IR SPECTRA OF (Ni, Zn) FERRITE MICROPOWDERS

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The results of experimental investigations of reflection spectra in near and far regions of infrared wavelength range of $Ni_{1-x}Zn_xFe_2O_4$ ferrite micropowders with different content of Ni and Zn in them are given. The intensity dependence of IR-spectrum of these ferrites on concentration change of cations Fe^{2+} and Fe^{3+} in ferrite different compositions is established. The dependence of dispersion on ferrite compositions is determined and the presumptive interpretation of observable spectral structures is given.

Keywords: IR spectra, ferrite micropowders
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1. INTRODUCTION

In spite of the fact that *Ni-Zn* ferrites are well-known, appeared in former century, they are of big scientific interest that is shown in big amount scientific publications, among which the investigations of IR and Raman spectra take the especial place. In works [1-2], devoted to investigations of neutron small-angel scattering, Mossbauer effect, EPR micropowder spectra and AFM magnetic profiles of thin films of $Ni_{1-x}Zn_xFe_2O_4$ ferrites with different content of *Ni* and *Zn,* the effects connected with not only two types of B-sublattice ordering but additional magnetic ordering and declination of sublattice spin collinearity are revealed. To interpret these peculiarities it was necessary to study in detail IR and Raman spectra. The results of experimental investigations of IR spectra of $Ni_{1-x}Zn_xFe_2O_4$ ferrite micropowders under consideration are given in present work.

2. SAMPLE PREPARATION

All compositions of ferrites are obtained by the way of high-temperature synthesis of ultrapure powders of *ZnO, NiO,* Fe_2O_3 compounds. The synthesized $Ni_{1-x}Zn_xFe_2O_4$ compositions are annealed at temperature 960° and grinded into micropowders with grid sizes about 20nm. The quality of synthesized compositions of ferrite micropowders is controlled by roentgen micropowder diffractograms on XRDD8 ADVANCE, Bruker, Germany and also by Raman spectra. The roentgen investigation results are published in [4]. IR spectra of $Ni_{1-x}Zn_xFe_2O_4$ ferrites of x=0;0,25;0,4;0,5;0,6;0,75;1,0 compositions are studied on infrared Fourier-spectrometer Vertex70 (Bruker, Germany) with attachment of diffuse reflection in vacuum camera in spectral range from 4000cm^{-1} up to 50cm^{-1}, the standard spectral resolution is better than 0,5cm^{-1} (fig.1-2). The positions of genetically connected spectral lines determining the form of main absorption maximums are given in table 1. The sample temperature in all experimental investigations is equal to 300K.

The positions of spectral lines from experimental works [3,4,5] are also given in table 1.

By analysis of obtained spectra, it is established that their profiles have the complex structure and not only shift but the splitting into spectral components in process of “x” change are observed.

