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SPECTRAL STUDIES OF THE SPINEL FERRITE SYSTEM $Ni_xZn_{1-x}Fe_2O_4$

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X-ray diffraction, DTA, IR and SEM investigations were carried out for a series of samples of the system $Ni_xZn_{1-x}Fe_2O_4$ (with $x = 0.0$, 0.2, 0.4, 0.6, 0.8 and 1.0) prepared using the usual ceramic technique. The analysis of X-ray diffraction indicates that the samples have single phase with spinel cubic structure. The lattice constant (a), radius of tetrahedral ions (r_{tet}), bulk density (D) and theoretical density (D_x) were found to decrease while the porosity (P) increases as the content of nickel ions (x) increases. SEM images indicate observable variations between the different compositions. IR absorption spectra showed the four characteristic peaks of ferrites. The position and intensity of the peaks are markedly composition dependent.

1. *Introduction*

NiZn ferrites attracted the attention due to their wide field of applications [1-4]. The physical, electrical, thermal, magnetic and dielectric properties of any material depend very much on its structure. Therefore, the structure of NiZn ferrites was studied using X-ray diffraction [5-12]. Infrared (IR) spectra were studied for CoZn and MgZn ferrites [13], NiZn ferrites [14] and for LaCu ferrites [15].

The aim of the present work was to study X-ray diffraction, IR absorption spectra, DTA and SEM images to investigate the effect of the replacement of zinc ions by nickel ions on the lattice constant, radius of tetrahedral ions, bulk and theoretical density, grain size, the position and intensity of the four peaks characterizing spinel ferrites.

2. *Experimental*

2.1. *Sample preparation*

A series of samples of $Ni_xZn_{1-x}Fe_2O_4$ was prepared using the usual ceramic technique taking $x = 0.0$, 0.2, 0.4, 0.6, 0.8 and 1.0, respectively. Pure NiO, ZnO and Fe_2O_3 oxides were mixed well in molecular ratios to form the system $Ni_xZn_{1-x}Fe_2O_4$. The mixed oxides were sintered at 1173 for four hours, then finely powdered in agate mortar made of carborundum and pressed at constant pressure in the form of discs. The discs were finally sintered at 1573 K for 15 hours.

2.2. *Analysis of samples*

Powder from each sample was used for X-ray diffraction, IR and DTA investigations. X-ray diffraction was studied at room temperature using Fe-K_α radiation of wavelength $\lambda = 0.193597$ nm from X-ray difractometer of the type Jeol model JSX-60 PA at the Minia University.

IR absorption spectra were recorded at room temperature (300 K) for the wave numbers in the range 200–4 000 cm^{-1} using radio recording infrared spectrometer of the type Perkin Elmer 1430. DTA was recorded in the temperature range 300–1170 K using Dupont instrument 990 thermal analyzer.

Scanning electron microscopic images (SEM) were taken for the samples using scanning electron microscope of the type Amray 1200B. The surfaces of the samples were carefuly polished to get smooth parallel surfaces. These surfaces were coated with a very thin layer of gold deposited by thermal evaporation under vacuum. Sample preparation, SEM, DTA and IR investigations were carried out at the Tanta University.

3. *Results and discussion*

3.1. *X-ray diffraction analysis*

The analysis of X-ray diffraction proved that the $Ni_xZn_{1-x}Fe_2O_4$ ferrites have single phase cubic spinel structure. The lattice constant a was calculated using special computer program PDP [16].

