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RESEARCH ARTICLE

FT-IR Studies of Nickel Substituted Polycrystalline Zinc Spinel Ferrites for Structural and Vibrational Investigations

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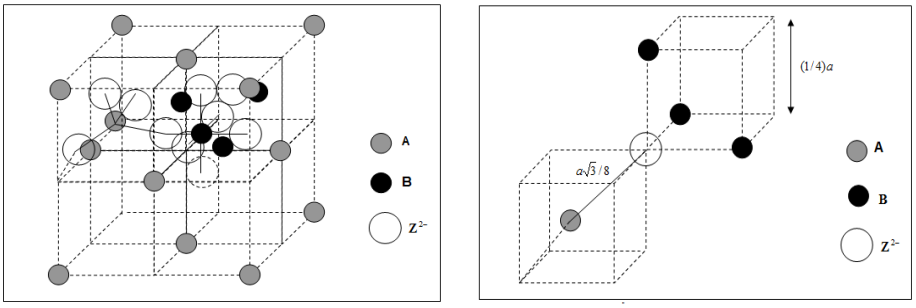
Abstract: FT-IR spectra of $Ni_{1-s}Zn_sFe_2O_4$ spinel ferrite, *s* changed by 0.2 according to $0.0 \leq s \leq 1.0$, have been analyzed in the frequency range (350−1000) cm^{-1}. Six polycrystalline ferrites samples were synthesized using the conventional standard double sintering ceramic method. Two main absorption bands were observed, their positions were found to be strongly dependent on *s*-value. The high frequency band in the range 550-600 cm^{-1} and a low frequency band at around 400 cm^{-1} were assigned to tetrahedral T_d and octahedral O_h sites, respectively, of spinel lattice. Force constant (F_C) was calculated for $T_d$and O_h sites and was found to decrease with increasing Zn ions. Threshold frequency ν^{th} for the electronic transition was determined and found to increase with increasing Zn ions. Cations distribution for the prepared mixed ferrite was concluded based on the FT-IR spectra. The ionic radii for each site were correlated to the cations distribution of the given ferrite.

Keywords: Spinel, Ferrite, Nickel, Zinc, Cation

Introduction

Spinel ferrites have been studied extensively due to easy synthesis and abundant uses in technological and industrial applications[1]. A general chemical formula of spinels is DT_2O_4, D and T is divalent and trivalent cations, respectively[2-4]. The generic structural formula or cations distribution of spinels can be expressed by $(D_{1-s}T_s)_{Tet.}\{D_sT_{2-s}\}_{Oct.}O_4^{2-}$, with $0.0 \leq s \leq 1.0$ which is the inversion parameter (degree of inversion), $(\ )_{Tet.}$ and $\{\ \}_{Oct.}$ are tetrahedral (T_d) and octahedral (O_h) sites, respectively[5,6]. Depending on cations distribution, spinel consists of three types of magnetic structures, they are; normal (S=0.0), perfectly inverse (S=1.0) and otherwise partially inverse or intermediate ($0.0 < s < 1.0$)[5-7]. The degree of inversion in the spinel lattice depends on ionic radii, ionic charge, electrostatic (Madelung) energy, electronic configuration, relative stabilization energies in the T_d and O_h fields, short-range

Born repulsion energy, crystal field effects and polarization effects[6-9]. For spinel ferrites with $T = Fe^{3+}$ *i.e.* $DFe_2^{3+}O_4^{2-}$, the distribution of the different ions in the T_d and O_h sites mainly depends on the method of preparation and processing conditions[10]. The mixed polycrystalline soft spinel ferrites $(Zn,Ni)Fe_2O_4$ have been intensely studied because of their remarkable high-frequency operation (1-100 GHz) as well as because of their favorable properties such as low eddy current losses and high of resistivity, permeability, Curie temperature and saturation magnetization in the radio frequency (RF) region[11-14]. Therefore, it plays a significant role in many applications[1,11,13-19]. The structure of $(Zn,Ni)Fe_2O_4$ spinel ferrite belongs to a close-pakced spinel face-centered cubic (*fcc*) with $O_h^7(Fd3m)$ space group symmetry (Figure 1)[6,17,20-22]. In the present investigation, we are measured and discussed the fourier transformation infrared (FT-IR) spectra of mixed polycrystalline soft ferrites of cubic spinel structure $Ni_{1-s}Zn_sFe_2O_4$ powders, where *s* = 0.0 to 1.0 in step of 0.20, which have been carried out by normal conventional ceramic method.



a b

Figure 1. (a) Two octants of the unit cell of the spinel lattice structure. A and B ions are at T_d and O_h sites of the Z^{2-} anions packing. (b) An anion Z^{2-} in the spinel lattice structure with its nearest cations neighbors[9].