3. EXPERIMENTAL RESULTS AND DISCUSSION

It is well known that IR active triply degenerate modes of F_{lu} symmetry type should be observed in IR spectra of spinel reflection, i.e. oscillations are asymmetric ones in respect of inversion center and symmetric ones in respect of twofold axis or vertical reflection planes (σ_v). On the other hand, masses of *Fe, Ni* and *Zn* ions consisting in the composition of investigated ferrite significantly exceed the oxygen ion mass. Moreover, the oxygen ion oscillations in respect of metal heavy ions practically don’t influence on positions of heavy ions whereas heavy ion oscillations influence on oxygen ion ones. The shift of oxygen ion can take place either along the C_3 triad axis order or perpendicular to it [5]. In first case the F_{1u}^1 oscillation of $Me^{2+}-O-3Me^{3+}$ bond (where Me^{2+} is octahedral cation and $3Me^{3+}$ are three tetrahedral cations) is observed. The high-frequency spectral band corresponds to this oscillation. In second case, the F_{1u}^2 oscillation of $Me^{3+}-O-2Me^{3+}$ bond, in which only octahedral cations take part, is observed. The low-frequency spectral band corresponds to this oscillation. The cation oscillations F_{1u}^3 $(Me^{3+}-Me^{3+})$ and F_{1u}^4 $(Me^{2+}-Me^{2+})$ in respect of each other take part at more low frequencies and have the weak intensities. As the frequencies of these oscillations is determined by dimensions and ion masses then the shift of spectral lines towards to low frequencies will be observed at exchange of Fe^{2+}on Zn^{2+} or Ni^{2+} (masses of Zn^{2+} and Ni^{2+} ions are bigger than Fe^{2+} mass) in tetrahedral and octahedral spinel fragments $Fe^{2+}Fe_2^{3+}O_4$. The three wide bands associated with lattice oscillations of *Fe-O, Ni-O* and *Zn-O* bonds are observed for all ferrite compositions in IR spectrum long-range region. The obtained frequency values in IR spectrum long-range region for micropowders of all compositions of $Ni_{1-x}Zn_xFe_2O_4$ ferrites are given in table 1. The light lines in tables correspond to spectral lines along compositions from $NiFe_2O_4$ up to $ZnFe_2O_4$: 604-542cm^{-1}; 425-388cm^{-1}; 249-241 cm^{-1}, which according to agreed classification are interpreted as oscillations of F_{1u}^1,F_{1u}^2, F_{1u}^3 and F_{1u}^4 symmetry type correspondingly. The presence of thin structure in IR spectra of investigated compositions and absorption maximum positions are established as a result of multiply carried out experiments.

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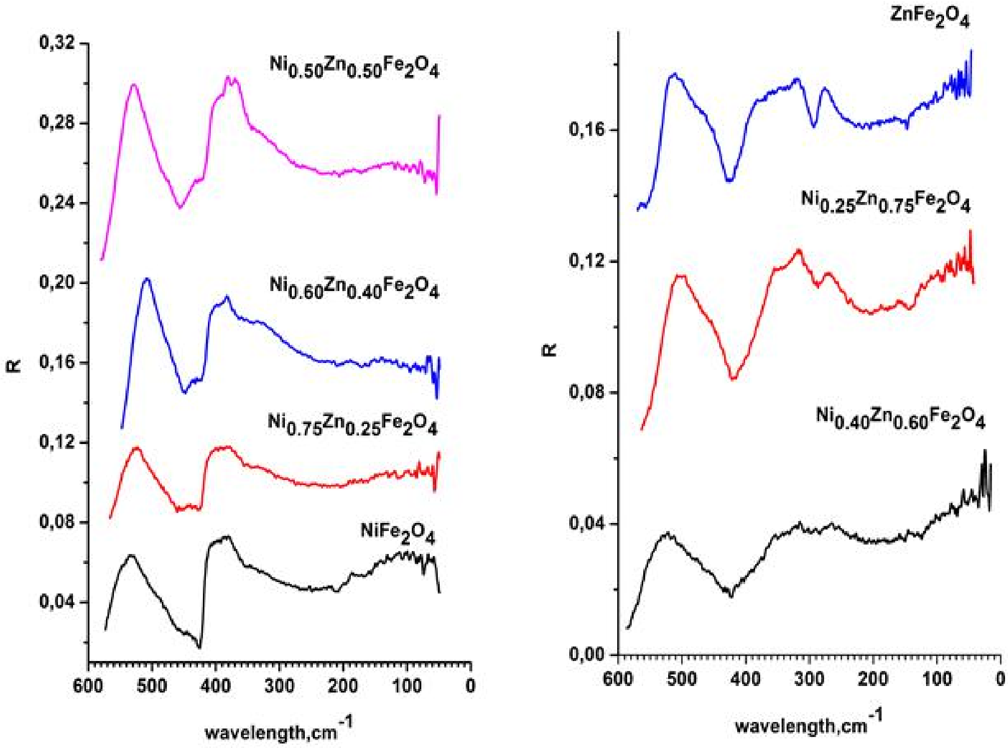

Fig. 1. IR spectra of $Ni_{1-x}Zn_xFe_2O_4$ ferrites in FIR mode.