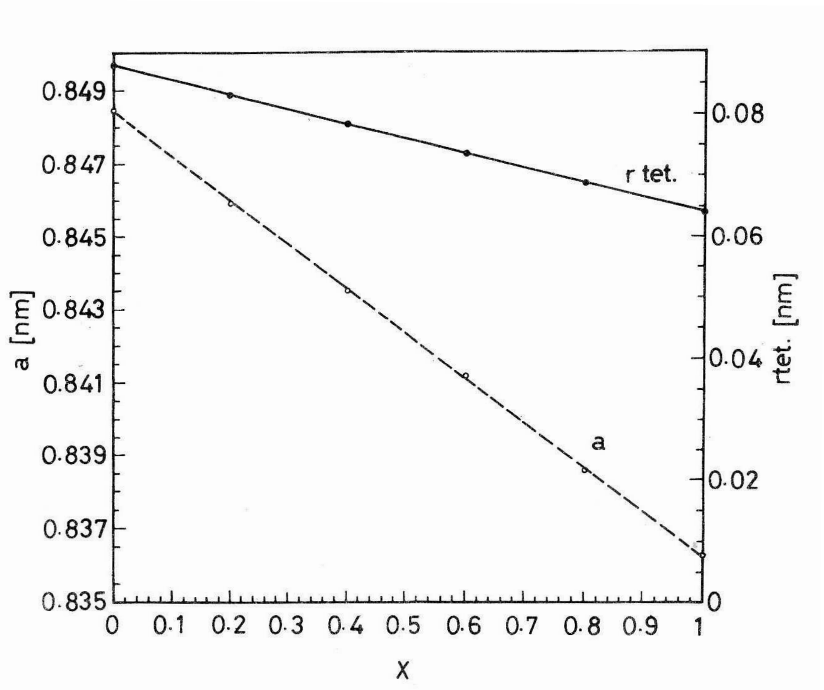

Fig. 1. The lattice constant and the radius of the tetrahedral ion as a function of Ni *ion content.*

The mean ionic radius of any molecule on the tetrahedral site A for any composition x is given by the following equation [17]:

$$r_{\text{tet.}} = (1-x)r_{\text{tet.}^{3+}} + xr_{\text{tet.Me}^{2+}} \tag{1}$$

where Me^{2+} is the divalent metal. Using Eq. (1) the radius of tetrahedral ions $r_{\text{tet.}}$ can be calculated. The lattice constant and the radius of the tetrahedral ion are presented in Fig. 1 as a function of Ni ion content (x). It is clear that the lattice constant and radius of tetrahedral ion decrease as the nickel ion content increases. As the nickel ions of smaller radius 0.062 nm replace zinc ions of larger radius 0.074 nm [18], the lattice constant and the radius of tetrahedral ion will decrease as this replacement increases. The values of the lattice constant for the system $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$, indicate that the present values of the lattice constant agree to within few parts in thousands with the published results [8,10]. The present value may be a little higher than those published earlier. This can be attributed to the fact that our sintering temperature (1573 K) and sintering time (15 hours) are larger than those of earlier work [8,10,19-21].

Theoretical density [22] was calculated using the equation:

$$D_x = \frac{ZM}{NV} \tag{2}$$

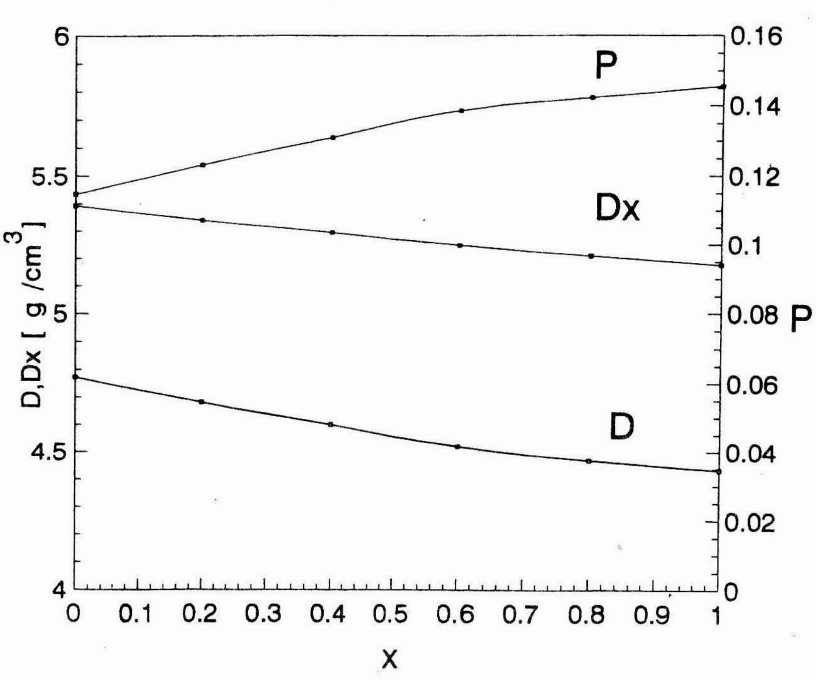

Fig. 2. Variation of the bulk density, theoretical density and porosity with composition.

where the unit cell volume is $V = a^3$ for cubic structure, M is the molecular weight, N is the Avogadro's number and the number of molecules per unit cell is $Z = 8$ for spinel structures.

The bulk density (D) was determined using the principle of Archimede's. The porosity (P) was calculated from the following equation [23]:

$$P = \frac{D_x - D}{D_x}. \tag{3}$$

The calculated values of the bulk density (D), theoretical density (D_x) and porosity (P) are drawn in Fig. 2 as a function of composition x. Both bulk and theoretical densities were found to decrease while porosity increases as nickel ion content increases. The density of zinc 7.13 gm cm^{-3} is lower than that for nickel 8.91 gm cm^{-3} [24]. Therefore the bulk and theoretical densities decrease while porosity increases as the content of nickel ions increases. The theoretical density is bigger than the bulk density. This can be related to the pores formed during the preparation of the samples which depends markedly on the sintering conditions. The reason that the bulk density D decreases with x in spite of the decrease in a is the difference in atomic masses of nickel and zinc.

DTA spectra for $Ni_xZn_{1-x}Fe_2O_4$ ferrite samples do not show any observable exo- or endo-thermic peaks. Therefore DTA can not be considered as a quick test for phase transition temperatures where exo- or endo-thermic peaks can appear. Differential gravimetric analysis measurements will be carried in the future for these samples to determine the transition temperature for the studied samples.

3.2. SEM investigations

The scanning electron microscopic images for $Ni_xZn_{1-x}Fe_2O_4$ ferrite samples with $x = 0$, 0.2, 0.4, 0.6, 0.8 and 1.0, respectively, indicate that the size of the grains decreases as the nickel ion content increases instead of zinc ions. This may be related to the well known fact that Ni ions have a smaller ionic radius (0.062 nm) than the Zn ions (0.074 nm). This means that at 1573 K the crystal growth in Zn ferrite is faster than in Ni.

3.3. IR spectral analysis

The position and the intensity of the absorbed IR spectra are presented in Fig. 3 and are listed in Table 1. The position and intensity of the bands are markedly composition dependent. Generally, there are four bands covering a range of wave numbers from 209 to 561 cm^{-1}. There are two high-frequency bands: ν_1 in the range from 544 to 561 and ν_2 in the range from 389 to 410 cm^{-1}. The band at frequency ν_1 is related to the intrinsic vibration of the tetrahedral groups while the band at ν_2 is attributed to the octahedral metal complex [25]. These two high-frequency bands are broad and depend on the conditions of preparation as mentioned earlier [26]. The other two bands are the low-frequency bands ν_3 in the range from 291 to 327 and ν_4 in the range from 209 to 270 cm^{-1}. The band at ν_3 is attributed to the divalent octahedral metal-ion–oxygen-ion complexes, while the weakest band ν_4 is due to thermal vibrations [27]. The first two bands ν_1 and ν_2 for ZnFeO

Table 1. The position and intensity of the four peaks characterizing ferrite samples.

