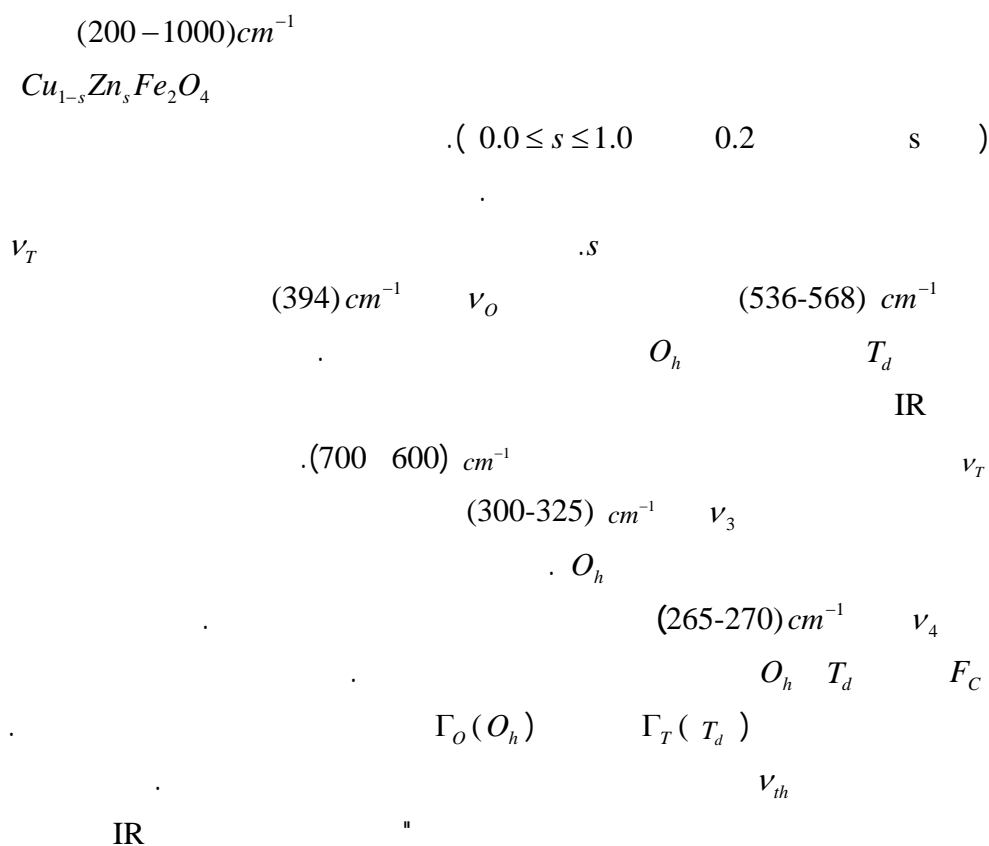


A Structural Study of Cu-Zn Ferrites by Infrared Spectra *

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ABSTRACT

Infrared (IR) spectra of Zn^{2+} ions substituted Cu spinel ferrite, having the general formula $Cu_{1-s}Zn_sFe_2O_4$, (where s stepped by 0.2 such that $0.0 \leq s \leq 1.0$), have been analyzed in the frequency

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range $(200-1000)cm^{-1}$. The above mixed ferrites were prepared by the conventional standard double sintering ceramic method. Four absorption bands were observed, their position and intensity were found to be strongly dependent on s -value. Mainly, two prominent bands were observed, a high frequency band ν_T at around $(536-568) cm^{-1}$ and a low frequency band ν_O at around $(394) cm^{-1}$ were assigned to tetrahedral T_d and octahedral O_h sites, respectively, of spinel lattice. Upon introducing Zn^{2+} ions, IR spectra indicated new shoulders or splitting in the absorption bands, such the first primary band ν_T which consists of two shoulders at about $(700$ and $600)cm^{-1}$. A small absorption band ν_3 was observed at about $(300-325)cm^{-1}$. This may indicate the presence of the divalent metal ion-oxygen complex on O_h sites. Other small weak absorption band ν_4 was, also, observed at about $(265-270)cm^{-1}$. Its intensity increased with the addition of Zn^{2+} ions. Force constant F_C was calculated for T_d and O_h sites, and was found to decrease with increasing Zn^{2+} ions. Half bandwidths of T_d sites (Γ_T) and O_h sites (Γ_O) changed linearly with increasing Zn^{2+} ions. Threshold frequency ν_{th} for the electronic transition was determined and found to increase with increasing Zn^{2+} ions. On the basis of the analysis of IR absorption bands, we concluded the cations distribution for the given mixed ferrite. The ionic radii for each site were correlated to the cations distribution of the given ferrite.

Keywords: Ferrites, Infrared, copper zinc ferrites.