Experimental

The mixed polycrystalline ferrites $Ni_{1-s}Zn_sFe_2O_4$, where *s* is the percentage increment of *Zn* ions on the compound which have the value *s* = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0, were prepared by using the standard double sintering (SSR) by mixing pure metal oxides in the calculated proportions according to the formula

$$(1-s)NiO + sZnO + Fe_2O_3 \rightarrow Ni_{1-s}Zn_sFe_2O_4$$

25.0 g from high purity metal oxides were used to prepare each composition of the investigated polycrystalline spinel ferrites. The metal oxides were weighed using a sensitive electric balance (ADAM model PW124) with an accuracy $1x10^{-4}$ g. The weighed metal oxides were mixed and then grounded to a very fine powder for 5 h. The mixed powder of metal oxides was pre-sintered at 750 ^oC for 3 h soaking time using a laboratory Furnace (BIFATHERM model AC62). Then the prefired powder was well ground for 3 h and pressed with hydraulic press under constant pressure of $3x10^8$ pa, After that, samples were sintered at 1200 ^oC for soaking time of 5 h using a laboratory Furnace (BIFATHERM model A C62). After sintering process, the samples were cooled down gradually to room temperature.

For recording FT- IR spectra, the powder of the samples was mixed with Potasium Bromide (KBr) at a ratio of 1:200 by weight to uniform dispersion in KBr pellet. The mixed powder of samples were pressed at $3x10^8$ pa by a hydraulic press. Clean discs with a thickness approximate of 1.0 mm were obtained. FT-IR spectra in the range from 350 to 1000 cm^{-1} were recorded in room temperature using FT-IR Spectrophotometer (Cary 660 FT-IR spectrometer).

Results and Discussion

The FT-IR spectrometer technique is depended on that a chemical material shows marked selective absorption in the infrared region. It is an important and non-destructive characterizing tool, which provides qualitative information regarding structural details of crystalline and non-crystalline substances, the position of ions in the crystal, local symmetry and the ordering phenomena[23]. The FT- IR spectra absorption bands mainly appear due to the vibrations of the oxygen ions with the cations producing various frequencies of the unit cell. Various absorption bands exist in FT-IR spectrum from functional groups and their linkages can be explored, are found to be dependent on atomic mass, cation radius, cation-anion bond distances, cation distribution *etc*[23]. Therefore, FT-IR spectra indicate to the valance state of the ions and their occupation in the spinel lattice crystal. The electrical and magnetic properties of spinels depend on the chemical composition, cation distribution and the method of preparation. The vibrational, electronic and magnetic dipole spectra can give information about the position and valency of the ions in the crystal lattice[19]. In a certain mixed spinel ferrites, as the concentration of the divalent metal ions increasing, it gives rise to the structural change in spinel lattice crystal without affecting the spinel ferrite structure[21]. The structural changes brought about by the metal ions that are either lighter or heavier than divalent ions in the ferrites, which strongly influence the lattice vibrations. The vibration frequency depends on the cations mass, the cations oxygen distance and the bonding–force[22].

The room temperature FT-IR spectra of the prepared $Ni_{1-s}Zn_sFe_2O_4$ samples were recorded between the wave numbers 350 cm^{-1} to 1000 cm^{-1}, which is a common feature of ferrites as shown in Figure 2. The measured FT-IR spectra confirm the formation of a single phase of spinel ferrites having two sites T_d and O_h of spinel structure. Here in, two prominent bands are present two different wave numbers ν_T and ν_O. The higher wave number, ν_T, band lies between 550 cm^{-1} to 600 cm^{-1} corresponding to the highest restoring force, which is attributed to the stretching vibrations of metal-oxygen (*M-O*) bond in T_d group complexes. The lower wave number, ν_O, at around 400 cm^{-1} is caused by the intrinsic vibrations of M-O bond in O_h group complexes. This is a good agreement with the observation by many researchers for various spinel materials[19,24-29]. The obtained FT-IR results confirm that the normal mode of vibration of T_d cluster is higher than that of O_h cluster[30]. The difference in frequencies of the characteristic vibrations (ν_T and ν_O) has been attributed to the long bond length of M-O ions in O_h sites and short bond length of M-O ions in T_d sites. The difference in band positions for T_d and O_h group complexes of spinel structure is due to the difference in values of Fe-O bond lengths[19,20,27,28,31,32]. It was also found that, the Fe-O bond distance of the T_d sites (0.189 *nm*) and this is smaller than that of the O_h sites (0.199 nm)[33]. The change in the frequency band position is due to perturbation occurring in the Fe-O inter nuclear distances[19,23]. This has been interpreted due to the more covalent bonding of the Fe ions at T_d sites. The positions of absorption bands in terms of wave number ν_T and ν_O for all samples are summarized in Table 1.