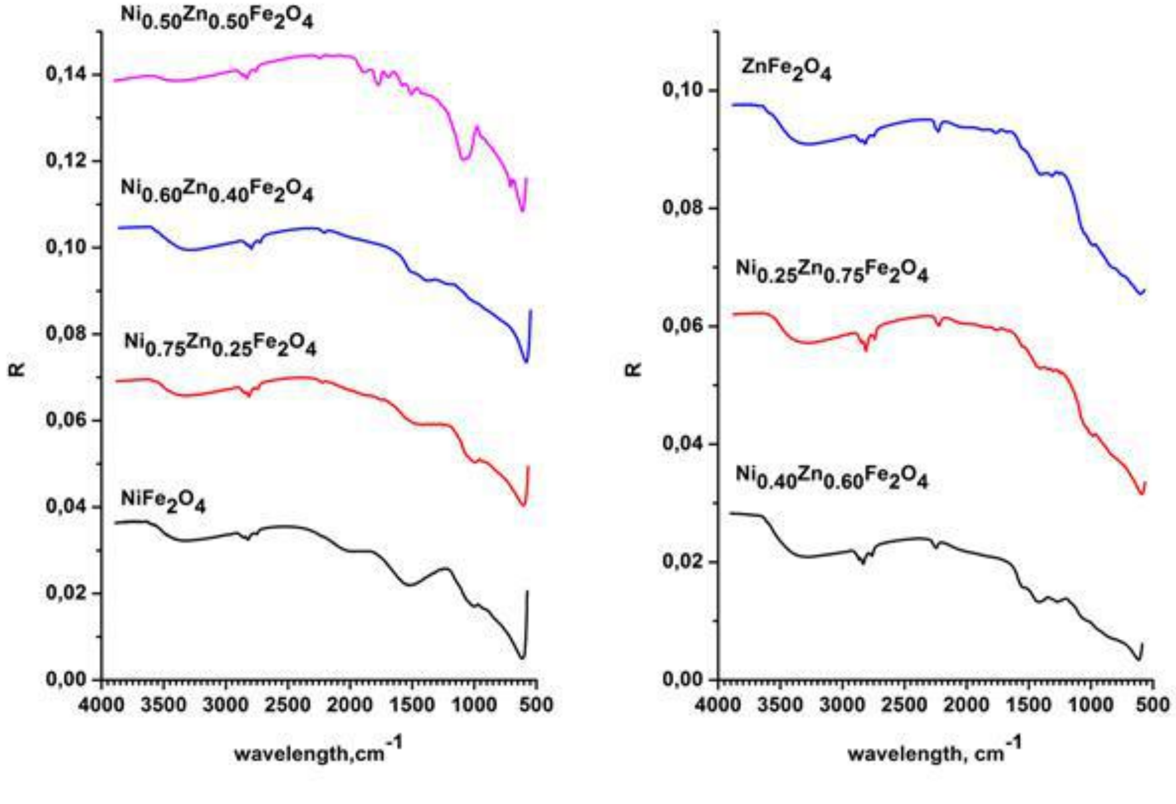

Fig. 2. IR spectra of $Ni_{1-x}Zn_xFe_2O_4$ ferrites in MIR mode, *x(Ni)=1;0.75; 0.6;0.5;0.4; 0.25; 0*

The absorption bands in frequency region with maximums in neighborhood of 430 cm^{-1}and 545 cm^{-1} which present themselves the oscillation combined bands of *Fe–O* valence bonds in octahedral positions with Zn^{2+} ions in nearest coordination surrounding *Fe–O–Zn* evidence on spinel structure formation, for example in $ZnFe_2O_4$. The absence or presence of wide intensive absorption bands at 3440 cm^{-1}and 1630 cm^{-1} shows the presence of adsorbed water or OH-groups [6, 7]. This fact is confirmed by absorption bands at 823cm^{-1} and

1045cm^{-1}, which are to deformation oscillations of $Zn–O–H$ and $Fe–O–H$ bonds.

