Effect of V2O5 Additive on Structural and Magnetic Properties of Ni-Zn ferrite

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Abstract
The In this work, the structural and magnetic properties of Ni-Zn ferrite by addition of additive V2O5 powders were investigated. Ni0.7Zn0.3Fe2O4+xV2O5 (where x = 0.0 and 0.2) powders were prepared by solid state reaction method. The identification of phase impurity by the addition of V2O5, examined by X-ray diffractometer and infrared spectroscopy, X-ray patterns reveal that all the samples have single-phase cubic spinel structure. Infrared spectroscopy was used to locate the absorption bands and to study the influence of addition V2O5 on the spinel structure of the presently investigated system. The lattice constant and x-ray density were calculated from the XRD data. The density of the samples was measured and consequently the porosity was calculated too. Magnetic properties were carried out by means of magnetization measurement to study the magnetic interaction between the ions. This paper mainly focused and discussed the effect of additive V2O5 on properties of Ni-Zn ferrite.

Keywords: Additive, Structural, Magnetic, Ferrite, V2O5.

1. Introduction

The Ferrites are the class of magnetic materials which consist of a mixed oxide of iron and other elements that are used prepared crystalline structure. The crystalline structure is made by heating the ferrite material at an ultra high temperature for a proper time and protocol. The general formula of composition of ferrites is MFe2O4 where M any divalent metals. One of the most attractive metal combinations in ferrite is nickel and zinc (Ni-Zn) which can be easily magnetized. Magnetic nanoparticle has several applications in industrial and medical field [1].

Ni-Zn ferrites has widely used in many technological applications. Ni-Zn ferrites is a soft magnetic ceramic that has spinel configuration based on a face-centered cubic lattice of the oxygen ions. Nowadays, these materials are largely studied in the search for improved properties [2] and new applications [3] especially in the nano-metric scale as ultrafine powders [4] and thin films [4]. Ni-Zn have been used as high-frequency ferrites for transformers core, rod antennas, radio frequency and more recently as microwave absorbing materials. Ferrite nanoparticles have received increased attention due to its chemical stability and high magnetocrystalline anisotropy, which can lead to a broad range of applications, from medicine and pharmacy to electronics and mechanics. [5-7]

The magnetic properties of Ni-Zn ferrites are strongly dependent on their chemical composition [8], porosity, grain size, etc. [9]. Regarding to the applications, the most important properties of spinel ferrites are conductivity and type of dominant charge carriers, saturation magnetization, coercivity etc. The spinel ferrites exhibit relatively high resistivity, sufficient low eddy current and dielectric loss for microwave applications. Moreover, the magnetic properties of ferrites, as well as the others iron oxides, change considerably when they are prepared as nanoparticles. Ferrites are commonly produced by a ceramic process involving high-temperature solid-state reactions between the constituent oxides or carbonates. In general, spinel ferrites are prepared by ceramic technology in which oxides or carbonates of the respective ions are used as a raw material [10-12]. The ceramic method is most convenient, easy and cost effective to obtain dense and high quality spinel ferrite materials. This method requires high temperature about 1100°C to complete the solid state reaction. Besides, the preparation technique and additives play an important role in modifying the properties of spinel ferrite. Usually various oxides like niobium oxide, vanadium oxide, tungsten oxide etc. are used as additives. It is reported that additives play an important role in governing the structural, electrical and magnetic properties of spinel ferrite [13-15]. In the literature, various additives like V2O5, WO3, Nb2O5 etc were incorporated in the spinel lattice to understand their effect on the structural, electrical, and magnetic properties [16]. To the best of our knowledge, effect of V2O5 additive in mixed Ni-Zn spinel ferrite on the various properties has not been systematically investigated. In this work, we report the effect of V2O5 additives in Ni0.7Zn0.3Fe2O4 spinel ferrite prepared using solid state reaction method on the structural and magnetic properties as a function of V2O5 mole percent.
2. Experimental

Nickel zinc spinel ferrite of chemical formula \( \text{Ni}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4 \) was prepared by the solid state reaction method. The oxides used as Nickel oxide (NiO), Zinc oxide (ZnO), Ferric oxide (Fe\( _2 \text{O}_3 \)) and Vanadium oxide (V\( _2 \text{O}_5 \)) of high purity (\( \geq 99.9\% \)) were used as a raw material. The respective oxides were weighed accurately and mixed homogeneously using agate pestle mortar to yield the given compositions \( \text{Ni}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4+x\text{V}_2\text{O}_5 \) (\( x =0.0, 0.2 \)).

