International Journal on
"Technical and Physical Problems of Engineering"
(IJTPE)
Published by International Organization of IOTPE

ISSN 2077-3528
IJTPE Journal
www.iotpe.com
ijtpe@iotpe.com

March 2021 | Issue 46 | Volume 13 | Number 1 | Pages 81-90

# LUMINESCENT AND OPTICAL PROPERTIES OF (Ni, Zn) FERRITES

**T.R. Mehdiyev [1] A.M. Hashimov [1] Sh.N. Aliyeva [1] I.F. Yusibova [1] A.V. Agashkov [2] B.A. Bushuk [2]**

*1. Institute of Physics, Azerbaijan National Academy of Sciences, Baku, Azerbaijan*
*jophphysics@gmail.com, ahashimov@azerenerji.gov.az, Shahla-aliyeva22@rambler.ru, yusibova78@mail.ru*
*2. B.I. Stepanov Institute of Physics, National Academy of Sciences of Belarus, Minsk, Belarus*
*a.agashkov@ifanbel.bas-net.by, bushuk@dragon.bas-net.by*

**Abstract-** The development of new technologies and instrument engineering has significantly stimulated the experimental potential of scientific researches, their reliability and efficiency. Not only research methods have changed, but also the requirements for materials. Investigations of microscopic objects and their submicron thickness of films entered the picture, and the role of studies of the relief and topology of surfaces by atomic force microscope investigation and methods rose sharply. Thus, it is not surprising that the study of ferrite materials has become one of the promising areas of research. Among those materials, already in the first half of the last century there were nickel-zinc ferrites, which found wide application in magnetic elements, electronic devices, computing systems, communication devices, transmit and receive devices and information processors, etc. In this case, we were interested in the use of these ferrites in solving the problem of limiting the effect of external high-frequency electromagnetic fields on the flow of alternating currents, and in studying the properties of these ferrites in a wide spectral range, characteristic for the noise spectrum, arising, for example, in lightning discharges, etc.

**Keywords:** High Voltage Engineering, Thin Film, Nanopowder, Ferrite, Hyper Resonant Effect, Afm, Thz Spectroscopy, Raman Spectroscopy, Luminescence of Spinels, Magnetic Properties.

## 1. INTRODUCTION

Despite the apparent simplicity of the solution, the problem of limiting the effect of external high-frequency electromagnetic fields on the flow of alternating currents still appears relevant. The solution of this problem is important in all cases when the amplitudes of alternating currents and voltages, due to the effect of high-frequency interference, exceed the acceptance limits and, as a result, lead to the failure of elements and blocks of electronic and electrical devices.

A new line of research of the problem under consideration that emerged in the 80-s of the last century was associated with the idea of using the skin effect, the effect of which is especially noticeable when alternating high-frequency currents flow through conductors and magnetic elements of electronic devices, or when they are exposed to external pulse and alternating electromagnetic fields. It is well known that skin effect in conductor elements manifests itself in a non-uniform distribution over cross section of density of the AC (alternating current) flowing through the conductor, which, with an increase in the AC frequency, is increasingly concentrated near the surface of the conductor. For cylindrical conductors, this distribution has axial symmetry, which corresponds, for example, for the normal skin effect, to an increase in the current density from the central part of the conductor to its surface.

With the increase of frequency, the thickness of the skin layer decreases and reaches values of the order of nanometers, that is, the skin layer becomes two-dimensional, which significantly changes the motion of carriers in it. Thus, the extension of the frequency domain of operation of frequency-dependent resistors, which was reported in [1, 2], required the investigation of the properties of the ferromagnetic sheath of resistor in the super high frequency (giga- and terahers) range. Accordingly, as shown by preliminary studies of nanocrystalline powders and granular nanofilms, it became necessary to apply the methods of advanced nanotechnology.

The reasons for this formulation of the problem lie in the wide noise microwave spectrum, arising, for example, in lightning discharges, etc. To date, a plenty of experience has been accumulated in the development of elements of nanoelectronics and computer engineering, their operation being based on the principles of quantum mechanics. This experience testifies that by stacking atoms with an accuracy of one-two layers, it is possible to create artificial atomic structures, quantum dots, quantum wells with specified properties. For example, quantum wells are created by placing a thin layer of semiconductor with a narrow band gap between two layers of material with a wider band gap. As a result, the electron gets trapped in one direction, which leads to the quantization of the energy of transverse motion.