INTRODUCTION:

Magnetic and electric properties of the ferrite materials strongly depend on their chemical and physical structure, in the determination of the precise configuration of the atoms and the ions in the ferromagnetic semiconductor [1].

In particular, the *IR* spectra of the ferrite materials are an important tool to describe the various ordering problems, also, in the investigation of the structural properties of the mixed ferrites. They give information not only about the positions of the ions in the spinel lattice crystal, but, also, about their vibration mode. The vibration spectra can be indicated to the valance state of the ions and their occupation in the spinel lattice crystal. Application of the *IR* spectroscopy to the ferrite materials is to detect the completion of the solid-state reaction, the cations distribution and the deformation of spinel structure [2].

The *IR* spectral absorption bands mainly appear due to the vibrations of the oxygen ions with the cations producing various frequencies in the unit cell. In a certain mixed spinel ferrite materials, as the concentration of the divalent metal ions increasing, it gives rise to a structural change or cation distribution in the spinel crystal lattice without affecting the spinel ferrite structure [1]. The structural changes brought about by the metal ions that are either lighter or heavier than divalent ions in the ferrites strongly influence the lattice vibrations. The vibration frequency depends on the cation mass, the cation oxygen distance and the bonding-force [3].

Many researchers studied the IR spectra of several ferrites [4-8]. However, no reports were found in the literature regarding IR spectra of Zn^{2+} ions substituted *Cu* spinel ferrite. Therefore, in the present communication we analyzed the IR spectra of mixed *Cu-Zn* spinel ferrite.

EXPERIMENTAL TECHNIQUE:

Polycrystalline mixed ferrite of the general formula $Cu_{1-s}Zn_sFe_2O_4$, (where *s* stepped by 0.2 according to $0.0 \leq s \leq 1.0$), was prepared by the conventional standard double sintering ceramic method. Weighted high purity metal oxides were mixed, and then ground to a very fine powder for 5 hours. Then the mixed powders were presintered at ($750^\circ C$) for 3 hours soaking time. After that, the prefired powder was well ground for 3 hours and by using a small quantity of butyl alcohol as a binding material. Samples pressed with hydraulic press under constant pressure of

($3 \times 10^8 \text{ Kg.cm}^{-2}$) in the form of a disc shape with diameter (11mm). All samples sintered for 5 hours soaking time at (1100°C). For each sintering of the samples were cooled down gradually to room temperature with a rate of $1^\circ \text{C}/\text{min}$. For recording IR spectra, the powder of the samples were mixed with (*KBr*) in the ratio (1:200) by weight to ensure uniform dispersion in *KBr* pellet. The mixed powder of samples were then placed in a cylindrical disc and pressed at ($3 \times 10^{10} \text{ Kg.cm}^{-2}$) by a hydraulic press. Clean discs of (1mm) thickness were obtained. IR spectra measurements were carried out at room temperature in the range from ($200\text{-}1000$) cm^{-1} using Berkin Elmer Model 883 infrared Spectrophotometer.

RESULTS AND DISCUSSION:

The values of the absorption bands frequency are given in Table (1), while Figure (1) indicates the *IR* spectra of the mentioned compounds. It illustrates the presence of two prominent absorption bands, along with some side bands in the range from 200 cm^{-1} up to 800 cm^{-1} regions. It shows that, the higher absorption bands ν_T are in the range from 536 cm^{-1} up to 568 cm^{-1} and the lower absorption bands are ν_O located around 394 cm^{-1} . This is in a good agreement with the observation of many researchers for various ferrite materials [4-6]. They found that, ν_T accure in the frequency range from 550 cm^{-1} up to 600 cm^{-1} , attributed to the stretching intrinsic vibrations of the T_d group complex corresponding to the highest restoring force. However, ν_O was observed in the frequency range from 300 cm^{-1} up to 450 cm^{-1} , which can be correlated with the stretching intrinsic vibrations of the O_h group complex (bond-bending vibrations). Several scientific research [1,2,7] have reported that ν_T greater than ν_O , and the bands ν_T and ν_O are characteristic of the lattice vibration of the metallic oxides, arise from the vibration of the oxygen ions against the metal ions in the lattice T_d and O_h complex.