From Table 1, it is clear that only the position of ν_T band is shifted with the incorporation of *Zn* ions in the *Ni* matrix. The same behavior was reported in previous work of different ferrite systems[31,34]. FT-IR results clearly indicate that Ni ions is stabilized in the O_h crystal field whereas Zn ions prefers T_d sites because of its ability to form covalent bonds[10,25,26,35].

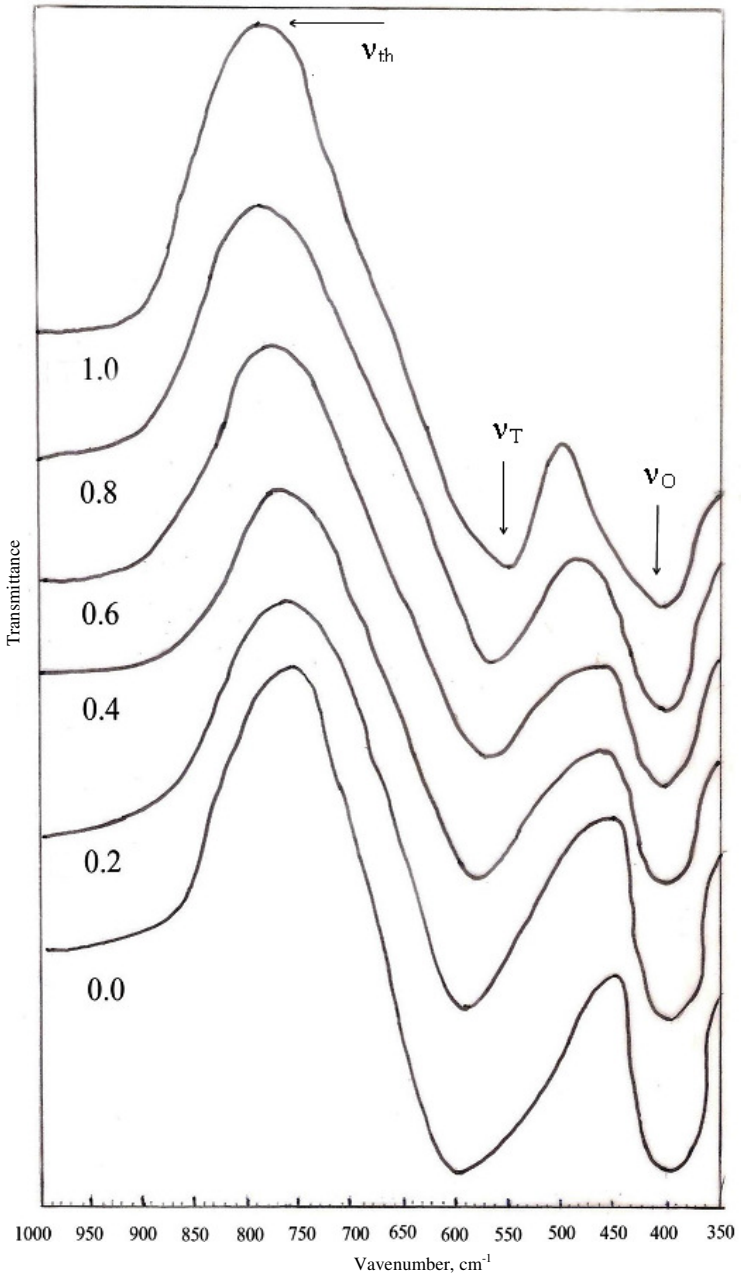


Figure 2. FT-IR absorption spectra of the mixed $Ni_{1-s}Zn_sFe_2O_4$ spinel ferrite

