PHOTOLUMINESCENCE PROPERTIES OF $Ni_{1-x}Zn_xFe_2O_4$ NANOPOWDERS

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The photoluminescence spectra of $Ni_{1-x}Zn_xFe_2O_4$ ferrite nanopowders with different Zn contents were studied. The experiments were carried out at 300K, spectral lines were used to excitation luminescence: Xe-lamp with the wavelength 280 nm, 290 nm, 300 nm, 325 nm, 350 nm, 375 nm, 388 nm, 400 nm, 425 nm, and also YAG Nd laser (λ= 532 nm). The obtained spectra were interpreted in the framework of the proposed model in [1] for Fe_3O_4, a structural analogue of $Ni_{1-x}Zn_xFe_2O_4$ ferrites.

Keywords: ferrites, photoluminescence, nanopowders, sublattice
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1. INTRODUCTION

In this study, the results of experimental investigations of the effect of magnetic inhomogeneity on the luminescence spectra of $Ni_{1-x}Zn_xFe_2O_4$ ferrite nanopowders with different concentrations of Ni and Zn. It is known that $Ni_{1-x}Zn_xFe_2O_4$ ferrites are still of great scientific interest because of the high practical relevance, as shown by an unrelenting amount of scientific publications. The characteristic features of these ferrites [2] is the presence of two magnetic sublattices bound by indirect exchange interaction (the dipole interactions between the atoms of each of the sublattices are much smaller than the exchange interaction between the atoms of different sublattices). Another feature of the studied ferrite compositions is a gradual (with the concentration of zinc) conversion of the inversed spinel structure into the normal spinel structure without changing symmetry, but there is a transition from the ferromagnetic to antiferromagnetic ordering. It is known that nickel-zinc ferrites having a spinel structure are widely used in the field of modern radio engineering, nanoelectronics, automation, data processing and transmission systems, and also for the development of various functional elements. Therefore, obtaining these materials and studying their optical properties in a wide range of wavelengths is of scientific interest. The studies of Mössbauer [3, 4] spectra showed that there is a weak magnetic phase [5] in nanopowders of magnetite a structural analogue of $Ni_{1-x}Zn_xFe_2O_4$ ferrites with the grain size about from 15 to 45 nm. The parameters of this phase could not be determined because of the low intensity of the respective peaks and impossibility of their separation from the intense peaks of iron ions of the A and B sublattices. Therefore, the weak magnetic sublattice parameters are not defined.

From this point of view, the main purpose of studying the photoluminescence processes of $Ni_{1-x}Zn_xFe_2O_4$ (x=0; 0.25; 0.4; 0.5; 0.6; 0.75; 1) excited by sources with different wavelengths is to investigate of magnetic excitations, optical properties and weak magnetic phase parameters in the nano-powders of these materials.

2. SAMPLES PREPARATION

The $Ni_{1-x}Zn_xFe_2O_4$ nano-powders, where x = 0; 0.25; 0.4; 0.5; 0.6; 0.75; 1 were synthesized by the method of high-temperature sintering of high purity NiO, ZnO and Fe_2O_3 compounds followed by annealing for 2 hours at 960^0 C [6]. The particle sizes of the nanopowders of all the compositions were about 20- 40 nm. The quality of nanopowders was monitored by X-ray diffractograms and optical methods. It is shown that lattice distortions resulting from deviation from stoichiometry have little effect on Raman spectra. Detailed X-ray studies of the formation of $Ni_{1-x}Zn_xFe_2O_4$ ferrite films have shown that the process of their formation, as pointed in [7], goes through three stages: at the first stage $ZnFe_2O_4$ is obtained, while part of NiO and Fe_2O_3 remain in the free state; in second stage the process of including Ni^{2+} ions in the $ZnFe_2O_4$ lattice begins and compound with an excess of Ni content are formed against stoichiometry; in the third stage the composition compound is finally formed. All observed changes are in good agreement with changes in the content of Fe^{3+} cations [8] in the compositions of $Ni_{1-x}Zn_xFe_2O_4$ films.

We note that it was established in [9] that the most homogeneous composition of $ZnFe_2O_4$, accompanied by the largest incorporation of Fe ions into the ZnO structure, is achieved when using α-Fe_2O_3 powders. A significantly smaller amount of Fe is included into the ZnO structure in samples obtained on the basis of FeO and Fe_3O_4.