Table (1): Absorption bands frequency for the T_d and the O_h sites of the mixed Cu-Zn spinel ferrite.

s	T_d sites			O_h sites		
	$\nu_{1sh}.cm^{-1}$	$\nu_{2sh}.cm^{-1}$	$\nu_T.cm^{-1}$	$\nu_O.cm^{-1}$	$\nu_3.cm^{-1}$	$\nu_4.cm^{-1}$
0.0	-	600	568	395	300	265
0.2	-	600	564	394	305	265
0.4	700	600	556	394	310	267
0.6	700	600	546	394	315	270
0.8	700	600	540	394	320	266
1.0	700	600	536	394	325	266

It is clear that, ν_T are caused by the stretching of the T_d metal ions and the oxygen bonding, while ν_O are caused by the vibrations of the oxygen ions in the direction perpendicular to the axis joining the T_d ions and the oxygen ions [2]. The IR spectra in Figure (1) indicate the existence of new shoulders or splitting in the absorption bands, i.e. the first primary band ν_T consists of two shoulders at $\nu_{1sh.} = 700\text{ cm}^{-1}$ and $\nu_{2sh.} = 600\text{ cm}^{-1}$. Similar results have been observed in various ferrite systems [2,8]. It has been shown by Potakova [9] that, the presence of the Fe^{2+} ions in spinel ferrite can produce splitting or shoulders on the absorption bands. This is Jahn–Teller distortion produced by the Fe^{2+} ions. This distortion causes local deformation in the spinel lattice owing to the noncubic component of the crystal field potential and, hence, leads to splitting of the band ν_T [10].

A third absorption band ν_3 appears in the range from 300 cm^{-1} up to 325 cm^{-1} , because a small amount of Fe^{2+} ions are produced in the mentioned compounds. This band is attributed to the $Fe^{2+} - O^{2-}$ bond of the O_h sites [8,10]. It appears relatively narrow and weak in intensity, and the intensity increases with the increasing Zn^{2+} ions. This tends to the ν_O band becomes narrow and the ν_3 more intense, therefore, ν_3 could be seen very clearly at high concentration of the Zn^{2+} ions.

Another absorption band ν_4 appears in the range from 265 cm^{-1} up to 270 cm^{-1} . It is attributed to some types of lattice vibration involving displacement of

the T_d cations in the samples.