In such a structure, the energy spectrum in each direction can be described by formula $E_n = \left(\frac{h_n}{a}\right)^2 / 8m$, where, $a$ is the thickness of the film in a given direction. In the remaining direction ($x$), electrons can move freely. The formed potential well must be considered infinitely deep; therefore, $E_n$ must be small in comparison with the actual depth of the well Φ. This condition leads to a filament thickness of the order of nanometers. The total energy of carriers in a quantum-dimension filament, similar to thin films, has a mixed discrete-continuous spectrum: $E = E_{nm} + \frac{p_x^2}{2m}$, in here, $p_x$ is the pulse component in the direction of the filament ($x$).

## 2. AFM CONTROL OF SAMPLES

Using any known technologies, the obtained nanothickness $Ni_{1-x}Zn_xFe_2O_4$ films were granular. This fact is illustrated in Figure 1, which shows, obtained with a scanning probe microscope, surfaces profiles and histograms of granules distribution on them: 1.$NiFe_2O_4$, 2.$Ni_{0.75}Zn_{0.25}Fe_2O_4$, 3.$Ni_{0.5}Zn_{0.5}Fe_2O_4$, 4.$Ni_{0.25}Zn_{0.75}Fe_2O_4$ thin films.

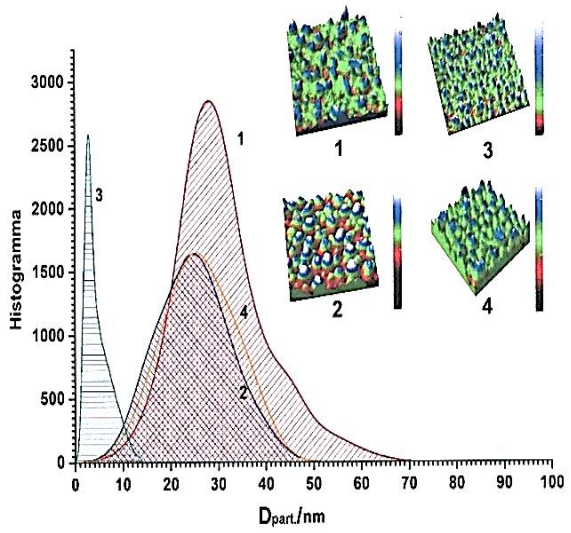


Figure 1. AFM profiles of the surface: 1. $NiFe_2O_4$, 2. $Ni_{0.75}Zn_{0.25}Fe_2O_4$, 3. $Ni_{0.5}Zn_{0.5}Fe_2O_4$, 4. $Ni_{0.25}Zn_{0.75}Fe_2O_4$ of micro-inhomogeneity distribution histograms

Further studies, the results of which were published in [5], showed that the size of the observed granules and the distance between them in thin films of $Ni_{1-x}Zn_xFe_2O_4$ ferrites on a $SiO_2$-substrate depended primarily on the composition. The experimental scheme is given in Figure 2,a. The modification of $Ni_{0.4}Zn_{0.6}Fe_2O_4$ nanopowder is carried out by the radiation from Spectra - Physics Tsunami laser. The micro-photos of substrate regions with particles of ferrite powder without influence (b) and at the influence of magnetic field (c) with a resolution bigger than 250 nm shown in Figure 3 are obtained at the following radiation parameters: radiation wavelength 1.064 μm, impulse duration 10 ns, energy density 480 mJ/cm$^2$.

The melting of conglomerates of submicron particles and their union into drop-shaped structures is carried out under the influence of laser impulses with duration ~10 ns. The analysis of the microcrystal structure presented in Figure 2,a shows that ferrite film is formed by spheroid different dimensions distributed in thin-crystal equal main grain mass with rare crystallographic shapeless isometric inclusions.

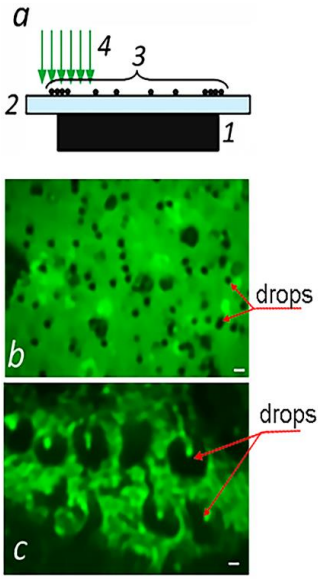


Figure 2. Experimental scheme (a): 1- permanent magnet; 2- glass substrate; 3- submicron powder particles $Ni_{0.4}Zn_{0.6}Fe_2O_4$; 4- laser radiation), (b): radiation without influence and (c): at the influence of magnetic field, Scale = 1 μm