The role of Ni and Zn cation reproportioning in different compositions of $Ni_{1-x}Zn_xFe_2O_4$ ferrites in formation of their IR spectra is established by experimental investigations. As it follows from experiments the shift, the appearance of new spectral lines and disappearance of “old” ones are observed in IR spectra of investigated compositions of $Ni_{1-x}Zn_xFe_2O_4$ ferrites depending on Ni^{2+} and Zn^{2+}cation inclusions. The dependences of obtained IR spectra of investigated $Ni_{1-x}Zn_xFe_2O_4$ compositions are easily interpreted within framework of model taking under consideration the changes of Fe^{3+}[3] and Fe^{2+}[8] cation concentrations in different ferrite compositions (fig.1). The comparison of these data with intensity taken for the example of experimental spectra band 425cm^{-1} shows on the fact that decrease of $Fe^{2+}$and Fe^{3+}contents in ferrite composition leads to the decrease of absorption intensity of this band in IR spectra. The change of $Fe^{2+}$and Fe^{3+} contents in ferrite compositions obviously indicates on the change of “jump” electron number and consequently on the change of indirect exchange interaction [9]. Thus, the interconnection of elementary cell “a” parameter and shift of normal oscillation frequency at isomorphous substitutions becomes understandable one. The indirect exchange interaction value is necessary to take under the consideration besides the changes of elementary cell “a” parameter in calculations of shift of normal oscillation frequency at isomorphous substitutions. As it has to be expected, the shift of IR spectra of $Ni_{1-x}Zn_xFe_2O_4$ ferrites towards to low frequencies is observed depending on Ni^{2+} and Zn^{2+}cation reproportioning. It is established that spectral line 604cm^{-1} observed in $NiFe_2O_4$ spectrum depending on “x” and interpreted as oscillations of $Me^{2+} - O - 3Fe^{3+}$ bonds (Me is Ni or Zn ions) related to F_{1u}^1 symmetry type shifts to 542cm^{-1} position in $ZnFe_2O_4$. At detail consideration, it is established that the form of considered spectral line has the complex structure. The shift and splitting of spectral components forming the given line profile is revealed in inclusion process of $Ni^{2+}$and Zn^{2+} ions in ferrite composition (see table 1). The profile change in neighborhood and maximums themselves from 425cm^{-1} ($NiFe_2O_4$) up to 388cm^{-1} ($ZnFe_2O_4$) more obviously demonstrates the process of substitution of Ni^{2+} by Zn^{2+}. Earlier this absorption maximum (in magnetite) is related to oscillations of $Fe^{3+} - O - 2Fe^{3+}$ bond of F_{1u}^2 symmetry type and oscillation frequency change takes place because of distance changes between Fe^{3+} cations. The analogous situation obviously should be observed for oscillations of F_{1u}^3 and F_{1u}^4 symmetry types influencing on the bonds between the same cations. This fact is seen by the behavior of spectral line 249 cm^{-1} ($NiFe_2O_4$), which shifts to the position 206cm^{-1} ($ZnFe_2O_4$). The continuous (at the decrease of concentration of Ni ions or at the increase of concentration of Zn ions) changes of absorption band form leading to the appearance of well marked maximum at 206 cm^{-1} which corresponds to oscillations of Zn-O bond are observed in 200-300cm^{-1} range. The analogous absorption maximum is shown in [10-14].

Table 1

Phonon frequency $Ni_{1-x}Zn_xFe_2O_4$, cm^{-1}							
	x=0	x=0.25	x=0.4	x=0.5	x=0.6	x=0.75	x=1.0
F_{1u}^1	604	592	584	578	582	570	-
	-	-	-	544	544	550	542
	533	538	522		535	-	-
	529	528	512	529	525	516	519
	-	524	508	-	518	506	507
	-	456	497	454	-	500	471
	443	442	437	436	-	-	-
	432	433		429	430	-	-
F_{1u}^2	425	426	426	424	-	421	426
	-	403	401	-	403	394	398
	392	391	389	389	388	391	388
	-	367	363	356	-	330	332
F_{1u}^4	349	345	346	343	324	-	-
	306	306	304	300	299	308	313
	273	275	270	266	284	287	294
F_{1u}^3	249	247	-	248	236	-	247
	-	204	204	206	195	206	206
	169	169	171	173	163	177	183
	96	93	95	95	128	81	84
	95	90	89	88	55	77	80
	-	85	84	83	52	73	76
	74	76	71	72	43	58	69