x	composition	ν_1 cm^{-1}	I	ν_2 cm^{-1}	I	ν_3 cm^{-1}	I	ν_4 cm^{-1}	I
0.0	$ZnFe_2O_4$	547	10	393	8	327	13		
0.2	$Zn_{0.8}Ni_{0.2}Fe_2O_4$	544	13	391	10	326	18	209	3
0.4	$Zn_{0.6}Ni_{0.2}Fe_2O_4$	552	6	408	6	269	28		
0.6	$Zn_{0.4}Ni_{0.6}Fe_2O_4$	549	4	410	3	291	2		
0.8	$Zn_{0.2}Ni_{0.8}Fe_2O_4$	547	15	389	12	297	22	270	21
1.0	$NiFe_2O_4$	561	6	391	7	299	5		

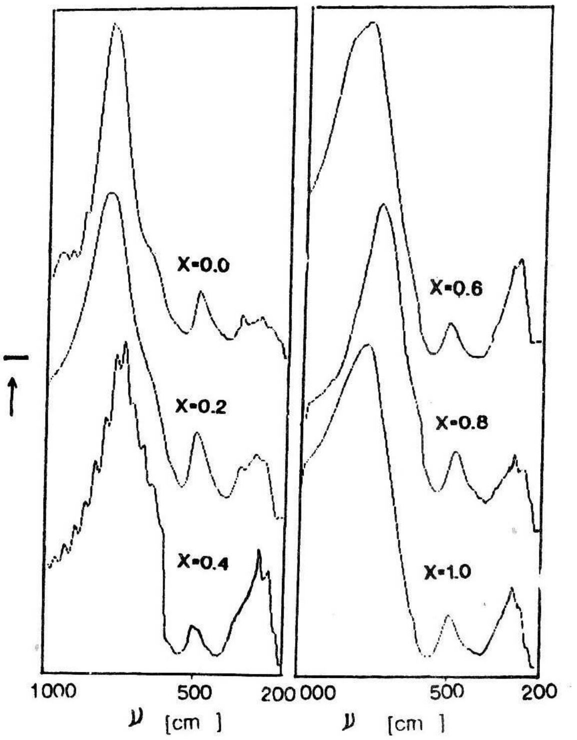

Fig. 3. IR absorption spectra for $\mathrm{Ni}_x\mathrm{Zn}_{1-x}$ *ferrites.*

are found to be 547 and 393 cm^{-1} and are in a good agreement with the published values 555 and 393 cm^{-1} [25,28]. The fourth peak appears for two compositions only. This may be related to the fact that it is very weak and not easily observed. Extensive IR analysis will be carried out in the future for the samples under investigations.

4. Conclusions

The results of this study can be summarized as follows:

1. The analysis of X-ray diffraction proved that the samples have single phase with cubic spinel structure.

2. The lattice constant, the radius of tetrahedral ions, the bulk and theoretical densities decrease while porosity increases as the nickel ion content increases.

3. The size of the grains decreases as the nickel ion content increases.

4. IR absorption spectra indicate the presence of the four peaks characterizing spinel ferrites. The intensity and position of the peaks are composition dependent.

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SPEKTRALNA ISTRAŽIVANJA SPINELNOG FERITNOG SISTEMA $Ni_xZn_{1-x}Fe_2O_4$

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Na nizu uzoraka sistema $Ni_xZn_{1-x}Fe_2O_4$ (za x = 0,0, 0,2 , 0,4 , 0,6 , 0,8 i 1,0) pripremljenih uobičajenom keramičkom tehnikom, izvršena su mjerenja difrakcijom rendgenskog zračenja, diferencijalna termička analiza, optička mjerenja u infracrvenom području i snimanja skanirajućim elektronskim mikroskopom. Analiza difrakcije rendgenskog zračenja indicira da uzorci imaju jednu fazu sa spinelnom kubičnom strukturom. Nađeno je da konstanta rešetke, promjeri tetrahedralnih iona, volumna i teoretska gustoća padaju a poroznost raste s porastom sadržaja nikla. Slike dobivene skanirajućim elektronskim mikroskopom indiciraju primjetne promjene među različitim smjesama. Spektri infracrvene apsorpcije pokazuju četiri karakteristična vrha za ferite. Položaj i intenzitet vrhova značajno ovise o sastavu sistema.