The appearance of drops with plane toes is seen, that confirms the glass substrate surface wetting by melted ferrite. The experiments show that the concentration of drop-shaped formations is insignificant without the influence of magnetic field (by order 250-300 Oe) (Figure 2,b) and non-structural regions by the order of several quadratic millimeters in which the particles, contrasting on film background, are absent and depolarization radiation which is seen more clear that glass surface, is revealed. The analogous results are observed in work [17] at the influence of external magnetic field with symmetry $C_3$: $H = 7.87\times10^3$ A/m (1 Oe = 79.577 A/m) in which the peculiarities of powder microstructure formation on $Al_2O_3$ after treatment without lapping of the electromagnetic field and with it.

The phase transformations taking place in the sample annealing process, are the reason of the observable peculiarities of macroscopic construction of obtained granular films on $SiO_2$ substrates: formations of different type defects, partial microstructure reconstruction, non-equal change of dimensional parameters, apparently, were phase transformations occurring during the firing of samples.

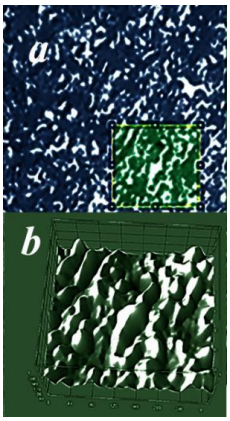


Figure 3. AFM investigations: (a) ferrite nanofilm; (b) AFM profile of the nanofilm

The analysis of experimental data obtained in the given work, confirms the results of earlier published works [18, 19] in which the average values of magnetic moments for A and B sublattices in the dependence on ferrite granule dimensions $\left(Fe^{2+}_{0.32}Zn^{2+}_{0.68}\right)\left[Ni^{2+}_{0.32}Fe^{2+}_{1.68}\right]O^{2-}_{4}$ confirming not only dominant mechanism of magnetic property dominating mechanism connected with oxygen vacancies but with the influence of magnetic cation redistribution between crystallographic positions of A and B sublattices, are calculated and temperature dependences of spin concentrations on A and B sublattices in different compositions $Ni_{1-x}Zn_xFe_2O_4$ which show Morin effect, i.e. the anisotropy constant change and reorientation of magnetic moments from one direction to another one.

The process of technological control earlier published in work [20] is carried out for achieving of required effect on both nano-meter level and on the levels from submicron one up to hundred microns for parameter repeatability and effective device functioning. From this, it is followed that the fact of plane "toes" presence in some drops $Ni_{0.4}Zn_{06}Fe_2O_4$ can be considered as established one and by other words, that given ferrite melt wets the glassy surface. This fact can be easily explained by considering the property of the components that make up the ferrite composition to react with silicon dioxide, namely:

The reaction $SiO_2+2Fe_3O_4 \rightarrow 3Fe_2SiO_4+O_2$, in which $SiO_2$ is an acid, and $Fe_3O_4$ is an alkali, takes place with the formation of iron orthosilicate, that is, the fayalite mineral:

$2O^{-II}-4e^- \rightarrow 2O^0$ (oxidation)

$6Fe^{8/3}+4e^- \rightarrow 6Fe^{II}$ (reduction)

On the other hand, this reaction is reversible $3Fe_2SiO_4+O_2 \rightarrow 2Fe_3O_4+3SiO_2$

Analogically, the reaction of the interaction of nickel oxide with $SiO_2$ leads to the formation of nickel silicate $2NiO+SiO_2 \xrightarrow{t\ ^\circ C} Ni_2SiO_4$, and the reaction $ZnO+SiO_2=ZnSiO_3$ - zinc metaxilicate. At ~1200 °C, all three ferrite components react with $SiO_2$.

Detailed studies of strengthening wetting characteristics in solders with glasses [15] indicated that in case of Fe-Ni alloy or $Ni_{0.4}Zn_{0.6}Fe_2O_4$ the maximum stress compensation is achieved at thicknesses of the glass and Fe-Ni alloy (1-1.5) μm and (0.5-0.75) μm, correspondingly. The parameters of optimal mode for seal obtaining are established: temperature rise to 900 °C at a rate of 10 °C/min, cooling from 900 °C to 500 °C at a rate of 10 °C/min, at a temperature of 500 °C isothermal holding 40 min. With subsequent cooling of the junction at a rate of 3 °C/min. The influence of the external magnetic field on macrostress change character and the role of mutual orientation of domain and external magnetic fields are also established in these investigations.