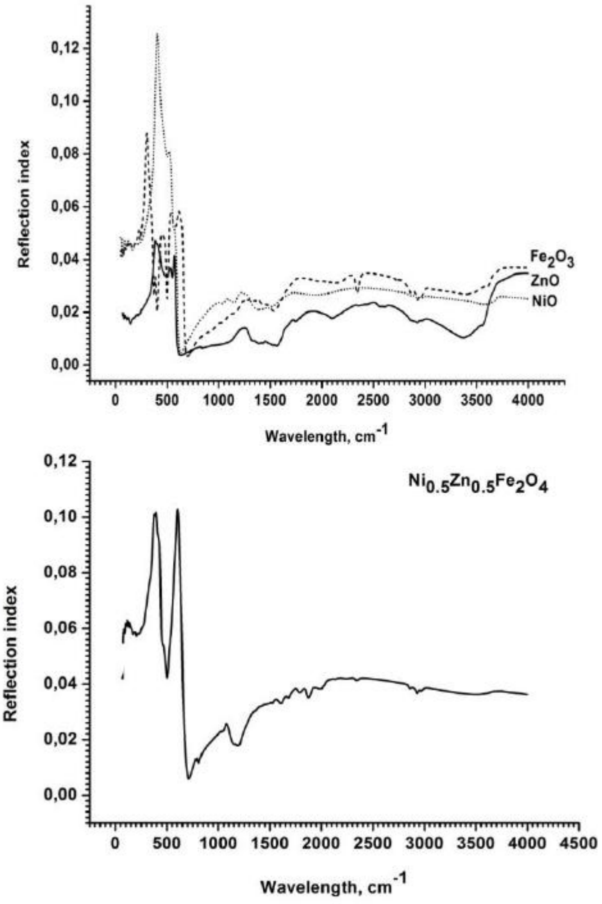

Fig.3. IR spectra of Fe_2O_3, NiO and ZnO powders used in synthesis process of $Ni_{1-x}Zn_xFe_2O_4$ ferrites and $Ni_{0.5}Zn_{0.5}Fe_2O_4$ composition chosen for example.

The analysis of IR spectra of investigated compositions of $Ni_{1-x}Zn_xFe_2O_4$ ferrites in 4000cm^{-1} - 500cm^{-1} range shows that the information about IR spectra of *ZnO*, *NiO* and Fe_2O_3 components is necessary for interpretation of spectral peculiarities (see fig.3). As it was shown earlier $Ni_{1-x}Zn_xFe_2O_4$ ferrites don't solve the excess quantity of *NiO* and *ZnO*. The excess quantity of Fe_2O_3 leads to formation of solid solution consisting of magnetite Fe_3O_4. By other hand for achievement of stable state in spinel structures the different forms of disorder appear in the form of point defects and vacancies (for example *ZnO* and *NiO*), the stability and concentration of which practically don't change until to thermodynamic equilibrium doesn't disturb. The concentration of these defects is enough to reveal them in IR spectra.

The weakly intense absorption band in (3627-3500) cm^{-1} range corresponds to the contribution in spectrum from OH ions and oxygen. The spectral band (2852-2829) cm^{-1} corresponds to the contribution from Ni^{2+} and Zn^{2+} ions in spectrum. The exchange process can be divided on stages: 1) composition change from $NiFe_2O_4$ up to $Ni_{0.5}Zn_{0.5}Fe_2O_4$ (the line 2852cm^{-1} shifts to 2829cm^{-1} decreasing in intensity; 2) composition change from $Ni_{0.5}Zn_{0.5}Fe_2O_4$ up to $ZnFe_2O_4$ spectral line shifts to 2850cm^{-1} , earlier in $ZnFe_2O_4$ this line haven't been registered). Note that this line is the doublet, the second component of which has very weak intensity. The analogous line 2904cm^{-1} is observed in *NiO*. The spectral structure observed in *ZnO* (1577cm^{-1} and 1409cm^{-1}) is revealed in spectral band (1550-1400)cm^{-1} in compositions of $Ni_{1-x}Zn_xFe_2O_4$ ferrites gradually appear in exchange process of Ni^{2+} by Zn^{2+}. Note that the spectral lines 1586cm^{-1} and 1585cm^{-1} are always observed in IR spectra of $Ni^{2+}$and Fe^{2+} ions correspondingly.

