higher frequency ($\nu_1 = 590$ cm$^{-1}$) are for stretching vibrations of the M-O clusters at the tetrahedral site. Lower frequency bands ($\nu_2 = 365$ cm$^{-1}$) are assigned to the stretching mode of the M-O bond in the octahedral sites [59].

**Table 2.** The vibrational frequencies of two prominent IR bands corresponding to tetrahedral and octahedral sites of Ni$_{0.7}$Zn$_{0.2}$Co$_{0.1}$Fe$_{2-x}$V$_x$O$_4$ (0 $\leq$ x $\leq$ 0.12) ferrites.

| V-content (x) | $\nu_1$(cm$^{-1}$) | $\nu_2$(cm$^{-1}$) |
|---------------|--------------------|--------------------|
| 0.00          | 578.49             | 372.19             |
| 0.02          | 590.09             | 379.88             |
| 0.05          | 583.69             | 381.18             |
| 0.07          | 583.69             | 370.99             |
| 0.10          | 579.69             | 373.58             |
| 0.12          | 574.70             | 364.59             |

**Magnetic properties**

Figure 5 shows the magnetic hysteresis (M-H) loops of Ni$_{0.7}$Zn$_{0.2}$Co$_{0.1}$Fe$_{2-x}$V$_x$O$_4$ (0 $\leq$ x $\leq$ 0.12) ferrites. The parameters such as saturation magnetization ($M_s$), coercivity ($H_c$), magnetic remanence ($M_r$), etc were obtained.
from the M-H loops and listed in Table 3. The narrow hysteresis loops assure the soft magnetic nature of all the samples [60]. In the present study, the value of saturation magnetization is 71.6 emu/g for un-doped Ni–Zn–Co ferrites. Then it decreased due to V substitution which shows non-magnetic nature. The V\(^{5+}\) ions have tendency to occupy B-sites. The net magnetic moment is given by the equation:

\[ M = M_B - M_A, \]

where \( M_B \) represents the total magnetic moment at B-sites and \( M_A \) indicates the total magnetic moment at A-sites. The total magnetic moment of B-sites is lowered by replacing Fe ions with V substitution and it causes the reduction of the magnetic moment of the ferrites system. Therefore, the lowering of saturation magnetization due to V substitution is reasonable. However, the \( M_s \) is observed to increase for \( x = 0.12 \), which might be owing to the increased grain size at \( x = 0.12 \) because of the proportional relationship between magnetization and grains size [61].

The values of \( M_s \) decrease with V contents, making the demagnetizing process easier. Another important parameter, known as Bohr magneton (\( \mu_B \)) is also calculated using the relation:

\[ \mu_B = \frac{M_s}{585}, \]

\( M' \) is the molecular weight. The calculated values of \( \mu_B \) also follow the trend of \( M_s \) with V contents.

### Study of temperature-dependent permeability: Curie temperature

The magnetic properties such as saturation magnetization, permeability, etc are very sensitive to temperature. One of the characteristic parameters, Curie temperature (\( T_C \)) can be obtained from the temperature-dependent permeability. The permeability remains almost constant up to a certain temperature and after that it increases slightly by exhibiting a peak, known as Hopkinson’s peak before dropping sharply to zero. The temperature at which completely disorderliness of atomic moments took place and the ferrimagnetic materials converted to paramagnetic is known as Curie temperature (\( T_C \)). The temperature-dependent initial permeability was measured and shown for different compositions in figure 6(a). The mentioned features are also observed for our obtained data and the calculated Curie temperature is shown in figure 6(b).

The measured \( T_C \) is noted to decline with the V substitution. The transition temperature attributed to the distribution of cation over A- and B-site and the value of exchange coupling constant (\( J_{AB} \)) [62]. The \( J_{AB} \) attributed...