Table 1. Absorption bands frequency for T_d, O_h and ν_{th} positions for the prepared mixed $Ni_{1-s}Zn_sFe_2O_4$ spinel ferrite samples

s	ν_T cm^{-1}	N_O cm^{-1}	ν_{th} cm^{-1}
0.0	600	400	755
0.2	590	400	760
0.4	580	400	765
0.6	570	400	770
0.8	560	400	775
1.0	550	400	780

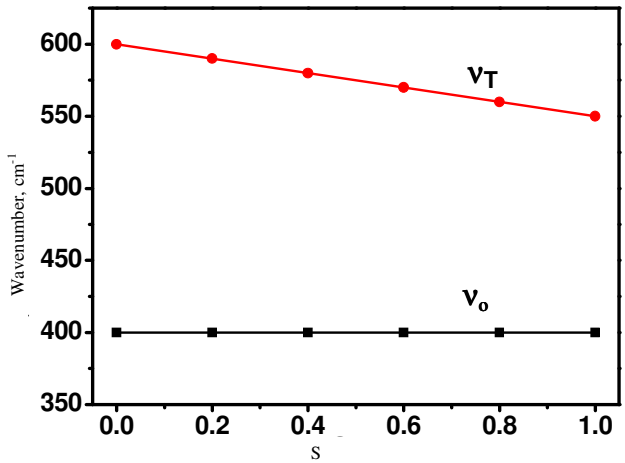


Figure 3. The positions of ν_T and ν_O with respect to the *Zn* ratio" *s"*

The calculated values of the force constant F_{CT} and F_{CO} for T_d and O_h sites, respectively, are listed in Table 2 using the following relation[31]

$$F_C = 4\pi^2 c^2 \nu^2 m \quad (1)$$

where
c is the light velocity ≈2.99x10^{10} cm. sec^{-1}
ν is the vibration frequency of T_d and O_h sites.
M is the reduced mass of Fe and O ions, which is found ≈2.061x10^{-23} g.

Table 2. Calculated values of the force constant F_{CT} and F_{CO} or the mixed $Ni_{1-s}Zn_sFe_2O_4$ spinel ferrite

s	F_{CT}x10^5, $dyne.cm^{-1}$	F_{CO}x10^5, $dyne.cm^{-1}$
0.0	2.61	1.16
0.2	253	1.16
0.4	2.43	1.16
0.6	2.36	1.16
0.8	2.28	1.16
1.0	2.20	1.16

Since the applied vibration frequency is proportional to the force constant F_C, so ν_T shift of the Fe-O bond vibration to lower frequency with increasing of the Zn ions. This indicates that, F_C of the Fe-O bond decreasing in the mixed *Ni-Zn* spinel ferrite. The observed change

in ν_T and decrease in F_{CT} indicate the occupancy of *Zn* ions at T_d sites[19]. The results show the compositional dependent behavior of force constant are attributed to the cation oxygen bond distances[1]. It is attributed to the shorter bond length of T_d cluster and longer bond length of O_h cluster[29]. Normally, it is expected that an increase in bond length should lead to a decrease in force constant. If the radius of the impurity ion is larger than the displaced ion then the bond length increases, lowering the force constant for either site or a reduction in the repulsive forces between the ions leading to a lower electrostatic energy implying lower wave number. Reverse will hold if a smaller impurity ion replaces a metal ion of the regular lattice. A decrease in wave number and force constant is expected with Zn^{2+} ion substitution because of its larger ionic radius than the displaced Zi^{2+} ion.

The FT- IR spectra of the composition $Ni_{1-s}Zn_sFe_2O_4$ shows a change in the absorption bands by introducing the Zn ions, which has larger ionic radius and higher atomic weight, on the T_d sites. This tends to increase the ionic radius of the T_d sites with addition of the Zn ions[32]. This is attributed to the method of preparation, the grains size and the porosity that influences the band position[20,21,28]. This affects Fe-O bond-stretching vibration[36]. Therefore, there are slight shift towards low frequency side in the ν_T band.