Thus, it becomes obvious that the created ferrite microstructures will have specific spatially modulated magnetic and electric profiles. On the other hand investigations on luminescence and Raman scattering of Ni-Zn ferrite thin films of different compositions [21-23] really always having the microscopic heterogeneity and absorption, shows us the observation possibility of the hyper resonance effects in them [24].

Note that experimental studies carried out on AFM allowed us to assume that the granular structure of the obtained ultra-thin films can be considered as a system of magnetic quantum dots and used for interpretation the conclusions of the percolation theory [25, 26]. Following this work, to calculate the magnetic permeability depending on temperature, frequency and concentration of particles, in the general case, we can use the following expressions

$$\mu'_{xx}(\omega)=1-\left(\frac{p}{p_{cr}}\right)+\left(\frac{p}{p_{cr}}\right)\left(\frac{9\mu_e}{2a^3H_a}\right)\left(\frac{T}{J_{ex}}\right)^{\frac{3}{2}}\cdot \cdot\left[\frac{\omega^2\tau_1^2}{1+\omega^2\tau_1^2}+\xi(p)\left(\frac{\Delta_0^2 J_{ex}}{T\hbar^2}\right)\left(\frac{\omega^4\tau_1^6}{\left(1+\omega^2\tau_1^2\right)^2}\right)\right] \quad (1)$$

$$\mu''_{xx}(\omega)=\left(\frac{p}{p_{cr}}\right)\left(\frac{9\mu_e}{2a^3H_a}\right)\left(\frac{T}{J_{ex}}\right)^{\frac{3}{2}}\cdot \cdot\left[\frac{\omega^2\tau_1^2}{1+\omega^2\tau_1^2}+\xi(p)\left(\frac{\Delta_0^2 J_{ex}}{T\hbar^2}\right)\left(\frac{\omega^4\tau_1^3}{\left(1+\omega^2\tau_1^2\right)^2}\right)\right] \quad (2)$$

Quasi-equilibrium magnon distribution function is determined from the collision integral

$$L\{l,h_0,\omega\}=2\pi\sum_{\{k\}}\psi^2(\{k\})\Phi\{f\}\delta\left(\sum\varepsilon(p)\right)\Delta\left(\sum k\right)+0\left(x^2,\omega\right) \quad (3)$$

in condition $L\{l,h_0,\omega\}=0$, where, $p$ is fraction of granules, $p_{cr}$ is critical fraction of granules; $a$ is granule size; $H$ is film thickness; $T$ is temperature; $\omega$ is frequency; $\tau$ is relaxation time; $J_{ex}$ is Bessel function; $\Phi\{f\}$ is functional of the distribution function, which depends on the number of particles participating in the scattering process.

Finally, using the expression from [25] that takes into account the pair interaction of magnetic moments for the case of $p<<p_{cr}$, that is, small concentrations, one can

determine the force acting on a magnetic particle from other particles and, naturally, its dependence on the concentration of granules.

$$U(p) = -\left(\frac{\pi^2 n^2 ZC}{36}\right)\left(\frac{p}{p_{cr}}\right)^2; \quad C = \frac{3\hbar}{\pi}\int_0^\infty d\omega\, \chi^2(i\omega)$$

where, $\chi_2(i\omega)$ is susceptibility of atoms in magnetic particles; $n$ is average number of particles in granules.

However, note that the force determined in this way characterizes the attraction of macroscopic bodies according to Van der Waltz's law. The introduction of this stochastic force requires some artificial assumptions. It is assumed that the Van der waltz interaction remains unchanged when the concentration changes, and the force magnitude is formally replaced by $F_0$, that is, $\Delta_0 = \langle F_0 a \rangle$. Note that the conductivity of the ferrite film between the granules is extremely low. From AFM studies (Figure.1) for the compositions of 1. $NiFe_2O_4$, 2. $Ni_{0.75}Zn_{0.25}Fe_2O4$, 3. $Ni_{0.5}Zn_{0.5}Fe_2O_4$, 4. $Ni_{0.25}Zn_{0.75}Fe_2O_4$ ferrite films were determined: the granule sizes (in nm): 27, 23, 8, 24; average distances between two granules (in nm): 8.92, 8.62, 0.96, 8.56; the ratio $\left(\frac{p}{p_{cr}}\right)\times 10^3 : 4.83, 4.9, 0.2, 5.34.$

## 3. AN IMPORTANT FEATURE OF THE LUMINESCENCE SPECTRA OF $Ni_{1-x}Zn_xFe_2O_4$ THIN FILMS

The luminescence and Raman spectra of $Ni_{1-x}Zn_xFe_2O_4$ thin films were studied on a 3D Laser Raman Microscopy System with an attachment for confocal laser microspectroscopy Nanofinder®30 (Tokyo Instruments, Japan) with a YAG Nd laser excitation source ($\lambda$ = 532 nm) in single-mode regime with the ability to change the radiation power from 0.1mW to 10mW. The spectrometer resolution is 0.5 $cm^{-1}$.