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**Table 3.** Saturation magnetization (\( M_s \)), Magnetic remanence (\( M_r \)), Resonance frequency (\( f_r \)) coercivity (\( H_c \)), Magnetic moment (\( \mu_B \)), Curie Tem. (\( T_C \)), Real permeability (\( \mu' \)) and Relative quality factor (RQF) for Ni\(_{0.7}\)Zn\(_{0.2}\)Co\(_{0.1}\)Fe\(_{2-x}\)V\(_x\)O\(_4\) (0 \( \leq x \leq 0.12 \)) ferrites.

| V content (x) | Saturation magnetization \( M_s \) (emu/g) | Magnetic remanence \( M_r \) (emu/g) | Resonance freq. \( f_r \) (MHz) | Coercivity \( H_c \) (Oe) | Theoretical | Experimental | Curie Tem. \( T_C \) (°C) | \( \mu' \) | RQFx10\(^3 \) |
|---------------|--------------------------------------------|---------------------------------------|-------------------------------|------------------------|-------------|--------------|----------------------|--------|-------------|
| 0.00          | 71.6                                       | 22.08                                 | 60.97                         | 277.2                  | 3.70        | 3.21         | 478                  | 253    | 5.11        |
| 0.02          | 28.24                                      | 9.42                                  | 56.92                         | 20.39                  | 3.66        | 2.78         | 476                  | 237    | 27.5        |
| 0.05          | 25.16                                      | 7.96                                  | 59.00                         | 27.36                  | 3.60        | 2.36         | 474                  | 226    | 67.6        |
| 0.07          | 22.95                                      | 7.46                                  | 59.00                         | 29.5                   | 3.56        | 1.99         | 458                  | 213    | 164.3       |
| 0.10          | 18.98                                      | 6.22                                  | 49.91                         | 20.26                  | 3.50        | 1.86         | 436                  | 184    | 203.2       |
| 0.12          | 21.55                                      | 5.36                                  | 61.20                         | 15.64                  | 3.46        | 2.15         | 465                  | 202    | 220.9       |

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from the interaction between ions on A- and B-sites, is much stronger than the \( J_{AA} \) and \( J_{BB} \) attributed from the interaction between ions of the same sites (A or B). The replacement of Fe\(^{3+}\) ions by V\(^{5+}\) ions, decrease the magnetic ions in the B-sites causing a decrease in the strength of exchange coupling constant \( J_{AB} \) and thus decrease the \( T_C \) values.

Frequency dependence of real permeability and Relative Quality Factor

Figure 7(a) shows the real part of permeability (\( \mu' \)) as a function of frequency. The toroid-shaped samples were prepared for this characterization. The value \( \mu' \) remains almost constant up to \( \approx 30 \) MHz. Then, a noticeable increase is noted at which \( \mu' \) became maximum and finally, it falls sharply to certain low values. The steady value is important for many applications such as in transformer as a broadband pulse and in video recording system as read-write heads (wideband) [63].

In different circumstances, a significant peak is exhibited by \( \mu'' \) (figure is not shown) at the frequency where sharp decline \( \mu' \) is taken place. This phenomenon is termed as ferrimagnetic resonance [64] and the prepared compositions are found to follow Snoek’s limit [65].

Figure 7(b) illustrates the composition dependence of \( \mu' \) which revealed that the initial permeability decreased gradually with V contents up to \( x = 0.10 \) and then increased slightly for \( x = 0.12 \). The permeability of ferrites depends on various factors like grain size, density, porosity, saturation magnetization, anisotropy, etc [66]. A good correlation is observed among permeability, average grain size (Table 1) and saturation magnetization (figure 5(b)). The Globus-Duplex relation \( \mu' \propto \frac{K}{D^2} \) (where, \( M_s, D \) and \( K \), represent the saturation magnetization, average grain size and anisotropic constant, respectively) can be used to explore the variation of \( \mu' \) with V contents. The above relation exhibits that the initial permeability is proportional to \( M_s \) and \( D \) where \( M_s \) and \( D \) are also found to decrease with V contents up to \( x = 0.10 \) and then increases for \( x = 0.12 \).

The relative quality factor (RQF) was calculated from the relation, \( RQF = \frac{\mu'_i}{\tan \delta} \) where \( \mu'_i \) is the initial permeability and \( \tan \delta \) is the magnetic loss evaluated from the ratio of real part of the permeability (\( \mu' \)) and imaginary part of the permeability (\( \mu'' \)) as \( \tan \delta = \frac{\mu''}{\mu'} \). It measures the performance of a material for use in a filter. Figure 7(c) shows the usual behavior of RQF versus frequency for different V contents where a prominent peak is observed for each of the compositions [31, 67, 68]. The exhibition of the peak is followed by very low values in both low and high frequency regions. The declination of RQF corresponds to the frequency (~30 MHz) corresponds to the increase of \( \mu'' \) (loss component). Moreover, the value of RQF is observed to increase owing to V substitution with the maximum for \( x = 0.12 \). The values of RQF are given in Table 3.