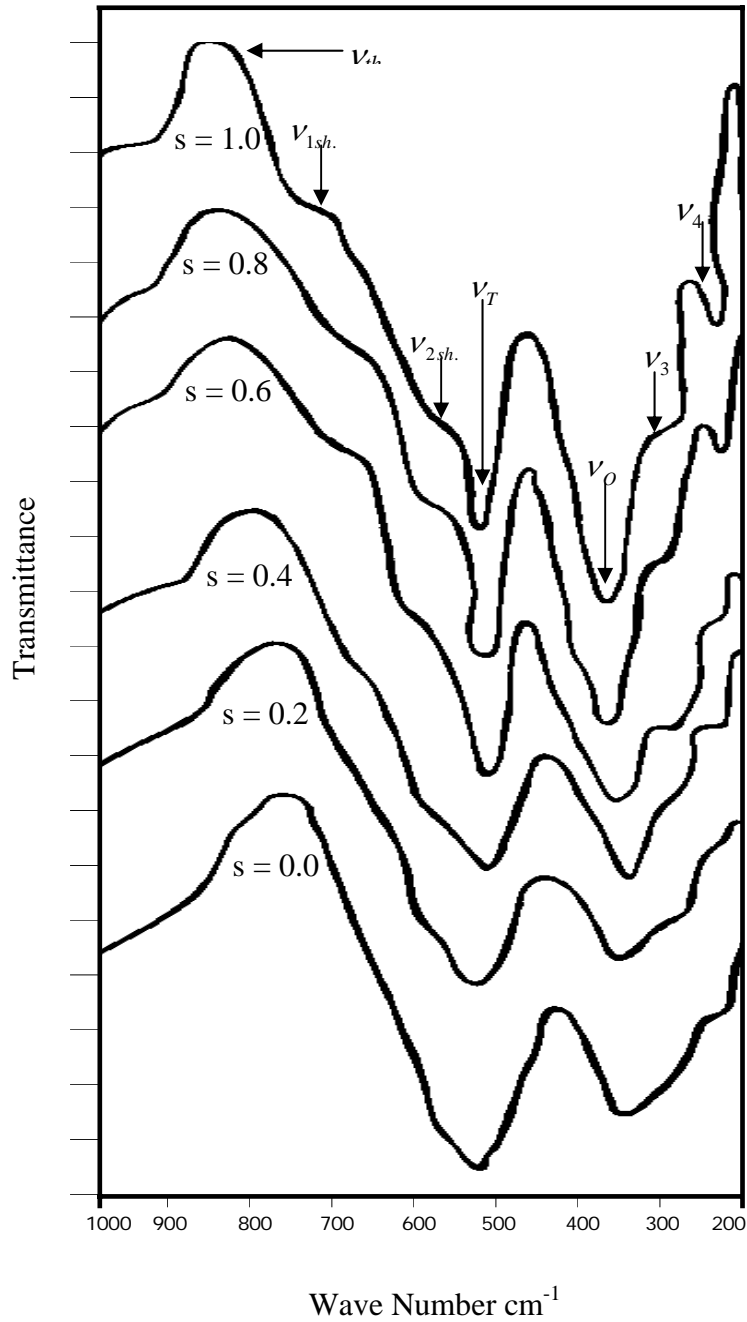


Fig.(1): IR absorption spectra of the mixed Cu-Zn spinel ferrite

Its frequency depends on the mass of the foreign atom occupying the T_d sites in the ferrite samples and the mass of the divalent cations [1,11]. Its intensity is small compared to any other absorption bands, which increases with increasing of the Zn^{2+} ions. The IR spectrum of $CuFe_2O_4$ was studied by **Mazen** [12]. His study indicated that, there were two mainly absorption bands where $\nu_T = 570\text{ cm}^{-1}$ and $\nu_O = 395\text{ cm}^{-1}$. However, $ZnFe_2O_4$ was studied by several investigators [4,10,13,14]. They reported that, there were four bands given by ($\nu_T = 555\text{ cm}^{-1}$, $\nu_O = 393\text{ cm}^{-1}$, $\nu_3 = 325\text{ cm}^{-1}$ and $\nu_4 = 169\text{ cm}^{-1}$).

Referring to Table (1), it is noticed that, ν_T shifts to the lower frequency with increasing the Zn^{2+} ions. The ν_T and the ν_O behavior with increasing of Zn^{2+} ions is illustrated in Figure (2). The same behavior was seen in previous works of different ferrite systems [8,15].

A difference in the band position of ν_T in the range from 536 cm^{-1} up to 568 cm^{-1} and of ν_O (which has a constant value) is expected because of the difference in the $Fe^{2+} - O^{2-}$ bond length for the T_d and the O_h complex [2,4,8,10]. It was found that, the $Fe^{2+} - O^{2-}$ bond length of the T_d sites (0.189 nm) is shorter than that of the O_h sites (0.199 nm) [16]. This has been interpreted on the base of covalent bonding of the Fe^{3+} ions at the T_d sites. Since the vibration frequency is proportional to the force constant F_C , so the $Fe^{2+} - O^{2-}$ bond vibration (ν_T) is shifted to a lower frequency with increasing the Zn^{2+} ions. This indicates that, F_C of the $Fe^{2+} - O^{2-}$ bond is decreasing in the mixed $Cu-Zn$ spinel ferrite. The calculated values of the force constant F_{CT} and F_{CO} for the T_d and the O_h sites, respectively, are listed in Table (2) using the following relation [8]

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

where:

- c is the light velocity $\approx 2.99 \times 10^{10}\text{ cm}\cdot\text{sec}^{-1}$.
- ν is the vibration frequency of the T_d and the O_h sites.
- m is the reduced mass for the Fe^{2+} ions and the O^{2-} ions, it is found equal $\approx 2.061 \times 10^{-23}\text{ gm}$.

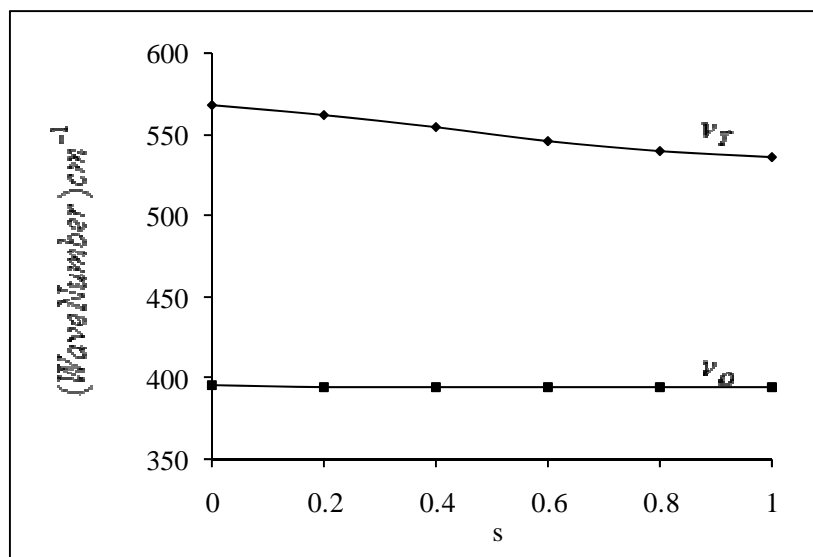


Fig. (2): Behavior of the absorption bands ν_T and ν_O with the composition s .