The luminescence spectra upon excitation from a xenon lamp were studied on LS-55 spectrometer with a Monk-Gillison monochromator (Perkin-Elmler Inc.). The fluorescence response, excited by two-photon mechanism, is registered by laser scanning microscope in combination with a micro-spectrometer and an argon laser of the Spectra-Physics Tsunami model working at $\lambda$ = 488 nm and generating radiation impulses with a duration of 100 fs and 82 MHz recurrence rate.

The luminescence intensity in experiments with non-modified particles (Figure 4,b) at excitation by $\lambda$=425nm radiation from xenon lamp is less than at excitation by radiation $\lambda$=400nm (Figure 4,c) that shows the observation of resonance effect, moreover, the spectrum structure (Figure 4,c) is more complex [21]. Studies carried out using laser radiation ($\lambda$ = 488 nm) of femtosecond duration have confirmed the obtained results. The obtained Raman spectrum in the region 200-1000$cm^{-1}$ (Figure 4,a) significantly differes from the Raman spectrum of non-modified particles. In comparison, Raman scattering spectra from nano-powder and nano-thick film $Ni_{0.4}Zn_{0.6}F_2O_4$ marked on $Al_2O_3$ substrate are given in Figure 4,a [21-23].

As it is seen in thin-film case the high-activity band, the appearance of which is connected with magnetic interactions in this ferrite, is observed.

Figure 5 shows the dependence of the band intensity on the power of the exciting radiation. Figure 1 shows AFM surface profiles of granular films of different compositions of $Ni_{1-x}Zn_xFe_2O_4$ ferrites and the size distribution of nanogranules on them. Note that at x=0.5, the size of the granules is the smallest. The analogous situation appears in [27] which the intensive maximum at 520 $cm^{-1}$ is revealed in Raman scattering spectra of $NiFe_2O_4$ ferrite thin films of different thickness (176, 118, 87 and 62 nm) synthesized on Si substrate, oriented in direction (100), this maximum is related to substrate Raman-spectrum by authors.

In work [3] it is mentioned that the most probable interpretation obtained by Raman-spectra of thin films of all ferrite compositions $Ni_{1-x}Zn_xFe_2O_4$, is connected with the contribution of normal oscillation spectra, magnons, and magnon-phonon interactions. The given statement is actual one especially in the relaxation phenomenon theory in two-sublattice ferrite [28] taking under consideration such experimental facts as the change of material magnetization and direction of sublattice magnetization during several pico-seconds at the heating of metallic ferromagnetics by impulses of femtosecond laser duration less than 100 fs.

The relaxation process of anti-ferromagnetism vector length caused by the exchange between sublattices and amplified by exchange interaction inside sublattices is very rapid. Moreover, the damping of optical mode is defined by the same exchange constant as the relaxation time of the anti-ferromagnetism vector length.

The actuality of the given statement is proved by the presence of giant anti-resonance in reflection of electro-magnetic waves on 3D-structure with nano-particles of ferrite-spinel, in particular $Ni_{0.5}Zn_{0.5}F_2O_4$ [29]. Note that, in works [30-32] it is established that plasmon nano-antenna consisting of metallic particles, concentrate the electromagnetic field and dielectric mediums with an occasional distribution of refractive index and irregular rough surface lead to the heterogeneous distribution of electromagnetic field intensity maximums in transmitted and reflected lights [32].

As the Raman scattering signal is proportional to the fourth power of local electric field in plasmon metamaterials taking under consideration that metallic nano-antennas allows to obtain the field gain in $10^2 - 10^3$ times, one can expect that the Raman scattering signal should be amplified more in $10^8$ times [33]. Note that different medium absorption for the radiation with frequencies $\omega$ and $\omega'$, is typical for hyper-Raman scattering, which is observed at two-photon excitation. However, the signals of non-resonant hyper Raman scattering, which can be easily estimated by the relation $E/E_m$, where $E$ is intensity of the electrical field strength of electromagnetic wave incident on the sample, which in ordinary experiments is much lower than the microscopic electric field strength $E_m$ in the sample which communicates with the part of the electronic subsystem

whose polarizability is responsible for optical processes and equal ~$10^8$ V/cm. The experiments with two-photon excitation of the luminescence of granular films do not confirm the presence of reasonable hyper Raman scattering in them.