Dielectric behavior

A very common dielectric behavior of ferrites is that the \( \varepsilon' \) and \( \varepsilon'' \) decrease with frequency exhibiting three different responses in three ranges of frequencies: (i) a sharp decrease with low frequency in \( \varepsilon' \) and \( \varepsilon'' \) (\( \varepsilon'' \) is not shown), (ii) a slow decrease within mid-frequency range in \( \varepsilon' \) and \( \varepsilon'' \) and (iii) finally become almost frequency
independent at high frequencies \([31, 67, 69, 70]\). The frequency dependent dielectric constant \((\varepsilon')\) and dielectric loss factor \((\tan\delta = \varepsilon''/\varepsilon')\) of \(\text{Ni}_{0.7}\text{Zn}_{0.2}\text{Co}_{0.1}\text{Fe}_{2-x}\text{V}_x\text{O}_4\) \((0 \leq x \leq 0.12)\) ferrites are shown in figures 8(a) and (b). The decrease of dielectric constant can be explained by Koop's theory considering that the grains of high
conductivity are being separated by grain boundary of high resistivity in the studied ferrites [71–74]. With the increasing frequency the orientational and ionic polarization gradually decreases. Hence, the dielectric constant also reduces slowly in the mid-frequency region. It becomes almost constant at very high-frequency region because only electronic polarization happens to contribute [75]. Therefore, the decrease of $\varepsilon'$ and $\varepsilon''$ with increasing frequency is expected. From figure 8(a), it is obvious that the dielectric constant is decreased due to V substitution. The hopping mechanism is responsible for the dielectric mechanism [76, 77]. The charges produced through electron hopping between Fe$^{3+}$ and Fe$^{2+}$ are responsible for electrical conduction in ferrites. With the substitution of V in place of Fe, Fe$^{3+} \leftrightarrow$ Fe$^{2+}$ hopping decreases. Consequently, the dielectric constant reduces with the increasing vanadium concentration.

Figure 8(b) demonstrates the unusual behavior of dielectric loss (tan\(\delta\)) as a function of frequency. The curves tan\(\delta\) versus frequency exhibit resonance peak at high frequencies. Such peaks usually occur when the jumping frequency of electron hopping becomes approximately equal to that of the externally applied ac electric field [78]. This peak is observed to shift to the high-frequency side with the increasing V substitution. A similar behavior (of tan\(\delta\)) has also been reported for V substituted Ni-Zn-Cu ferrites [41], Sn substituted Ni-Zn ferrites [67] and Y substituted Mg-Zn [70].

**Frequency dependence of AC resistivity**

The frequency-dependent ac resistivity ($\rho_{ac}$) is shown in figure 9(a) within the frequency range 1 kHz – 120 MHz. The resistivity is observed to decrease with increasing frequency and then becomes invariant at high frequency [67]. Figure 9(a) also demonstrates that the ac resistivity is noted to increase with V contents as shown in figure 9(b). It is seen from figures 8(a) and 9 that the dependence of dielectric constant and ac resistivity on V contents follows the opposite trend that is normal trends in ferrites. The dependence of dielectric constant or ac resistivity on V contents can be explained by assuming two mechanisms. Firstly: the V is substituted for Fe$^{3+}$ ions at the B-sites that lead to the decrease of electronic hopping between Fe$^{3+}$ and Fe$^{2+}$ occurs at B-sites due to reduced Fe$^{3+}$ ions. Thus, The reduction of electronic conductivity responsible by the electronic hopping process is expected. Such a type of reducing electronic conductivity is also reported using Fe$^{3+}$ ions replacement with ions that tend to occupy the B-sites [67]. Secondly: the decrement of grain sizes with V contents also contributed to the enhanced resistivity.

The FESEM micrographs show that the average grains size is observed to decrease (table 1) with V contents that lead to the increase in the number of grain boundaries, the more grain boundaries results in more insulating barriers in the way of charge carriers [71]. Consequently, the decrease of grain size also revealed the reduction of the conductive area [79]. Hence, the electrical resistivity increases owing to V substitutions as shown in figure 9(b).