Table (2): Calculated values of the force constant F_{CT} and F_{CO} .

s	$(F_{CT} \times 10^5) \text{ dyne.cm}^{-1}$	$(F_{CO} \times 10^5) \text{ dyne.cm}^{-1}$
0.0	2.361	1.142
0.2	2.312	1.136
0.4	2.247	1.136
0.6	2.182	1.136
0.8	2.125	1.136
1.0	2.103	1.136

The IR spectra of the mentioned compositions show a change in the absorption bands by introducing the Zn^{2+} ions, of larger ionic radius and higher atomic weight, on the T_d sites. This tends to increase the ionic radius of the T_d and the O_h sites with addition of the Zn^{2+} ions [2]. This can be ascribed to the method of preparation, the grain size and the porosity that influence the band position [1,4,10]. Consequently this affects the $Fe^{2+} - O^{2-}$ bond stretching vibration [17]. Therefore, there are slightly shifts towards low frequency in the ν_T and the ν_O bands. Clearly, for the

normal spinel ferrites both the two prominent bands depend on the nature of the O_h ions and fewer on the T_d ions [18], such as Zn spinel ferrite.

Referring to the IR spectra, it is noticed that, the half bandwidths of the T_d sites, Γ_T , and of the O_h sites, Γ_O , change linearly with the increasing the Zn^{2+} ions.

Table (3) shows the values of Γ_T , Γ_O and Γ_T/Γ_O . The behavior of Γ_T and Γ_O with the composition s is illustrated in Figure (3), while the ratio Γ_T/Γ_O is represented in Figure (4). The ratio Γ_T/Γ_O seems to increase linearly with the composition s . Γ_T and Γ_O depend on the statistical distribution of the various cations over the T_d and the O_h sites [19]. This distribution depends on the replacement process of the smaller ionic radii of the Fe^{3+} ions with (0.067nm) and the Cu^{2+} ions with (0.076nm), by the larger ionic radius of the Zn^{2+} ions with (0.084nm). Thus, there is a good correlation of Γ_T and Γ_O with the ionic radii R_T and R_O of the T_d and the O_h sites, respectively, as will explained literally.

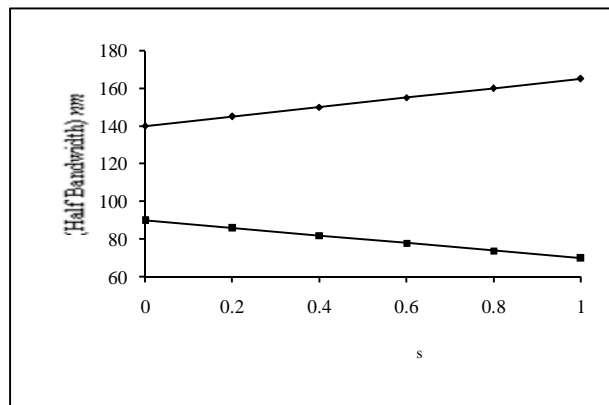


Fig. (3): Variation of Γ_T and Γ_O with the composition s .

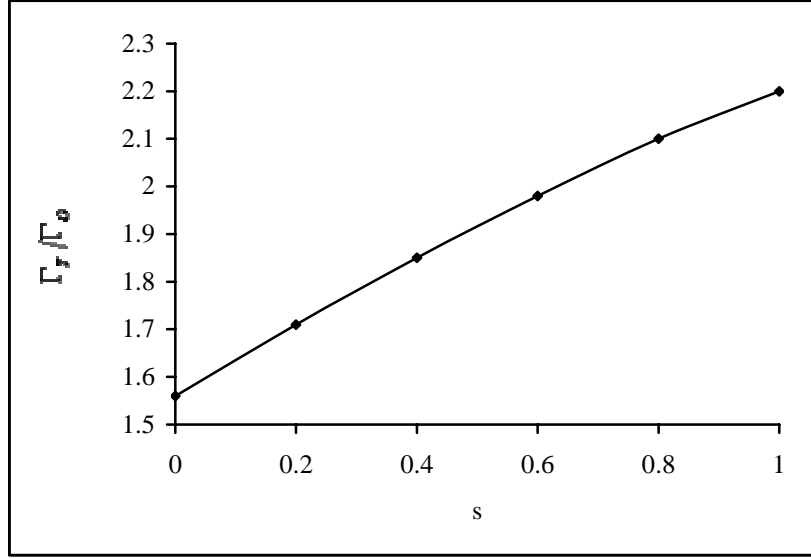


Fig. (4): Change of Γ_T/Γ_O with the composition s .

Table (3): Values of ν_{th} , Γ_T , Γ_O and Γ_T/Γ_O for the mixed Cu-Zn spinel ferrite.