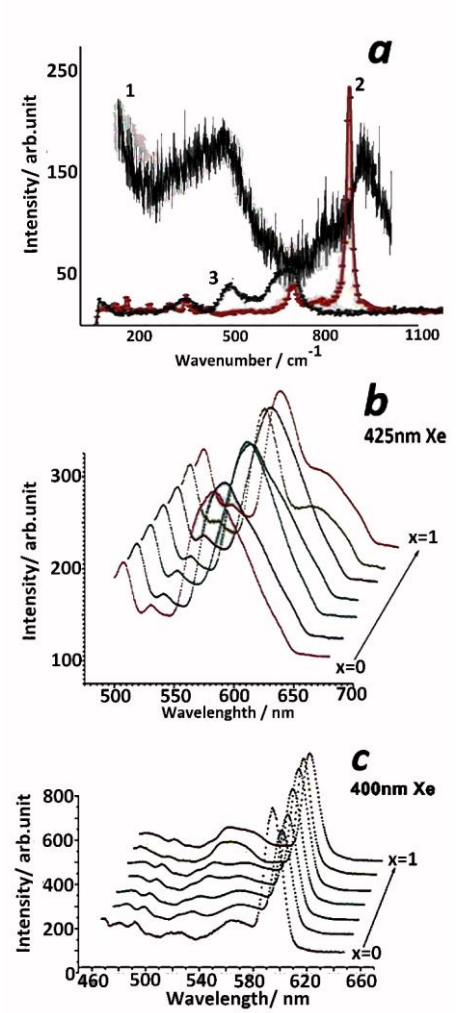


Figure 4. a. Raman-scattering spectrum (1) of $Ni_{0,4}Zn_{0,6}Fe_2O_4$ modified ferrite and its comparison with spectra of thin film (2) and nanopowder (3) of this material [25–27]. The spectrum intensities (2) and (3) are significantly higher than the Raman spectrum intensity for two-photon excitation (Figure 4,a); b. and c. The luminescence spectra $Ni_{1-x}Zn_xFe_2O_4$ of different compositions excited by radiation $\lambda$=425 nm (b) from xenon lamp and radiation $\lambda$ = 400 nm (c) [19]

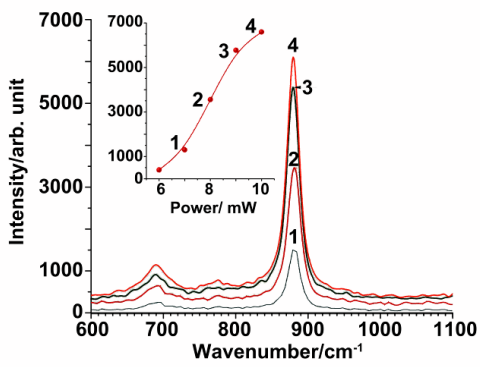


Figure 5. The intensity dependence of maximum 880 $cm^{-1}$ on excitation radiation power

Large frequency shifts of the scattered light can also be observed in cases of spontaneous and stimulated Raman scattering, which arise near the intrinsic absorption band of the crystal [24]. From previous studies [19, 21-23] shown that, the Raman scattering spectra in ferrite thin granular films $Ni_{1-x}Zn_xF_2O_4$ are shifted relative to Raman scattering spectra of nano-composite powders of analogous compositions. The shift value is different one for different scattering bands (in average, it is approximately equal to 200 $cm^{-1}$). Besides, intensity maximum is observed for the maximum 880$cm^{-1}$ in composition $Ni_{0.4}Zn_{0.6}F_2O_4$. In [30] it is shown that the shift of Raman scattering spectra if film silicon relative to monocrystalline one, is connected with stressed state appearing in process of film cooling according to theory [20, 28].