The spatial symmetry group of $Ni_{1-x}Zn_xFe_2O_4$ corresponded to $Fd\bar{3}m$. However, all $Ni_{1-x}Zn_xFe_2O_4$ ferrite compositions, except $ZnFe_2O_4$, referring to normal spinel (x = 1), have a reverse spinel structure, a good idea of which for the $NiFe_2O_4$ case (x = 0) can be seen in fig. 1 in [10, 11, 12, 13]:

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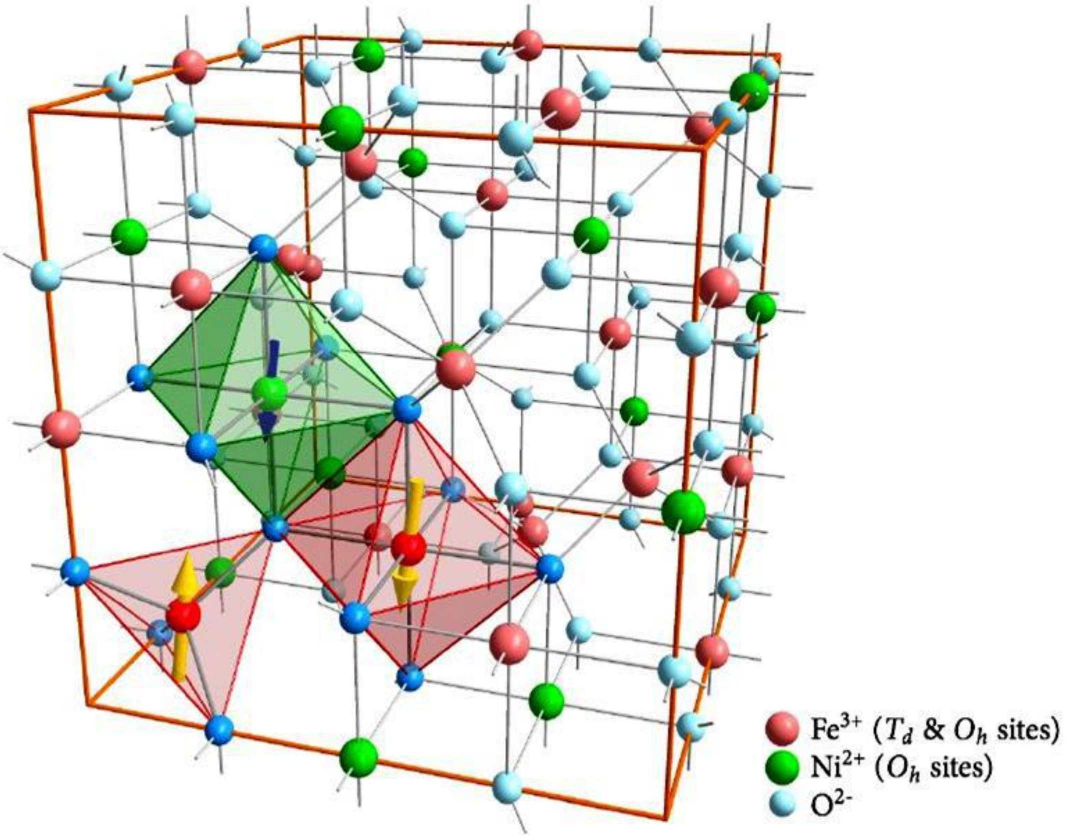

Fig.1. The unit cell of the inverse spinel lattice of $NiFe_2O_4$: Fe^{3+}-cations (red) are distributed equally across tetragonal (T_d) and octahedral (O_h) lattice sites, while Ni^{2+}-cations (green) occupy O_h sites. An antiferromagnetic coupling between the T_d and O_h sites compensates the magnetic moments of the Fe^{3+}-cations, why only the Ni^{2+}-cations account for the net macroscopic magnetization of 2 $\mu_B/f.u$ [10]