Initially, the oxide ingredients were heated at 200°C to remove the moisture. Then the mixed powder was heated at 900°C for 24 h and again ground it for 3h. The calcined mixed powder was pressed into circular disc shaped pellet of 10 mm diameter and ~3 mm thickness at a pressure of 5 tons using a hydraulic press. Polyvinyl alcohol (PVA) was used as binder which was burnt out during high temperature sintering. These pellets were then sintered at 1080°C for 6 h in an alumina crucible in air atmosphere. The prepared sample of each composition was used for the characterization and various measurements. The pellets were polished by a fine emery paper to make their faces smooth and parallel.

Characterizations

The \( \text{V}_2\text{O}_5 \) added \( \text{Ni}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4 \) spinel ferrite system was subjected to various characterization techniques like X-ray diffraction (XRD), Fourier transform infrared (FTIR) for its structural and functional group studies. Moreover, the magnetic measurements were carried out by using pulse field hysteresis loop tracer technique at room temperature. X-ray diffraction (XRD) measurements are obtained at room temperature (Bruker Advanced D8), operated at 40 kV and 20 mA, utilizing a CuK\( _\alpha \) radiation source (\( \lambda = 1.54056 \) Å) in the 2\( \theta \) range 20-80° with step of 0.01° and time/step 2 s. Bulk density and apparent porosity of sintered specimens were determined by the Archimedes principle. An infrared study of calcined powders was done using an FTIR instrument (NICOLET-NEXUS-870). Pulse field hysteresis loop tracer supplied by Magneta Pvt. Ltd. Mumbai was used to measure the magnetic properties of the samples at room temperature. The field applied during measurements was \( \pm 5000 \text{ Oe} \).

3. Results and Discussion

The crystal structure of Ni-Zn ferrites with the addition of \( \text{V}_2\text{O}_5 \) for various composition (\( x=0.00 \) and 0.2) was analyzed using an X-ray diffraction (XRD) technique to identify the formation of a single phase cubic spinel structure. The phase identification and structural analysis of the samples \( \text{Ni}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4+x\text{V}_2\text{O}_5 \) (\( x =0.0 \) and 0.2) was done by XRD patterns which are shown in figure 1. (a) and (b).

The observed peaks in XRD patterns are sharp and intense. The presence of planes as (220), (311), (222), (400), (422), (511) and (440) in the XRD pattern which are allowed in cubic spinel structure reveals the formation of cubic spinel structure of each sample. Thus, the obtained XRD pattern exhibits the single phase cubic spinel structure [17]. An additive forming a liquid phase during sintering gives rise to pore-free grains and improves mass transport mechanisms due to the capillary forces between particles. The oxides of transition elements \( \text{V}_2\text{O}_5 \) melt at 670°C and form a liquid phase [18, 19]. The incorporation of \( \text{V}^{5+} \) ions into the spinel introduces complexities in the system such as creation of \( \text{Fe}^{2+} \) ions and precipitation of \( \text{Fe}_2\text{O}_3 \) as a second phase. The structural parameters such as lattice parameter, crystallite size and X-ray density were determined using XRD data and their values are tabulated in table 1. The lattice constant of the samples
Ni_{0.7}Zn_{0.3}Fe_{2}O_{4}+xV_{2}O_{5} (x = 0.0 and 0.2) spinel ferrite was calculated using the following standard relation [20]

\[
\frac{1}{d^2} = \left(\frac{h^2+k^2+l^2}{a^2}\right) \beta F(t)
\]  

where, \((d)\) is interplanar spacing; \((h k l)\) is Miller Indices.