The threshold frequency (ν_{th}), according to Waldron[28] for the electronic transition can be determined from the maximum point in the absorption spectra, where it reaches a limiting value as in Figure 3**.** The values of threshold frequency ν_{th} are in Table 1, which are shown in Figure 4. It is noticed that, ν_{th} is increasing with the increase of *Zn* ions content. This increment in ν_{th} is not reflected on the value of the corresponding activation energy Ea. Which is calculated from the relation $E_{th}=h\nu_{th}$ that has a constant average value about 0.1 *eV*, where h is Planck's constant.

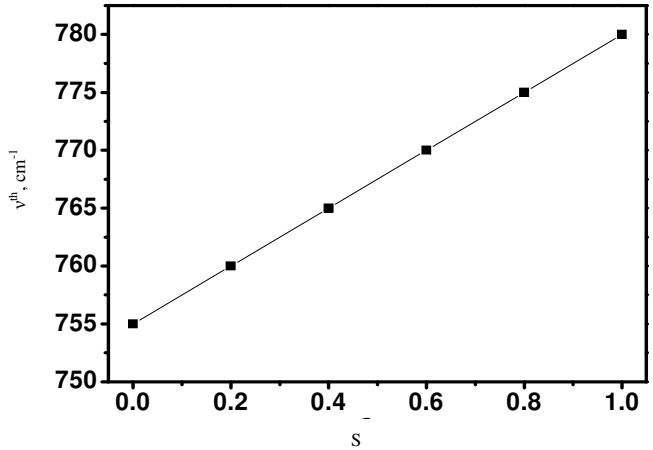


Figure 4. Variation of ν_{th} with the Zn ratio" *s"*

It is necessary to know the cations distribution, which could be described with the following considerations.

$$(Zn_s^{2+}Fe_{1-s}^{3+})\{Ni_{1-s}^{2+}Fe_{1+s}^{3+}\}O_4^{2-} \qquad (2)$$

The non-magnetic Zn ions occupy the T_d sites, which are favored by the polarization effect and this occurs by replacing the Fe ions in the T_d sites. However, the T_d sites preferences of the cations depend upon their electronic configuration[38]. The Zn ions show a marked stronger preference for the T_d sites than the Fe ions, where their (4s 3d) electrons form a covalent bonds with 2p electrons of the oxygen ion[38,39].

Depending on the cations distribution that is given in the considered cations distrubition, the ionic radii for T_d and O_h sites, we used the following equations[40,41]

$$R_T = sR_{Zn^{2+}} + (1-s)R_{Fe^{3+}} \quad (3)$$

$$R_O = \frac{1}{2}[(1-s)R_{Ni^{2+}} + (1+s)R_{Fe^{3+}}] \quad (4)$$

where

R_T and R_O are the mean ionic radii per molecule for T_d and O_h sites, respectively.

R_{Zn}^{2+} is the ionic radius of the Zn ion.

R_{Fe}^{2+} is the ionic radius of the Fe ion.

R_{Ni}^{2+}s the ionic radius of the Fe ion.

The ionic radii R_T and R_O *versus* the *Zn* ratio "*s*" are plotted in Figure 5, while R_T/R_O versus the *Zn* ratio "*s"* is plotted in Figure 6. It is noticed that, with increasing of the Zn^{2+}ions R_T increases while R_O decreases. This behavior is attributed to the replacement of the Fe ions with the large ionic radius of the Zn ions on T_d sites and *Ni* ions with the smaller ionic radius than Fe ions on O_h sites. The cations distribution, the calculated ionic radii R_T and R_O and ionic ratio R_T/R_O are tabulated in Table 3.

Table 3. Values of R_T, R_O and R_T/R_O for the mixed *Ni-Zn* spinel ferrite

s	Cations distribution	R_T, nm	R_O nm	R_T/R_O
0.0	$(Fe_{1.0}^{3+})\{Ni_{1.0}^{2+}Fe_{1.0}^{3+}\}O_4^{2-}$	0.063	0.076	0.82894
0.2	$(Zn_{0.2}^{2+}Fe_{0.8}^{3+})\{Ni_{0.8}^{2+}Fe_{1.2}^{3+}\}O_4^{2-}$	0.0652	0.0746	0.87399
0.4	$(Zn_{0.4}^{2+}Fe_{0.6}^{3+})\{Ni_{0.6}^{2+}Fe_{1.4}^{3+}\}O_4^{2-}$	0.0674	0.0732	0.92076
0.6	$(Zn_{0.6}^{2+}Fe_{0.4}^{3+})\{Ni_{0.4}^{2+}Fe_{1.6}^{3+}\}O_4^{2-}$	0.0696	0.0718	0.96935
0.8	$(Zn_{0.8}^{2+}Fe_{0.2}^{3+})\{Ni_{0.2}^{2+}Fe_{0.8}^{3+}\}O_4^{2-}$	0.0718	0.0704	1.01988
1.0	$(Zn_{1.0}^{2+})\{Fe_{2.0}^{3+}\}O_4^{2-}$	0.074	0.069	1.07246