The investigation of charge localization in magnetite on B-sublattice [35-37] shows that $t_{2g}$ electrons of B-sublattice not totally localize in the form of $Fe^{2+}$ states but they distribute on three ions of $Fe^{3+}$- $Fe^{2+}$- $Fe^{3+}$ trimeron and $d_{xy}$ energy is less than $d_{yz}/d_{zx}$ one, though it is accepted that the charge disproportionation is connected with change of $Fe^{2+}$ and $Fe^{3+}$ states. The deformation of all four Fe-O trimeron bounds forms the effective energy division $\Delta t_{2g}$ between $d_{xy}$ and $d_{yz}/d_{zx}$. Thus, the tetragonal-distorted $Fe^{2+}O_6$-octahedrons with deformed Fe-O bonds in xy plane are connected with $Fe^{3+}O_6$-octahedrons of trimeron. The tetragonal distortion of $Fe^{3+}O_6$-octahedrons remove the degeneracy of $t_{2g}$-orbitals (the transition from $O_h$ symmetry to $D_{4h}$). The effective division energy $\Delta t_{2g}$ between $d_{xy}$ and $d_{yz}/d_{zx}$ takes place at absent of spin-orbital bound if the four Fe-O bounds in $xy$ plane are prolonged or compressed ones.

The authors of [38, 39] works establish that intensity maximum 90meV observed in spectra of magnetite resonance inelastic X-ray scattering and corresponding Fe $L_3$-edge weakly depends on phonon excitation. Note that the multiple calculations carried out for $Fe^{3+}$ ions of B-position in exchange molecular field 90 meV show that excitation energy 90 meV agrees with Zeeman splitting 100 meV caused by molecular field [40]. Finally, this energy characterizes spin-flip-process, i.e., the magnetic phase transition, and agrees with energy of almost nondispersive mode at 80-85 meV observed at inelastic neutron scattering [40, 41].

The results of the work [35] on magnetite are quite applicable to the granular Ni-Zn-ferrites films of which contain the strongly distorted octahedrons $Fe^{2+}O_6$ connected with $Fe^{3+}O_6$ ones. Obviously, that the intensive maximum 880 $cm^{-1}$ (109 meV) observed in Raman spectra is explained within the framework of model [35]. Correspondingly the presence of this maximum in Raman scattering spectrum is the result of almost non-dispersive mode excitation in $Ni_{1-x}Zn_xFe_2O_4$ nanofilms, observed also in neutron inelastic scattering experiments. The last fact followed from [35], work suggests the presence of magnetic polarons in Ni-Zn ferrites.

All the considered assumptions, as experiments showed, for all their plausibility, did not explain other experiments. The appearance of new spectral bands in

luminescence and Raman scattering were more similar to the generation associated directly with the ferrite-substrate structure, that is, the effect depended both on the composition of the ferrite film, its thickness, and the substrate material (glass, sapphire) and on the intensity of the incident light. Investigations of the spectra of spontaneous and stimulated radiation of $Ni_{1-x}Zn_xFe_2O_4$ ($x$=0; 0.25; 0.5) films deposited on oxidized silicon or sapphire, with optical pumping by a laser and an increase in the radiation power, led to a sharp increase in the luminescence intensity (Figure 6).

The experimental model used by us was practically identical to those used in these works with the difference in taking into account the optical properties of the intermediate layer formed in the processes of creating and annealing of the ferrite film at 1200 C and 900 C temperatures, respectively, on the surfaces of glass or sapphire substrates. In all cases, the thicknesses of the produced films were about 60 nm. The experiments were carried out under the conditions of perpendicular incidence of the exciting radiation on the film surface. The power of the exciting radiation was varied in the intervals from 0.5 to 10 mW.