Figure 10 displays the variation of ac conductivity with the change of frequency. With the increasing frequency the resistivity decreases as shown in figure 9(a) and as a result, the conductivity increases.
Conclusion

Ni$_{0.7}$Zn$_{0.2}$Co$_{0.1}$Fe$_{2-x}$V$_x$O$_4$ ($0 \leq x \leq 0.12$) ferrites have been synthesized by the conventional ceramic technique. The decrease of lattice constant with V content is observed. A good correlation is noticed among lattice constant, density and porosity for different V contents. Average grain size decreases with V contents. The formation of spinel cubic ferrites is confirmed from the obtained values of vibrational frequency $\nu_1$ (in the range: 574 to 590 cm$^{-1}$) and $\nu_2$ (in the range: 364 to 382 cm$^{-1}$). Crystal sizes varies with the V substitution depending on the strain working on those. The soft ferromagnetic nature is observed from hysteresis loops with low coercive field. The lowering of $M_s$ (from 71.6 emu g$^{-1}$ to 18–28 emu g$^{-1}$) is due to non-magnetic V substitution. The Curie temperature obtained from temperature-dependent permeability decreases as V substitution reduces the strength of exchange coupling constant. The study of the frequency-dependent permeability exhibits a good correlation among average grain size and saturation magnetization. The dielectric constant reduces in V-substituted Ni–Zn–Co ferrites where the ac resistivity varies inversely with V contents. The ac conductivity increases with the increasing frequency and shows inverse relation with ac resistivity. It is also expected that the results obtained in this paper will encourage the materials scientist to investigate the effect of V substitution on other ferrites systems.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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References

[1] Carter C, Barry, Norton and Grant M 2007 Ceramic Materials: Science and Engineering (New York: Springer.Springer-Verlag) 1–728
[2] Sugimoto M 1999 The past, present, and future of ferrites J. Ame. Cera. Soci., 82 269–80
[3] Goldman A 2006 Modern Ferrite Technology (United States of America: Springer)
[4] Gul I, Ahmed W and Maqsood A 2008 Electrical and magnetic characterization of nanocrystalline Ni–Zn ferrite synthesis by co-precipitation route J. Magn. Magn. Mater. 320 270–5
[5] Knayzey A V, Zakharchuk I, Lahderenta E, Baidakov K V, Knayzeva S S and Ladenkov I V 2017 Structural and magnetic properties of Ni–Zn and Ni–Zn–Co ferrites J. Magn. Magn. Mater. 435 9–14
[6] Mikami I 1973 Role of induced anisotropy in magnetic spectra of cobalt-substituted nickel-zinc ferrites Japan. J. App. Phys. 12 678–93
[7] Abdeen A M 1998 Structural, magnetic and electrical properties of the sol-gel prepared Li$_{0.5}$Fe$_2$O$_4$ fine particles J. Magn. Magn. Mater. 185 199–206
[8] Jalaly M, Enayati M H, Kameli P and Karimzadeh F 2010 Effect of composition on structural and magnetic properties of nanocrystalline ball-milled Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ ferrite Physica B 405 507–12
[9] Kumar P S A, Shroti J J, Kulkarni S D, Deshpande C E and Date S K 1996 Low-temperature synthesis of Ni$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$ powder and its characterization Mater. Lett. 27 293–6

Figure 10. Room temperature variation of acConductivity in Ni$_{0.7}$Zn$_{0.2}$Co$_{0.1}$Fe$_{2-x}$V$_x$O$_4$ ($0, 0.02, 0.05, 0.07, 0.10$ and $0.12$) with the swiping of frequency from 10 Hz to 100 MHz
Zheng Z, Wu X, Feng Q and Harris V G 2019 Low loss and tailored high-frequency performances of BaO doped NiZnCo magneto-optical ferrites J. Magn. Magn. Mater. 428 623–6

Olsson R T, Salazar-Alvarez G, Hedenqvist M S, Gedde U W, Lindberg F and Savage S J 2005 Controlled Synthesis of Near-stoichiometric ferrite nanoparticles Nov. Magn. Mater. 30 117–20

Cartera D, Casula M F, Falqui A, Loche D, Mountjoy G, Sangregorio C and Corrias A 2009 A structural and magnetic investigation of the inversion degree in ferrite nanocrystalline MnFe2O4 (Mn = Co, Ni) J. Phys. Chem. C 113 8066–15