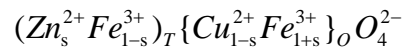
s	$(\nu_{th})cm^{-1}$	$(\Gamma_T)cm^{-1}$	$(\Gamma_O)cm^{-1}$	Γ_T/Γ_O
0.0	760	140	90	1.56
0.2	770	145	85	1.71
0.4	780	150	81	1.85
0.6	790	155	78	1.98
0.8	800	160	76	2.1
1.0	810	165	75	2.2

According to **Waldron** [4], the threshold frequency ν_{th} for the electronic transition can be determined from the maximum point of absorption spectra where it reaches a limiting value. Table (3) shows these threshold values, which are illustrated in figure (5). It is found that, the threshold frequency ν_{th} increases with increasing of the Zn content.

This increment in ν_{th} is not reflected on the corresponding value of the activation energy E_a . The threshold energy E_{th} was calculated from the relation $E_{th} = h\nu_{th}$ that has a constant average value about 0.1eV, where h is **Planck's** constant.

It is necessary to know the cations distribution, which will be suggested as the following considerations. When the non-magnetic Zn^{2+} ions occupy the T_d sites, which are favored by the polarization affect, this will occur by replacing the Fe^{3+} ions in the T_d sites. However, the T_d sites preference of the cations depends upon their electronic configuration [20]. The Zn^{2+} ions show a marked stronger preference for the T_d sites than the Fe^{3+} ions, where their (4s 3d) electrons form a covalent bond with 2p electrons of the oxygen ion [21,22].

In the light of the above considerations, the cations distribution for the mixed Cu-Zn spinel ferrite can be written as follows:



The above formula has a good agreement with the cations distribution, which was suggested by several authors [17,23-25].

To calculate the ionic radius for the T_d and the O_h sites, we used the following equations [9,26]

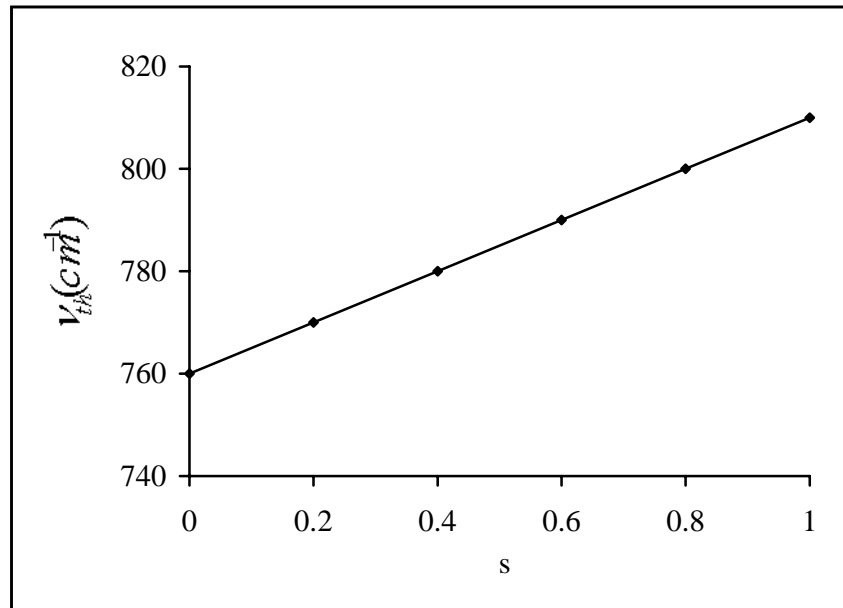


Fig. (5): Change of v_h with the composition s .

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

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

where:

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

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

$R_{Fe^{3+}}$ is the ionic radius of the Fe^{3+} ion.

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

In Figure (6), the ionic radii R_T and R_O are plotted versus the composition s , while R_T/R_O is, also, plotted versus the composition s in Figure (7). From these figures, it is clear that, R_T increases while R_O decreases with increasing of the Zn^{2+} ions. This behavior is attributed to the replacement of the Fe^{3+} ions to the larger ionic radius of the Zn^{2+} ions on the T_d sites and the Cu^{2+} ions to the smaller ionic radius of the Fe^{3+} ions on the O_h sites. Therefore, increase the Zn^{2+} ions leads to the change of Γ_T and Γ_O as shown in Figure (3).

From the IR spectra of the mixed Cu-Zn spinel ferrite in Figure (1), it is observed that, when the Zn^{2+} ions increase, a change in the intensity of T_d and O_h absorption band occurs. Other researchers found this behavior [2,8,12], for different ferrite materials.

The intensity of the IR absorption bands is function of the concentration and thickness of the samples in solid solutions [27]. This intensity of the T_d and the O_h bands depends on the ionic replacement and consequently on the magnetic dipole moment. Changing the magnetic dipole moment with the inter-nuclear distance during $d\mu/dr$ depends on the intensity E of the absorption band. It is defined by [28]

$$E = 10^{-3} \frac{N_o}{2mc^2} \left(\frac{d\mu}{dr} \right)^2 \quad (4)$$

where N_o is the **Avogadro's** number.