3. RESULTS AND DISCUSSION
3.1. EXPERIMENTAL DETAILS

The luminescence spectra of all synthesized $Ni_{1-x}Zn_xFe_2O_4$ nano-powders compositions were studied on LS-55 spectrometer with a Monk-Giddison monochromator at room temperature in the 300-700 nm wavelength range. The following symbols were used on the fig. 3: A, B, C, etc. - luminescence spectra when excited from the Xe source: 280 nm (4.427 *eV*), 290 nm (4.275 *eV*), 300 nm (4.132 *eV*), 325 nm (3.814 *eV*), 350 nm (3.542 *eV*), 375 nm (3.306 *eV*), 388 nm (3.195 *eV*), 400 nm (3.099 *eV*), 425 nm (2.917 *eV*); *a*, *b*, etc. - compositions: x = 0; 0.25; 0.4; 0.5; 0.6; 0.75; 1 respectively. The numbers 1, 2 and etc. in table 1 denote the energies and wavelengths of electronic transitions averaged over the investigated compositions. The top lines of the table cell are nm, the bottom lines- *eV*.

The luminescence spectra of all synthesized $Ni_{1-x}Zn_xFe_2O_4$ nano-powders compositions were also investigated on the Confocal Raman Spectrometer, 3D Confocal Laser Microspectroscopy System Nanofinder 30 (Tokyo Instruments, Japan). The source of excitation is the YAG Nd laser (λ =532 nm), with the possibility of changing the radiation power from 0.1 *mW* to 10 *mW*. These studies revealed the presence of a photoluminescence band in the region of 600-1000 nm, with a maximum at 822 nm, the intensity of which depended on the composition. The maximum band of this photoluminescence is practically independent on the power of the exciting radiation.

3.2. DISCUSSION

Ni-Zn ferrites exhibit red photoluminescence within excitation by xenon lamp radiation at 393 nm at room temperature. The emission spectrum is composed of a several groups of sharp lines in the range of about 530–710 nm with the most intensive line at 612 nm. The photoluminescence excitation spectra of emission lines at 587 nm, 612 nm and 700 nm have evidently similar structure. They are composed of broad band in the range of 250–320 nm with maximum at about 275 nm and a series of sharp lines in the range of 350–550 nm with the most intensive at 363 nm, 393 nm and 466 nm [1].

Fig. 2 shows the approximate band structures of the Fe_3O_4 nanoparticles, as estimated by our photoluminescence measurements. A near-infrared peak is observed at ~840 nm (1.47 *eV*), which can be attributed to the electron traps on the tetrahedral site, that are associated with the oxygen vacancies. Their mutual correlation is beyond doubt, as mentioned earlier, is a consequence of the exchange processes between Fe^{3+} and Fe^{2+} ions. It should be note that a similarity of this maximum is also performed in the photoluminescence spectra of the authors, for instance [1, 14]. For the following interpretation of the obtained results, we used the scheme of the energy bands of the Fe_3O_4 nanoparticle systems, published in [1]:

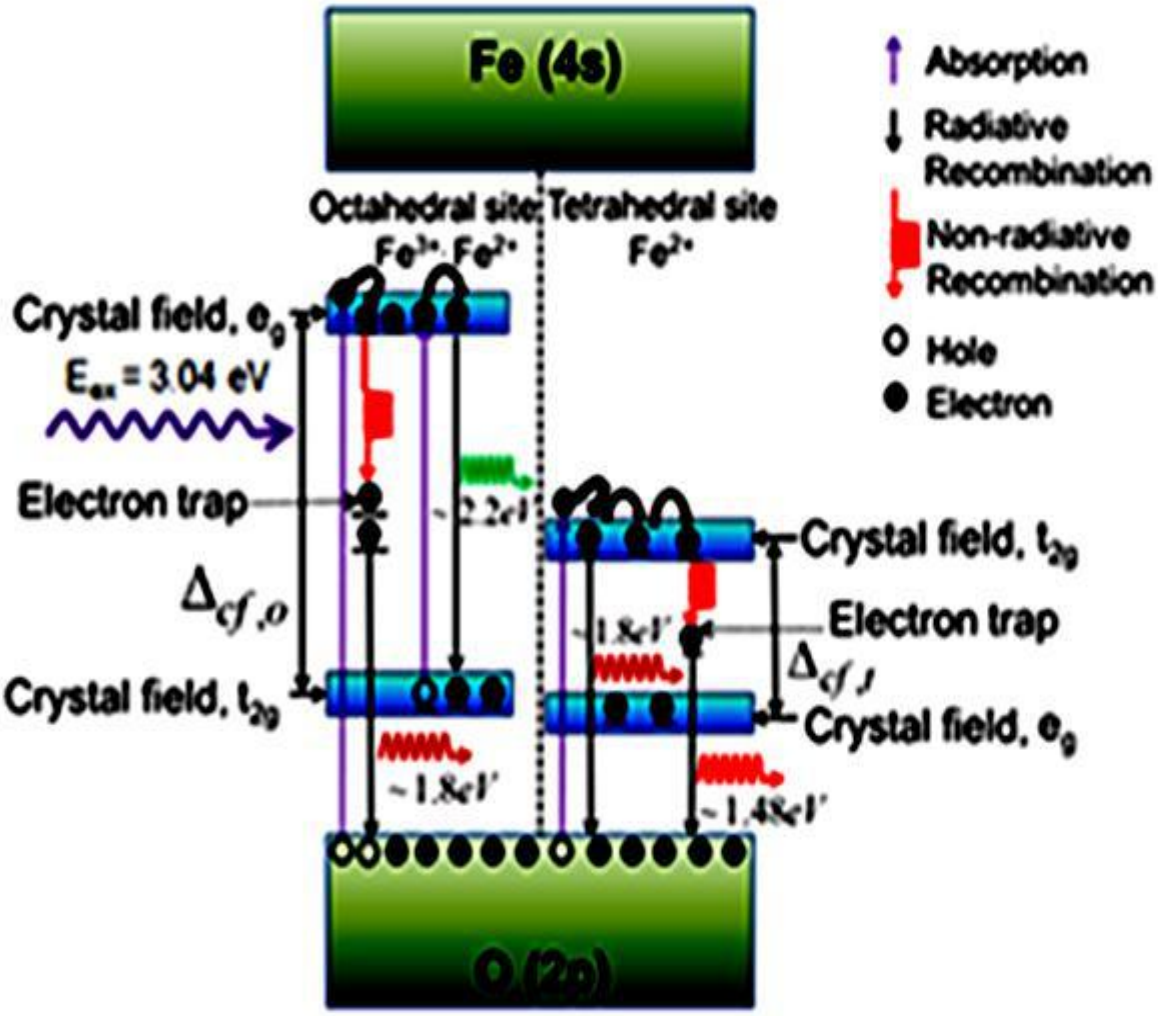

Fig. 2. The schematic of the energy bands of the Fe_3O_4 nanoparticle systems [1]

PAA-Fe_3O_4 photoluminescence measurements (PAA-hydrophilic coatings) when illuminated with 407 nm laser light (3.05 eV), published in [1], revealed three main peaks in the spectral range of 10–5000 nm: about 540 nm, 690 nm, and 840 nm. Similar photoluminescence spectra were obtained using 449 nm (2.76 *eV*) radiation for excitation. The photoluminescence spectra contained two main peaks: at 550 nm (2.10 *eV*) and 674 nm (1.84 *eV*) for the PAA-Fe_3O_4 samples, whereas for the Fe_3O_4 samples only one peak was observed at 674 nm (1.84 *eV*) [1]. In the present study, all these peaks were also observed.

According to [1], the photoluminescence peak near 550 nm (2.30 *eV*) is explained by the radiative recombination of mobile electrons from $t_{2g} \rightarrow e_g$ (2.2 *eV*) at the octahedral site. A much weaker peak at ~ 690 nm (1.79 *eV*) corresponds to recombination of trapped electrons from the octahedral site to O (2p) at the tetrahedral site. In addition, from [14], it is possible to see the intensity of the emission bands at 541.94 and 518.93 nm, which changes with increasing Zn/Ni substitution. Obviously, these intensities increase with increasing Zn content, except for x =0.5. This can be explained as follows: 1) based on the analysis of MAUD with increasing concentration of Zn^{2+} and leaving Ni^{2+} cations in the structure, Zn^{2+} ions occupy tetrahedral sites and transfer Fe^{3+} to octahedral sites, 2) these changes lead to a decrease in the structural isotropy of the synthesized nano-crystals, with the exception of the $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nano-crystals, 3) nano-crystals have the highest saturation magnetization among the synthesized nano-crystals and have structural isotropy in the tetrahedral regions, 4) the capture of half of the tetrahedral sites by Zn^{2+} ions and the rest by Fe^{3+} ions leads to a decrease in the transitions of Fe^{3+} ions in tetrahedral sites.