Mallapur M M, Shilkh P A, Kambarale R C, Jamadar H V, Mahamuni P U and Chougule B K 2009 Structural and electrical properties of nanocrystalline cobalt substituted nickel-zinc ferrite J. Alloys Comp. 479 797–802

Ghodake J S, Kamble R C, Salvi S V, Sawant S R and Suryavanshi S S 2009 Electric properties of Ni substituted Zn–Ni–Zn ferrites J. Magn. Magn. Mater. 321 1445–52

Khan A, Khan M A, Shahid M, Ashgar M, Shairk I, Naseem S, Riaz S and Wasi M F 2015 Nanocrystalline Zn1–xCo2xZn0.34Fe2O4 ferrites: Fabrication via co-precipitation route with enhanced magnetic and electrical properties J. Magn. Magn. Mater. 393 56–56

Mehdi K, Gupta V R, Gupta N and Rout S K 2014 Structural and microwave characterization of Ni0.5Co0.5Zn0.64Fe2O4 for antenna applications J. Cera. Inter. 40 1575–86

Stergiou C 2016 Microstructure and electromagnetic properties of Ni–Zn–Co ferrite up to 20 GHz Adv. Mater. Sci. and Eng. 2016 1-7 Article ID 1934783

Ghodake J S, Shinde T J, Patil R P, Patil S B and Suryavanshi S S 2015 Initial permeability of Zn-Ni-Co ferrite nanocrystalline ferrites J. Magn. Magn. Mater. 379 436–49

Hassan A, Khan M A, Shahid M, Ashgar M, Shairk I, Naseem S, Riaz S and Wasi M F 2015 Nanocrystalline Zn1–xCo2xZn0.34Fe2O4 ferrites: Fabrication via co-precipitation route with enhanced magnetic and electrical properties J. Magn. Magn. Mater. 393 56–56

Mattell I, Souriou D and Chevalier A 2018 Magnetic and dielectric properties in the UHF frequency band of half-dense Ni–Zn ferrites ceramics with Fe-excess and Fe-deficiency J. Magn. Magn. Mater. 447 9–14

Chen K, Jia L, Yu X and Zhang H 2014 A low loss NiZnCo ferrite, prepared using a hydrothermal method, for antenna applications J. Appl. Phys. 115 174508

Ren X and Gu G 2014 Electromagnetic and microwave absorbing properties of NiCoZn–ferrites doped with La3+ J. Magn. Magn. Mater. 354 44–48

Saini A, Thakur A and Thakur P 2016 Matching permeability and permittivity of Ni0.5Zn0.5Co,Fe2O4 ferrite for the substrate of large bandwidth miniaturized antenna J. Mat. Sci.: Mat. in Electr. 27 2816–23

Stergiou C and Litsardakis G 2014 Structural and magnetic properties of yttrium and lanthanum-doped Ni-Co ferrite J. Magn. Magn. Mater. 371 388–91

Hassan M D, Khan M N I, Nahar A, Ali M A, Matin M A, Hoque S M, Hakim M A and Jamil A T M K 2020 Tailoring the properties of Ni–Zn–Co ferrites by Gd3+ substitution J. Magn. Magn. Mater. 497 165978

Hankare P P, Jadhav S D, Sankpal U B, Chavan S S, Waghmare K J and Chougule B K 2009 Synthesis, characterization and effect of sintering temperature on magnetic properties of MgNi ferrite prepared by co-precipitation method J. Alloys Compd. 473 926

Harris V G et al 2009 Recent advances in processing and applications of microwave ferrites J. Magn. Magn. Mater. 321 2035

Kaiser M 2010 Influence of V2O5 ion addition on the conductivity and grain growth of Ni–Zn–Cu ferrites J. Appl. Phys. 107 975–84

Lu J, Yao G, Liu Y, Ma J and Zu G 2012 Obtaining and characterization of Zn–V2O5 and Mg–V2O5 pseudo-binary oxide nanomaterials by hydrothermal method J. Ceram. Int. 38 1707–11

Ji L, Shi G, Ni Z, Zheng L and Chen A 2012 Effects of V2O5 addition on NiZn ferrite synthesized using two-step sintering process Physica B 407 2205

Korkmaz A D et al 2011 Structural, optical, and magnetic properties of vanadium-substituted nickel spinel Nanoferrites J. Super. Nov. Magn. 32 1057–65