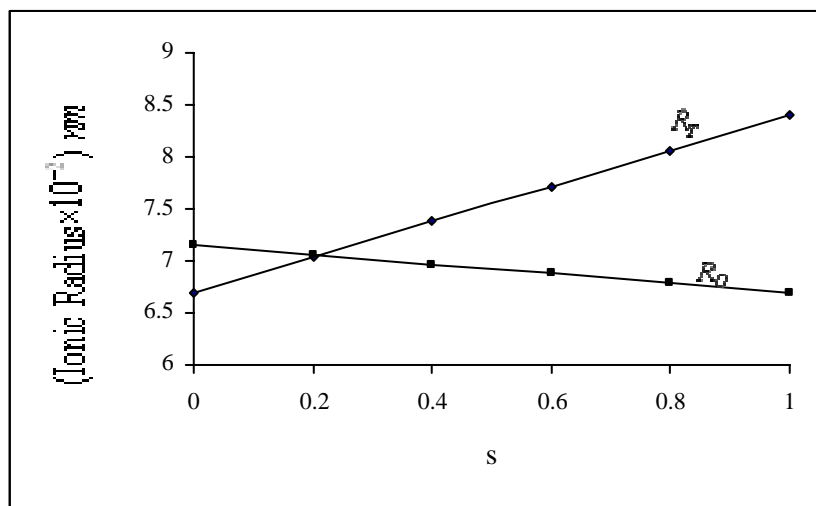


Fig. (6): Change of R_T and R_O with the composition s.

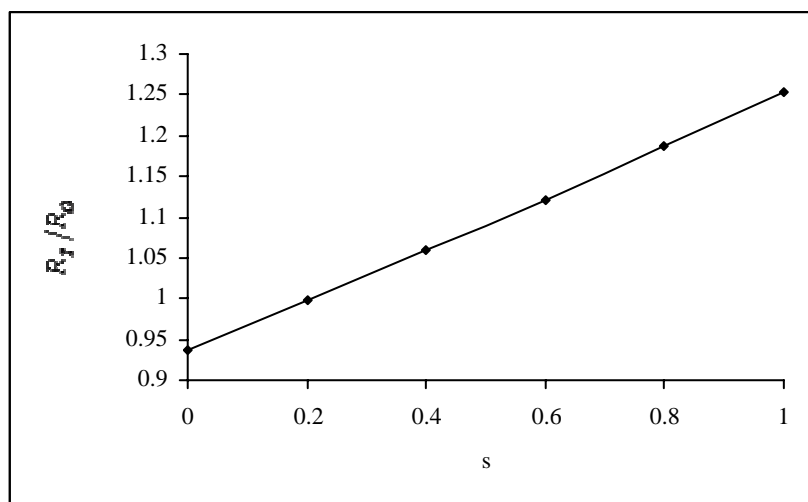


Fig. (7): Change of R_T/R_O with the composition s.

It is clear that, the intensity values give an induction of the $d\mu/dr$ values. The latter value represents the contribution of the ionic character of the $Fe^{2+} - O^{2-}$ bond in the spinel lattice [8,29].

The change of the intensity with increasing the Zn^{2+} ions is explained on the basis of the cations distribution of the mixed $Cu-Zn$ spinel ferrite, which is given before. From this form, it will be seen that, as the Zn^{2+} ions increase the Cu^{2+} ions decrease in the O_h sites and the Fe^{3+} ions leave the

T_d sites to the O_h sites. This may disturb the $Fe^{2+} - O^{2-}$ bond of T_d and O_h sites in the spinel lattice [8].

The $Fe^{2+} - O^{2-}$ bond exerted by the Fe^{2+} ions is formed in the samples during the sintering process. It is to be noted that, the sintering process affects the number of the Fe^{2+} ions in each site. On the other hand, the electronic distribution of the $Fe^{2+} - O^{2-}$ bond is greatly affected when the Zn^{2+} ions are introduced, which consequently affects the value of $d\mu/dr$ of the $Fe^{2+} - O^{2-}$ bond, as measured by the absorbance of the IR absorption bands.

From the previous discussion, one can conclude that the IR spectra can give information about changes in the molecular structure of the ferrites, due to the perturbation occurring in the $Fe^{2+} - O^{2-}$ bond upon introducing of the Zn^{2+} ions.

CONCLUSION:

Infrared spectra of the diamagnetic Zn^{2+} ions substituted on the Cu spinel ferrite have been analyzed in the frequency range $(200-1000)cm^{-1}$. Four bands were observed, their positions and intensities were found to depend strongly on the composition s .