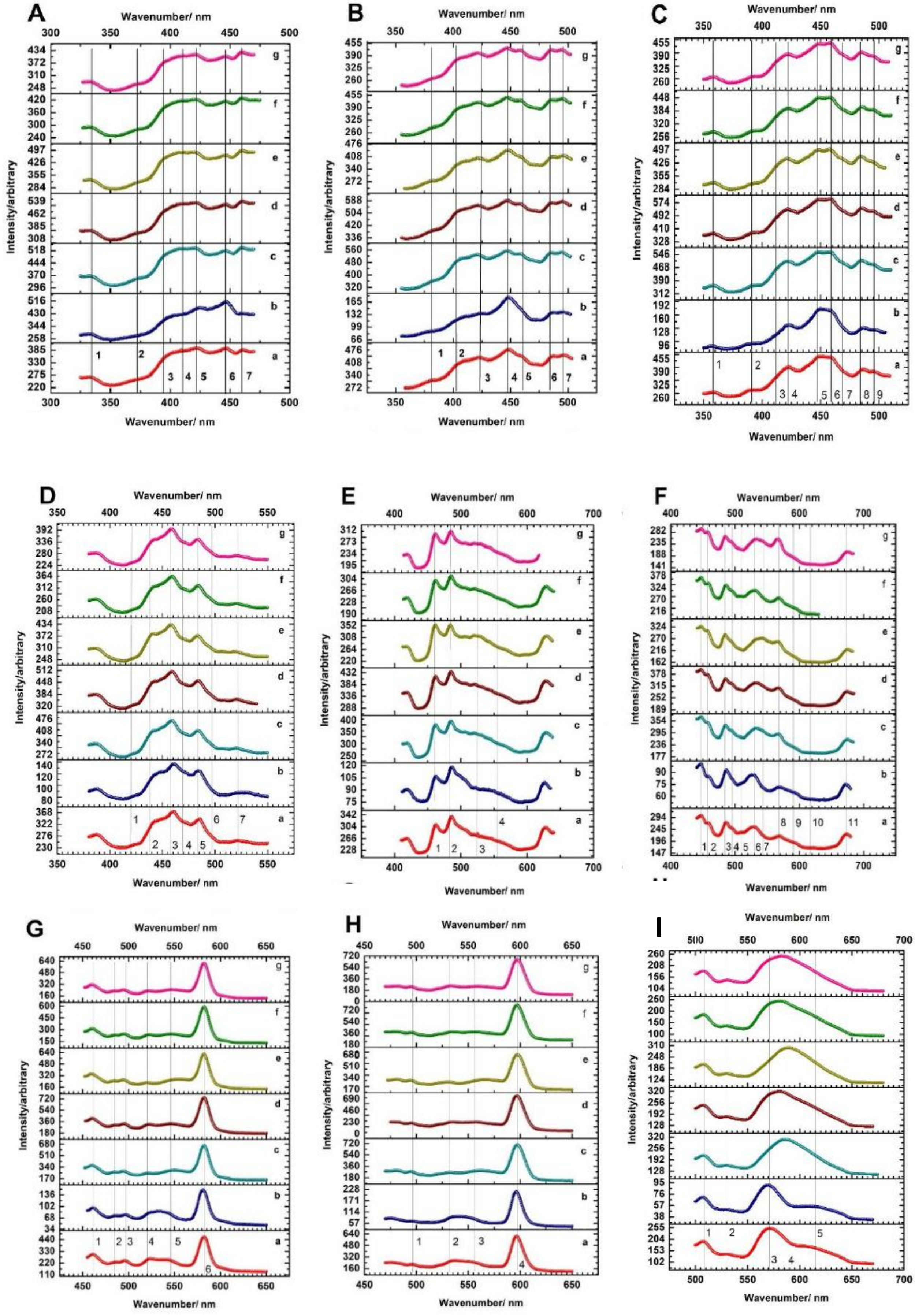

Fig. 3. Photoluminescence spectra of $Ni_{1-x}Zn_xFe_2O_4$ nanopowders (A, B, C, D, E, F, G, H, I - luminescence spectra when excited from the Xe source: 280 nm, 290 nm, 300 nm, 325 nm, 350 nm, 375 nm, 388 nm, 400 nm, 425 nm respectively)

Table 1.