Maismam M, Phanjoubam S, Sharma H K, Chandra P K, Devi L R and Thakur O P 2004 Magnetic properties of vanadium-substituted lithium zinc titanium ferrite Materials Letters 58 2412–412

Silmani Y, Almesiere M A, Guner S, Tashkandi N A, Baykal A, Sarac M F, Nawaz M and Ercan I 2019 Calcination effect on the magneto-optical properties of vanadium substituted NiFe2O4 nanoparticles J. Magn. Magn. Mater. 403 9145–9154

Helba Z K, Bakr Mohamed M and Ahmed S L 2017 Cation distribution correlation with magnetic properties of cobalt ferrite nanoparticles defective by vanadium doping Journal of Magnetism and Magnetic Materials 441 409–16

Kaiser M 2010 Magnetic and dielectric properties of low vanadium doped nickel–zinc–copper ferrites J. Phys. and Chem. of Solids 71 1451–7

Mizraee O, Golozar M A and Shafeyi A 2008 Influence V2O5 as an effective dopant on the microstructure development and magnetic properties of Ni1–xZnxFe2O4 soft ferrites J. Mater. Chem. 19 59689

Jain H and Lee C H 2001 Processing and Properties of Low-Fire Ni–Zn–Cu Ferrite with V2O5 J. Appl. Phys. 90 20232

Arulmurugan R, Jeydevan B, Vaidyanathan G and Sendhilnathan S 2005 Effect of zinc substitution on Co-Zn and Mn-Zn ferrite nanoparticles prepared by co-precipitation J. Magn. Magn. Mater. 288 470

Koseoglu Y, Baykal A, Gouzuk A and Fas Hava S 2009 Structural and magnetic properties of Co3Zn1–xFe2O4 nanocrystals synthesized by microwave method Polyhedron 28 2887

Baradpurkar P P, Shewale S S, Barde N P and Jadhav K M 2019 Structural, magnetic and catalytical properties of cobalt ferrite nanoparticles dispersed in silica matrix Mater. Res. Exp. 6 045035

Hewitt PG 1993 Conceptual Physics (New York, USA: Harper Collins College Publishers) 7th ed.