The lattice parameter \((a)\) as calculated from the XRD data has been observed for both the sample is 8.380 Å and 8.381 Å for \(x=0.0\) and 0.2 respectively. It is noticed from the values of lattice parameter does not vary much rather it remains almost constant. This can be explained from the compositional formula that, although \(V^{5+}\) ions have a smaller radius (0.59 Å) than \(Fe^{3+}\) ions (0.64 Å) and \(Ni^{2+}\) ions (0.69 Å), its incorporation into lattice results in the creation of some \(Fe^{2+}\) ions which have an ionic radius (0.74 Å) [21, 22]. Similar variation of lattice parameter is reported in the literature [23]. The bulk density of V_{2}O_{5} added Ni-Zn spinel ferrite specimens has been determined by the Archimedes principle, while the X-ray density for each composition was calculated using the relation [24, 25]:

\[
d_B = \frac{2M}{NV_A}
\]

where, \(Z\) is the number of molecules per formula unit \((Z = 8\) for spinel system), \(M\) the molecular weight, \(V\) is the unit cell volume and \(N_A\) is the Avogadro’s number.

The obtained values of bulk density and X-ray density are given in relation (2). It is observed that the bulk density found to be 4.246 and 4.286 by the addition of additive V_{2}O_{5}. The increase in density can be attributed to the fact that for the present samples anion vacancy concentration increases which prohibits the discontinuous grain growth with results in increase in the density. The percentage porosity \(P\) (%) was calculated using a standard relation [26].

\[
P\% = 1 - \left(\frac{d_B}{d_c}\right)\%
\]

where, \(d_B\) is the bulk density and \(d_c\) is the X-ray density.

The values of porosity for each sample were obtained and their values are given in Table 1. The porosity of given sample found to be 21.906 and 21.416. The change in the density and porosity with increasing \(V^{5+}\) content may be due to the reduction of oxygen vacancies which play a predominant role in accelerating densification; this means that the decrease in oxygen ion diffusion would retard the densification. The X-ray density was found higher than the bulk density. This can be attributed to the existence of pores which depend on the sintering condition [27].

Average crystallite size of V_{2}O_{5} added Ni-Zn spinel ferrite estimated using Scherrer’s equation [28].

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

where, \(\beta\) is the full width half maximum intensity of a Bragg’s reflection, \(\lambda\) is the wavelength of the X-ray radiation, \(t\) is the average crystallite size and \(\theta\) is the Bragg’s angle. It observed that the crystallite size increases from 2.453 to 2.666 due to change increases in lattice parameter by addition of V_{2}O_{5}. The distance between magnetic ions (hopping length) in the tetrahedral site \((L_A)\) and octahedral site \((L_B)\) was determined according to the relation [29].

\[
L_A = a\sqrt{(3/4)}
\]

\[
L_B = a\sqrt{2/4}
\]

The variation of the hopping length for A-site \((L_A)\) and the B-site \((L_B)\) with the \(V^{5+}\) dopant is tabulated in Table 3. It is observed that the distance between magnetic ions (hopping length) of \(L_A\) and \(L_B\) exhibits similar behavior as that of lattice constant. The values of the tetrahedral and octahedral bond length \((d_{AL} \text{ and } d_{BL})\), the tetrahedral edge \((d_{AE})\) and the shared and unshared octahedral edge \((d_{BE} \text{ and } d_{BEU})\) were calculated by using the relations [30] and their values are presented in Table 3.

\[
d_{AL} = a(3(\sqrt{u-1/4}))^{1/2}
\]

\[
d_{BL} = a[3u^2-(1/4)u+(43/64)]^{1/2}
\]

\[
d_{AE} = a[2(1-2u)]^{1/2}
\]

\[
d_{BE} = a[2u-1/2]^{1/2}
\]

\[
d_{BEU} = a\sqrt{(4u^2-3u+11/16)}
\]

These structural parameters are found to depend on lattice parameter. In the present case, the lattice constant changes with doping of \(V^{5+}\) ions in Ni-Zn ferrites hence \(d_{AL}, d_{BL}, d_{AE}\) and \(d_{BE}, d_{BEU}\) (shared, unshared) all these structural parameters changes. The radius of tetrahedral sites \((r_A)\) can vary, depending upon the nature and ionic radii of the constituent ions. The tetrahedral A-site ionic radii can be calculated using the values of lattice constant ‘\(a\)’ and oxygen positional parameter ‘\(u\)’ \((u = 0.381Å)\). Table 4 gives the values of tetrahedral radius \(r_A\), the values of ‘\(r_A\)’ increases with substitutions of \(V^{5+}\) ions in Ni-Zn ferrites. The octahedral radius ‘\(r_B\)’ of all the samples under investigation was calculated using the values of lattice constant ‘\(a\)’ and oxygen parameter ‘\(u\)’. Octahedral radius ‘\(r_B\)’ increases with doping of \(V^{5+}\) ions in Ni-Zn ferrite. The values of octahedral radius for each sample were found to be greater than tetrahedral radius which can be observed from Table 3. The theoretical lattice parameter \((a_{th})\) can be calculated using this equation. The values of \(a_{th}\) are shown in table 3. The variation of theoretical values of lattice constant is similar to that of experimentally determined lattice parameter.
Table 1: Lattice parameter (a), X-ray density (\(d_a\)), Bulk density (\(d_b\)), Porosity (\(P\) %), Unit cell volume (\(V\)) and Crystallite size (\(t\)) of Ni\(_{0.7}\)Zn\(_{0.3}\)Fe\(_2\)O\(_4\)+\(x\)V\(_2\)O\(_5\).