Comparison the results of [1] work and obtained from our investigation of energies and wavelengths of electronic transitions of photoluminescence spectra of $Ni_{1-x}Zn_xFe_2O_4$ ferrite nano-powders

Experimental data [1] **407 nm** **3.05 eV**	-	-	-	-	-	-	-	-	-	-
Our Investigation (nm, eV)	332 3.734	372 3.332	396 3.13	406 3.053	421 2.945	446 2.779	461 2.689	486 2.551	496 2,499	522 2.375

Experimental data [1] **407 nm** **3.05 eV**	540 2.3	-	-	-	-	690 1.8	840 1.47
Our Investigation (nm, eV)	548 2.262	558 2.222	598 2.073	628 1.974	636 1.949	683 1.81	873 1.42
YAG Nd laser (λ= 532 nm)	-	-	-	-	-	682.8	873

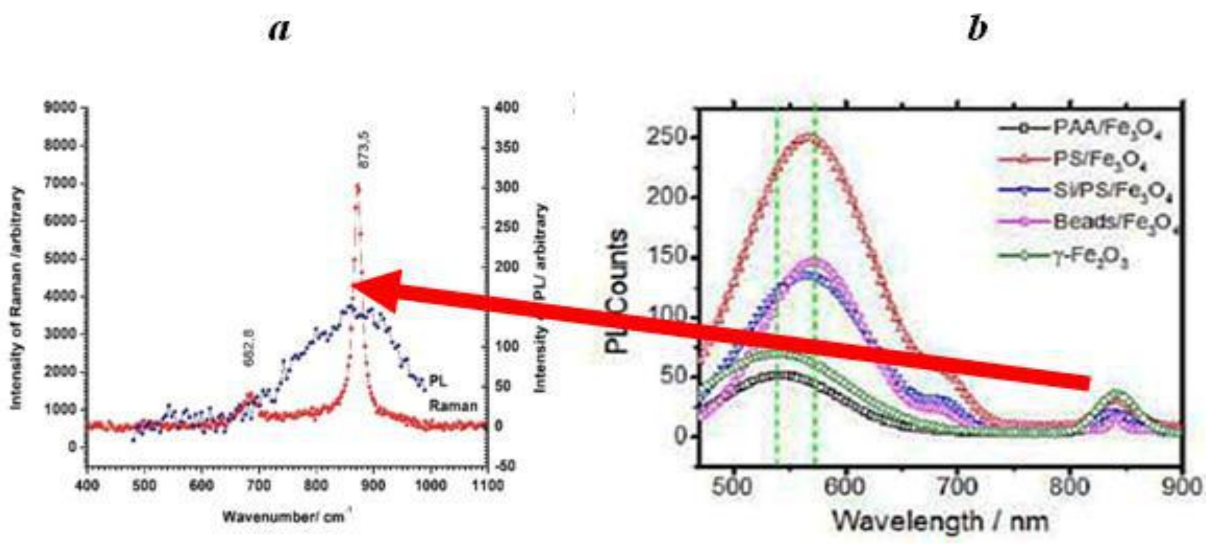

Fig.4. $Ni_{0.4}Zn_{0.6}Fe_2O_4$ thin film (a) [15] and Fe_3O_4 (b) ($840 cm^{-1}$) [1] to the maximum of oxygen vacancies is indicated by a red arrow. The blue color indicates the components of the photoluminescence spectrum of $Ni_{0.4}Zn_{0.6}Fe_2O_4$ nanopowders, and the red color indicates a maximum of 873 cm^{-1} in the Raman spectrum of $Ni_{0.4}Zn_{0.6}Fe_2O_4$ thin films (a)

Comparing the results obtained with the known studies [1, 15], we note that, with a common similarity, they contain information on previously unrecorded electronic transitions, as well as the dynamics of the change in the luminescence spectra with a change concentration in the composition.