Angadi V J, Rudrawantasy B, Sadhana K, Murthy S R and Praveena K 2016 Effect of Sm3+–Gd3+ on structural, electrical and magnetic properties of Mn–Zn ferrites synthesized via combustion route J. Alloy. Compd. 656 5–12
[49] Jacoboa S E and Berkofof P G 2016 Structural and electromagnetic properties of yttrium-substituted Ni–Zn ferrites J. cera. Inter. 42 1–5
[50] Gadkari A, Shinde T and Vasambekar P 2009 Structural analysis of Y 3+–doped Mg–Cd ferrites prepared by oxalate co-precipitation method Mat. Chem. Phys. 114 503–10
[51] Kamble R, Shahik P, Kamble S and Kolekar Y 2009 Effect of cobalt substitution on structural, magnetic and electric properties of nickel ferrite J. Alloys Comp. 478 599–603
[52] Shannon R D and Prewitt C T 1969 Effective ionic radii in oxides and fluorides Acta Crystaloggr. 25 925–46
[53] Panatage S M, Shirsath S E, Toksha B G, Jadhav S, Sukla S J and Jadhav K M 2009 Cation distribution by Rietveld, spectral and magnetic studies of chromium-substituted nickel ferrites J. App. Phys., A 95 629–34
[54] Globus A, Passcard H and Cagan V 1977 Distance between magnetic ions and fundamental properties in ferrites J. de Phys. Colloq. 38 C1–163–C1–168
[55] Machefert J M, Calvar M L and Lenglet M 1991 FTIR study of nickel and copper oxidation: Theoretical approach and experience J. Surf. Interface Anal. 17 137–42
[56] Lefez B and Jouen S 2001 FTIR microscopic base imaging system: Applications for chemical analysis of Zn and Ni atmospheric corrosion J. Appl. Spectrosc. 55 935–8
[57] Waldron R D 1955 Infrared Spectra of Ferrites Physica Review 99 1725–7
[58] Hemeda O M, Said M Z and Barakat M M 2001 Spectral and transport phenomena in Ni ferrite-substituted Gd2O3 J. Magn. Magn. Mater. 224 132–42
[59] White W B and De. Angelis W A 1967 Interpretation of the vibrational spectra of spinels Spectrochimica Acta Part A: Molecular Spectroscopy Part A 23 985–95
[60] Maxwell L R and Pickart S J 1953 Magnetization in Nickel Ferrite–Aluminates and Nickel Ferrite Gallates Phys. Rev. 92 1120
[61] Tukaram V, Shinde S B, Borade R B and Kadam A B 2019 Study of cation distribution, Structural and Electrical Properties of Al-Zn Substituted Ni-Co ferrite Physica B & Phys. Cond. Matt. 577 411783
[62] Alves T E P, Pessoni H V S and Franco A 2017 The effect of Y 3+ substitution on the structural, optical, Band Gap and magnetic properties of cobalt ferrites nanoparticles Jr. Phys. Chem. Chem. Phys. 19 16395
[63] Ashok K, Masin B, Sreemoolanadhan H and Mathew M 2019 Trans. Ind. Ceram. Soc. 78 1
[64] Brockman F G, Dowling P H and Steneck W G 1950 Dimensional effects resulting from high dielectric constant found in a ferromagnetic ferrite Phys. Rev. 77 85
[65] Snoek J L 1948 Effect of Sintering Time on the Structural, Magnetic and Electrical Transport Properties of MgFe0.35Cu0.2Zn0.45Fe1.94O4 Ferrites Physica 14 207–17
[66] Low K O and Sale F R 2002 Electromagnetic properties of gel-derived NiCuZn ferrites J. Magn. Magn. Mater. 246 30–5
[67] Ali M A, Khan M N I, Chowdhury F U Z, Hossain M M, Akhter Hossain A K M, Rashid R, Nahar A, Hoque S M, Matin M A and Uddin M M 2019 Yttrium-substituted Mg–Zn ferrites: correlation of physical properties with Yttrium content J. Mater. Sci.: Mater. Elect. 30 13258–70
[68] Ali M A, Uddin M M, Khan M N I, Chowdhury F U Z, Hoque S M and Liba S I 2017 Magnetic properties of Sn-substituted Ni–Zn ferrites synthesized from nano-sized powders of NiO, ZnO, Fe3O4, and SnO2 J. Chin. Phys. B 26 077501
[69] Ali M A, Khan M N I, Chowdhury F U Z, Akhter S and Uddin M M 2015 Structural properties, impedance spectroscopy and dielectric spin relaxation of Ni–Zn Ferrite synthesized by double sintering technique J. Sci. Res. 7 65–75
[70] Ali M A, Uddin M M, Khan M N I, Chowdhury F U Z and Haque S M 2017 Structural, morphological and electrical properties of Sn-substituted Ni–Zn Ferrite synthesized by double sintering technique J. Magn. and Magn. Mater. 424 148–54
[71] Koops C G 1951 On the dispersion of resistivity and dielectric constant of some semiconductors at audio frequencies Phys. Rev. 83 121
[72] Maxwell C J 1973 Electricity and Magnetism (New York: Oxford University Press)
[73] Wagner K W 1973 The Distribution of Relaxation Times in Typical Dielectrics Ann. Phys. 40 817–9
[74] Barde N P, Shewale S S, Solanki P S, Shah N A and Bardaparkar P P 2021 Effect of silica matrix on structural, optical and electrical properties of Zn0.55Y0.2Zn0.25Fe1.94O4 nanoparticles ScriptaMaterialia 194 113712
[75] Verma A and Chatterjee R 2006 J. Magn. Magn. Mater. 306 313
[76] Robinkin L T and Novikova Z I 1980 Ferrites IzV Acad. Nauk USSR Minish 1960 146
[77] Iwaoichi K and Ikeda Y 2008 Dielectric behavior and ac electrical conductivity study of Sm 3+ substituted Mg–Zn ferrites J. Mater. Chem. Phys. 112 68–73
[78] Hossain A K M, Mahmud S T, Seki M, Kawai T and Tabata H 2007 Structural, electrical transport, and magnetic properties of Ni1+xZn0.3Fe2O4 J. Magn. Magn. Mater. 312 210–19
[79] Esha I N, Tomo F T, Al-Amin M, Khan M N I and Maria K H 2018 Synthesis of type-II based (1-x)Bi1001-xFe2O3(Ca1/2Sr1/2)3Ti3Fe2O7 composites via traditional solid-state reaction method and investigation of multiferroic properties J. AIP Adv. 8 125207