4. CONCLUSION

The reflection spectra of $Ni_{1-x}Zn_xFe_2O_4$ (x=0, 0.25, 0.4, 0.5, 0.6, 0.75, 1.0) ferrite micro-powders in range from 4000 cm^{-1} up to 50cm^{-1} are investigated. The phonon frequencies for each ferrite composition and their changes with "x" change are established. It is shown that observable changes in reflection spectra of these ferrites connect with reproportioning of Ni^{2+}/Zn^{2+} ion concentration.

5. AKNOWLEDGMENT

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[1] *Sh.N.Aliyeva, A.I.Nadjafov, T.R. Mehdiyev.* AJP Fizika **XIX**, 107 (2013). (In Russian).

[2] *Sh.N.Aliyeva, Y.N.Aliyeva, A.I.Nadjafov, I.S.Hasanov, E.K.Huseynov, T.R. Mehdiyev.* Phys. Status Sol.(c) **12**, 615 (2015).

[3] *F. Shahbaz Tehrani, V. Daadmehr, A. T. Rezakhani, R. Hosseini Akbarnejad, S. Gholipour.* Journal of Superconductivity and Novel Magnetism **25**, 2443 (2012).

[4] *Jiaqi Wan, Xuehui Jiang, Hui Li, Kezheng Chen Facile.* Journal of Material Chemistry **22**, 13500 (2012).

[5] *M. Kalyan Raju.* Chemical Science Transactions **4**, 137(2015).

[6] *J.T. Keiser, C.W. Brown, R.H. Heidersbach.* J. Electrochem. Soc. **129**, 2686 (1982)

[7] *Ming Ma, Yu Zhang, Yu Wei, Hao-ying Shen, Hai-qian Zhang, Ning Gu and Yu.N. Mixaylov, V.A. Kazanchev.* FTT **52**, 894, (2010). (In Russian).

[8] *S. Jadhav Santosh, E. Shirsath Sagar, B. G. Toksha, S. J. Shukla, K. M. Jadhav.* Chinese Journal of Chemical Physics **21**, 381 (2008).

[9] *K.P. Belov.* UFN **166**, 669 (1996). (In Russian).

[10] *J.L.M. Vidales, A.L. Delgado, E. Vila, F.A.Lopez.* J. Alloys Comp. **287**, 276 (1999).

[11] *Paramita Das, Arghya Dutta, Asim Bhaumik and Chhanda Mukhopadhyay*. Heterogeneous ditopic $ZnFe_2O_4$ catalyzed synthesis of 4*H-pyrans*: further conversion to 1,4-DHPs and report of functional group interconversion from amide to ester, Electronic Supplementary Material (ESI) for Green Chemistry, This journal is © The Royal Society of Chemistry 2013, 13p

[12] *M. Thomas and K.C. George.* Infrared and magnetic study of nanophase zinc ferrite, Indian J. Pure Appl. Phys., 2009, 47, 81

[13] *F.A. Lopez, A.L. Delgado, M.Vidales J.L. and E. Vila.* Synthesis of nanocrystalline zinc ferrite powders from sulphuric pickling wastewater, J.Alloys Comp,1998,265, 291

[14] *M.A. Ahmed, E.H. El-Khawas, M.Y. Hassan and El-Desoky M.* IR Spectroscopy, Magnetic Susceptibility, Mössbauer and ac Resistivity of Co-Zn Ferrite, Indian J. Phys., 2000, 74A, 567.

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