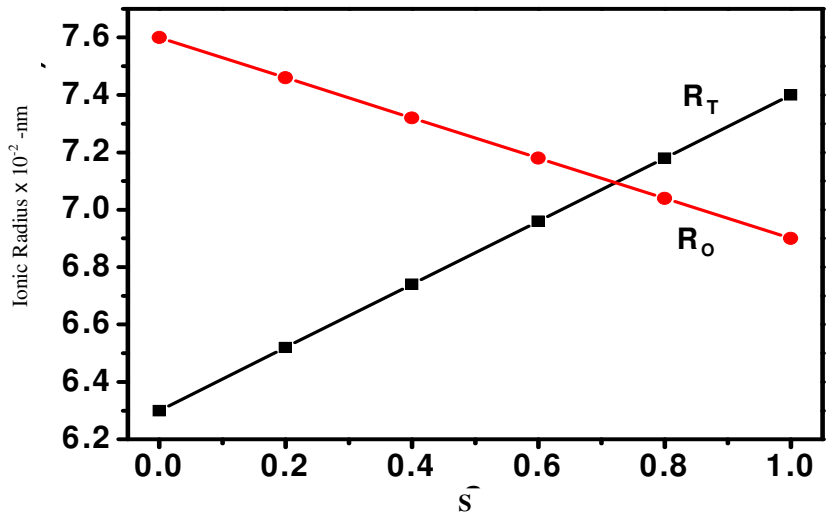


Figure 5. Variation of R_T and R_O with the *Zn* ratio" *s"*

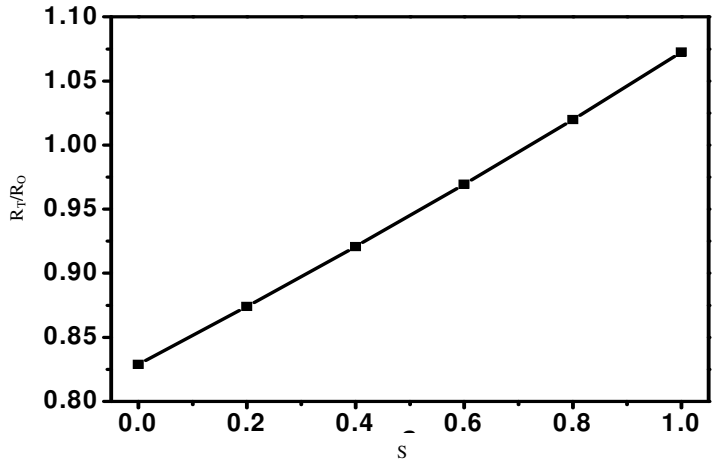


Figure 6. Variation of R_T/R_O with the *Zn* ratio" *s"*

Conclusion

FT-IR spectra of the diamagnetic Zn ions substituted on the *Ni* spinel ferrite have been analyzed in the frequency range (350-1000) cm^{-1}. Two bands were observed, their positions were found to depend, strongly, on *Zn* ions content.

1. FT-IR spectra indicated that two main prominent bands are detected, one of a high frequency band ν_T at around (550-600) cm^{-1} and the other of a low frequency band ν_O at 400cm^{-1} and are assigned to T_d and O_h sites, respectively.
2. Force constant F_C of T_d and O_h sites were calculated and found to decrease with increasing the Zn ions.
3. On the basis of analyzing the FT-IR absorption bands, we deduced the cations distribution for the given mixed ferrite as the following form $(Zn_s^{2+}Fe_{1-s}^{3+})\{Ni_{1-s}^{2+}Fe_{1+s}^{3+}\}O_4^{2-}$. This illustrated that the non-magnetic Zn ions has a preference to T_d sites, where the Niions occupy O_h sites.
4. The ionic radii of T_d and O_h sites were calculated and found to change linearly with increasing the Zn ions.

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