<table>
<thead>
<tr>
<th>(x)</th>
<th>(a) (Å)</th>
<th>(d_a) (gm/cm(^3))</th>
<th>(d_b) (gm/cm(^3))</th>
<th>(P) (%)</th>
<th>(V) (Å(^3))</th>
<th>Crystallite size ((t))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>8.380</td>
<td>5.437</td>
<td>4.246</td>
<td>21.906</td>
<td>588.5</td>
<td>2.453</td>
</tr>
<tr>
<td>0.20</td>
<td>8.381</td>
<td>5.454</td>
<td>4.286</td>
<td>21.416</td>
<td>588.7</td>
<td>2.666</td>
</tr>
</tbody>
</table>

Table 2: Ionic radii (\(r_A\), \(r_B\)), Theoretical lattice parameter (\(a_{th}\)) and Hopping length (\(L_A\), \(L_B\)), of Ni\(_{0.7}\)Zn\(_{0.3}\)Fe\(_2\)O\(_4\)+\(x\)V\(_2\)O\(_5\) system.

<table>
<thead>
<tr>
<th>(x)</th>
<th>(r_A) (Å)</th>
<th>(r_B) (Å)</th>
<th>(a_{th}) (Å)</th>
<th>(L_A) (Å)</th>
<th>(L_B) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.5814</td>
<td>0.7247</td>
<td>8.3800</td>
<td>3.6286</td>
<td>2.9628</td>
</tr>
<tr>
<td>0.20</td>
<td>0.5816</td>
<td>0.7250</td>
<td>8.3800</td>
<td>2.5283</td>
<td>2.4488</td>
</tr>
</tbody>
</table>

Table 3: Tetrahedral bond (\(d_{AL}\)), Octahedral bond (\(d_{BL}\)), Tetra edge (\(d_{AE}\)) and Octa edge (\(d_{BE}\)) of Ni\(_{0.7}\)Zn\(_{0.3}\)Fe\(_2\)O\(_4\)+\(x\)V\(_2\)O\(_5\) system.

<table>
<thead>
<tr>
<th>('x')</th>
<th>(d_{AL}) (Å)</th>
<th>(d_{BL}) (Å)</th>
<th>(d_{AE}) (Å)</th>
<th>(d_{BE}) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>1.9014</td>
<td>2.0460</td>
<td>3.1050</td>
<td>2.8206</td>
</tr>
<tr>
<td>0.20</td>
<td>1.9016</td>
<td>2.0602</td>
<td>3.1054</td>
<td>2.8209</td>
</tr>
</tbody>
</table>

Table 4: Saturation magnetization (\(M_s\)), Remanence magnetization (\(M_r\)), Coercivity (\(H_C\)), Remanence ratio (\(M_r/M_s\)) and Magneton number (\(n_B\)) for Ni\(_{0.7}\)Zn\(_{0.3}\)Fe\(_2\)O\(_4\)+\(x\)V\(_2\)O\(_5\) system.

<table>
<thead>
<tr>
<th>('x')</th>
<th>(M_s) (emu/g)</th>
<th>(M_r) (emu/g)</th>
<th>(H_C) (Oe)</th>
<th>(n_B) (μa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>62.70</td>
<td>2.15</td>
<td>23.79</td>
<td>2.041</td>
</tr>
<tr>
<td>0.20</td>
<td>74.60</td>
<td>2.26</td>
<td>18.71</td>
<td>2.429</td>
</tr>
</tbody>
</table>

Analysis of infrared absorption spectra for all the compositions of V\(_2\)O\(_5\) substituted Ni-Zn spinel ferrite in the range of 500-4000 cm\(^{-1}\) was recorded at room temperature by using SHIMADZU FTIR spectrometer as shown in Fig.2 (a) and (b).