1. The IR spectra indicated that two main prominent bands are detected, one of a high frequency band ν_T at around $(532-568)cm^{-1}$ and the other of a low frequency band ν_O at $395cm^{-1}$ and are assigned to the T_d and the O_h sites, respectively.
2. Upon introducing the Zn^{2+} ions, the IR spectra indicated new shoulders or splitting in the absorption bands, the primary bands ν_T are consisted of two shoulders at $700cm^{-1}$ and $600cm^{-1}$.
3. Other subsidiary absorption band ν_3 was observed in the range $300-325cm^{-1}$. It is related to the presence of the divalent metal band ion-oxygen complex on the O_h sites.
4. Other small weak absorption band ν_4 was observed at $266cm^{-1}$, its intensity increased with increasing the Zn^{2+} ions.

5. Force constant F_C of the T_d and the O_h sites were calculated and found to decrease with increasing the Zn^{2+} ions.
6. The half bandwidth of the T_d sites was assigned to Γ_T and of O_h sites was assigned to Γ_O , they change linearly with increasing the Zn^{2+} ions.
7. The threshold frequency ν_{th} of the electronic transition was determined and found to increase with increasing the Zn^{2+} ions.
8. On the basis of analyzing the IR absorption bands, we deduced the cations distribution for the given mixed ferrite as the following form $(Zn_s^{2+}Fe_{1-s}^{3+})(Cu_{1-s}^{2+}Fe_{1+s}^{3+})O_4^{2-}$. This illustrated that the non-magnetic Zn^{2+} ions has a preference to the T_d sites, where the Cu^{2+} ions occupy the O_h sites.
9. The ionic radii of the T_d and the O_h sites were calculated and found to change linearly with increasing the Zn^{2+} ions.

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REFERENCES:

1. Reddy P. and Salagram M. (1987): Phys. Stat. Sol. (A) ,100, 639.
2. Shaikh A. Jadhav S. Watawe S. and Chongnle B. (2000): Mat. Sci. lett.,44,192.
3. Patil S. , Otarl S., Mahajan V. , Patil M. , Patll A, Soudagav N., Patll B.and Sawant S. (1991): Solid State. Comm., 78, 39.
4. Waldron R. (1955): Phys. Rev., 99, 1717.
5. Hanfner S., Krist Z., (1961): 155, 331.
6. Patil R., Kakatkar S., Sanlepal A. and Sawant S., (1994): J.Pure Appl. Phys.,2,193.
7. Harris L. (1955): I. Opt. Soc. Amer ,45,27.
8. Mazen S. , Abed Allah M. , Nakhla R. and. Zaki. H. (1993): Mat. Chem. And Phys. ,34, 35.
9. Potakova V. , Zvera N. and Romanov V. (1972): Phys. Stat. Sol. (A) ,12, 623.
10. Josyulu O. and Obhanadri J. (1981): Phys. Stat. Sol. (A), 65, 479.
11. Trate J. and Preudhommed J. (1971): Spectrochim Acta, 27A, 961.

12. Mazen S. (2000): *Mat. Chem. and Phys.*, 62, 139.
13. Kamiyama T., Haneda K., Sato T., Lkeda S. and Sano H. (1993): *Sol. State Comm.* , 7, 563.
14. Mitsuishi A. Yoshin H., and Fuj S. (1958): *J. Phys. Soc. Jap.* ,13, 1236.
15. Mazen S., Hakeem N. and Sabrah B. (1984): *Phys. Status Sol. (b)*, 11,123.
16. Evans B. and Hanfner S. (1968): *J. of Chem.and Phys. Sol.* ,29,1573.
17. Sawant S. and Patil. R. (1981): *Solid State Comm.* ,40, 391.
18. Trate P. (1963): *Spectrochim, Acta*, 19, 49.
19. Trate P. (1963): *Acta Cryst.*, 16, 228.
20. Vishwanathan B. and Murthy V.(1990): " Ferrites Materials ", *Sci. Technol.*,6.
21. Tang Xioa-Xia, Manthiram A. and Good-enough. J. (1989): *J. of Sol. State Chem.*,79, 250.
22. Belled S., Pujar R. and Chougule B. (1998): *Mat. Chem. and Phys.*, 52,166.
23. Chikazumi S. (1964): "Physics of Magnetism", New York, John Wiley and Sons.Inc.
24. Morrish Allan. H. (1965): "The Physical Principles of Magnetism", John Wiley and Sons. Inc.
25. Smit J. and Wijn H. (1959): " Ferrites ", New York, John Wiley.
26. Standly K. J. (1972): " Oxide Magnetic Materials" Clarendon Press Oxford.
27. Mazen S. , Abed-El. Rahiem A., and Sabrah B. (1988): *J. Mat. Sci.* ,23, 2917.
28. Dwcius J., Nalu O. and Thomson A. (1963): *Proc. R. Soc. London. Ser. A*,27, 295.
29. El-Sayed A. (2002): *Ceramic International.* , 28, 363.