3. CONCLUSION

The photoluminescence spectra of $Ni_{1-x}Zn_xFe_2O_4$ nanopowders (x=0; 0.25; 0.4; 0.5; 0.6; 0.75; 1) were studied at various energies and excitation powers. The transition energies are determined and a tentative interpretation is given.

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[1] *M.E.Sadat, Masoud Kaveh Baghbador, Andrew W. Dunn, H.P. Wagner, Rodney C. Ewing, Jiaming Zhang, Hong Xu, Giovanni M. Pauletti, David B. Mast,* and *Donglu Shi*. Photoluminescence and photothermal effect of Fe_3O_4 nanoparticles for medical imaging and therapy, Applied Physics Letter, 105, 091903-1-091903-5, 2014.

[2] *E.W. Gorter*. Philips Res. Rep., 9, 4, 295, 5, 321, 6, 403, 1954.

[3] *M.Sorescu, L. Diamandescu, R. Peelamedu, R. Roy, P. Yadoji*. Structural and magnetic properties of NiZn ferrites prepared by microwave sintering, Journal of Magnetism and Magnetic Materials, 279 (2004), 195–201, doi:10.1016/j.jmmm., 01.079, 2004.

[4] *V. Blanco-Gutiérrez, M.J. Torralvo, Sáez-PucheR.* and *P.Bonville*. Magnetic properties of solvothermally synthesized $ZnFe_2O_4$ nanoparticles Journal of Physics: Conference Series 200,072013, 5 p., 2010.

[5] *V.G. Kostishyn, B.K.Ostafiychuk, V.V.Moklyak, A.V.Nuriev*. Materials of Electronics Engineering, 2013, 4, 22-29.

[6] *A.A.Sadigova, S.A.Ahmadova, Sh.N.Aliyeva, T.R.Mehdiyev*. IR Diffuse Reflectance Spectra of Nanopowders of $Ni_{1-x}Zn_xFe_2O_4$ Ferrites, AJP Fizika XXIV, p .26, 2018

[7] *N.N.Scholtz, K.A.Piskarev*. Ferrimagnetic materials for radio-frequencies, Publishing House Energy, Moscow, 2013.

[8] *S.Aliyeva, S.Babayev, T.Mehdiyev*. Raman spectra of $Ni_{1-x}Zn_xFe_2O_4$ nanopowders, JRS; 49 (2), 271, 2018.

[9] *Y.V.Kasyuk, L.A.Bliznyuk, N.A.Basov, A.K.Fedotov, A.S.Fedotov, I.A.Svito*. Structure and electrophysical properties of doped zinc oxide ceramics, International Scientific Conference, November 22-25, Minsk, Vol. 2, pp.84-86, 2016.

[10] *Michael Hoppe, Sven Doring, Mihaela Gorgoi, Stefan Cramm* and *Martina Muller*. Enhanced ferrimagnetism in auxetic $NiFe_2O_4$ in the crossover to the ultrathin film limit, Phys. Rev. B 91, 054418 – Published 24 February 2015.

[11] *J. B. Goodenough*. Magnetism and the chemical bond. (Interscience Publishers, New York, 1963.

[12] *J. Kanamori*. “Superexchange interaction and symmetry properties of electron orbitals”, Journal of Physics and Chemistry of Solids 10, 87, doi: 10.1016 /0022 -3697(59) 90061-7, 1959.

[13] *P.W. Anderson*. “Chapter 2 - Exchange in Insulators”, in G. T. Rado and H. Suhl, Magnetism. Academic Press. pp. 25–83, isbn: 978-0-12-575301-2, 1963.

[14] *F. Shahbaz Tehrani, V. Daadmehr, A.T. Rezakhani, R. Hosseini Akbarnejad, S. Gholipour*. Structural, magnetic, and optical properties of zinc- and copper- substituted nickel ferrite nano-crystals, Journal of Superconductivity and Novel Magnetism, October 2012, Vol. 25, Iss. 7, pp. 2443–2455.

[15] *I.F.Yusibova, Sh.N.Aliyeva, T.R.Mehdiyev*. Verwey transition in Raman scattering spectra of (Ni-Zn) ferrite nanofilms, AJP Fizika, Vol. XXIV, №3, Section: Az, 2018, 95-100.

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