The spectrum transmittance (%) against wave number (cm\(^{-1}\)) is used for interpretation of the results. The study of far-infrared spectra is an important tool to get the information about the position of ions in the crystal. Spectra for the compositions of Ni\(_{0.7}\)Zn\(_{0.3}\)Fe\(_2\)O\(_4\)+\(x\)V\(_2\)O\(_5\) (\(x = 0.0\) and 0.2) have been taken in the range of 500 - 4000 cm\(^{-1}\). Fig. 3 & 4 shows the spectra of V\(_2\)O\(_5\) substituted Ni-Zn (\(x = 0.0\) and 0.2) spinel ferrite. In the spectra, higher frequency band and lower frequency band are assigned to the tetrahedral and octahedral complexes respectively. The strong absorption bands (\(\nu_1, \nu_2\)) around 600 cm\(^{-1}\) and 400 cm\(^{-1}\) in each spectrum which are characteristic bands of the tetrahedral and octahedral metal ions have been reported in the literature\[31, 32\], which is attributed to tetrahedral and octahedral complexes of Fe\(^{3+}\)- O\(^2-\). These two bands have been reported by Waldron in spinel structure of ferrite \[33\]. No shift of absorption band \(\nu_1\) is observed. The absorption band \(\nu_2\) is slightly shifted to a higher frequency side with addition of V\(^{5+}\) ions and is attributed to increase in bond length on the B-site \[33\]. This suggests that the V\(^{5+}\) ions occupy the B-site. The difference in frequencies between \(\nu_1\) and \(\nu_2\) is due to changes in bond length (Fe\(^{3+}\)- O\(^2-\)) at tetrahedral and octahedral sites. The broadening of the \(\nu_2\) band is observed in V\(^{5+}\) substituted Ni-Zn, which suggests the occupancy of V\(^{5+}\) ions on the B-sites \[34\]. The IR band width depends on the cation distribution of the material.

Literature survey showed that the crystallite size is one of the most important parameters affecting the magnetic properties of ferrites. Grain growth kinetics; however, depend strongly on the impurity content \[34, 35\]. It is well known that the dominate microstructural parameters which are important for achieving high permeability are a high sintered density, a large average grain size and clean and stress-free grain boundaries \[36\]. Small amounts of additives can greatly affect the properties of ferrites \[37\]. The magnetic permeability of polycrystalline ferrite strongly depends on the grain size. When the grain size increases, the permeability increases \[38\]. V\(_2\)O\(_5\) is added because of its reactive liquid phase forming properties and because of its beneficial effects when substituted into the lattice. Addition of each V\(^{5+}\) ion, introduces two Fe\(^{2+}\) to satisfy the site and charge balance, which means that \([\text{Fe}^{2+}] / [\text{Fe}^{3+}]\) ratio increases.

4. Conclusions

The Ni\(_{0.7}\)Zn\(_{0.3}\)Fe\(_2\)O\(_4\)+\(x\)V\(_2\)O\(_5\) spinel ferrites have been synthesized successfully using standard solid state reaction method. X-ray studies of both the samples with additive (V\(_2\)O\(_5\)) ion exhibit a cubic spinel structure. The change in the values of lattice constant of V\(^{5+}\) ions doped in Ni-Zn ferrite is due to larger ionic radii of the V\(^{5+}\) ions as compared to the Fe\(^{3+}\) ions. The X-ray density and bulk
density increases with V$^{5+}$ doped in Ni-Zn spinel ferrites. However, decreasing trend in porosity was attributed to the substitution of V$^{5+}$ thereby making all samples denser. The analysis of FTIR spectra, it was found that when Fe$^{3+}$ is replaced with V$^{5+}$ ions, almost minor changes are observed in the band position of FTIR spectra. The saturation magnetization and the magneton number decreases with increasing of V$^{3+}$ content as compared to pure Ni-Zn spinel ferrite.

References


[36] O. Mirzaee, M. Golozar, A. Shafyei, Influence of V 2 O 5 as an effective dopant on the microstructure development and magnetic properties of Ni 0.64 Zn 0.36 Fe 2 O 4 soft ferrites, Materials characterization, 59 (2008) 638-641.