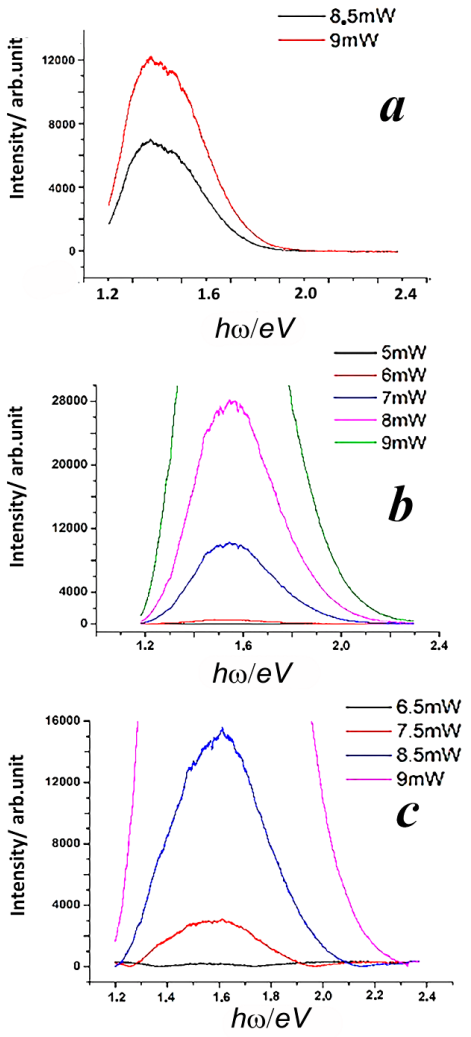


Figure 6. Luminescence spectra obtained when $NiFe_2O_4$ (a), $Ni_{0.25}Zn_{0.75}Fe_2O_4$ (b), $Ni_{0.5}Zn_{0.5}Fe_2O_4$ (c) films are excited by a Nd YAG laser ($\lambda$=532 nm) in a single-mode mode

The effect of radiation generation in non-epitaxial, polycrystalline, nano-thin $Ni_{1-x}Zn_xFe_2O_4$ ferrite films has been discovered. Generation was recorded both in the visible (1.8 eV) and in the far infrared (880 $cm^{-1}$) spectral regions (Figure 4-6) at an exciting laser radiation power of more than 4 mW (reflection density in $kW/cm^2$ ~ 20; 26; 31; 36; 41; 46; 51 Figure 6). All experiments were carried out at a temperature $T$ = 300 K.

## 4. TERAHERTZ SPECTRA OF $Ni_{1-x}Zn_xFe_2O_4$ THIN FILMS

The dipole photoconductive antenna excited by femtosecond radiation of ytterbium laser, $\lambda$ = 1.03 μm is used for generating the THz impulses. The photo-antenna-detector registering the amplitude and phase of electric field of THz impulses is gated by same radiation.

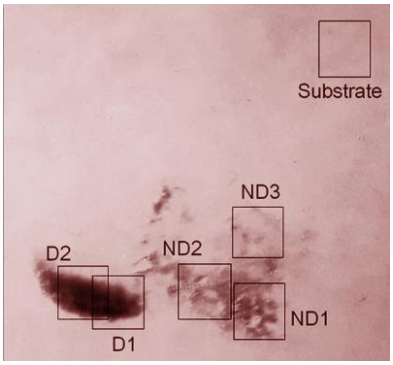


Figure 7. The sample with emphasized regions in which the investigation is carried out: D1, D2 (Dense); ND1, ND2, ND3 (Not Dense); substrate is pure glass

The sample type with granular film $Ni_{0.4}Zn_{0.6}Fe_2O_4$ and regions for which the measurements are carried out is shown in Figure 7. The regions with high concentrations of particles (Dense) are designated as D1 and D2, the regions with low concentrations (Not Dense) are designated as ND1, ND2 and ND3.

At measurements of reflection, the megahertz radiation is focused on the sample by an aluminum parabolic mirror with focal length $f$ = 5 cm and formed spot with diameter near 2 mm from the initial beam by diameter 15mm. Mirrors with a focal distance ~ $10^4$ mm carry out the beam focusing; the dimension of the exposed region is 5 mm.

The spectra of the reflected terahertz radiation in the frequency range 0.1-2.5 THz from $Ni_{0.4}Zn_{0.6}Fe_2O_4$ granular films obtained by the means of Furrier transformation after elimination of noise influence caused by water vapor absorption lines and also effects similar to interference from several re-reflection, substrate spectrum and aluminum mirror are shown in Figure 8,c. These results were obtained independently at different times in two scientific physics centers: the Institute of Physics of the National Academy of Sciences of Belarus and Azerbaijan.

It is known [42], in the absorption spectra of $Fe_3O_4$, a structural analog of $Ni_{1-x}Zn_xFe_2O_4$ ferrites, in the range 0.4-2.0 THz were observed weak structures with an interval of 0.24 THz (~0.9 meV) from 0.57 to 1.76 THz.

They were assigned to the acoustic phonon modes, and considered in work [43], in which the axisymmetric free vibrations of thin elastic spherical shells were studied (noted that magnetite nanoparticles can be represented in the form of nanohollow spheres). In [44] it was indicated that single peaks (0.57, 0.82, 1.05, 1.28 and 1.56 THz) decay into two consecutive peaks of acoustic phonons (0.49 and 0.62, 0.74 and 0.86, 0.97 and 1.08, 1.21 and 1.32, 1.45 and 1.55 THz), which is the result of the feature of the crystal structure of magnetite.

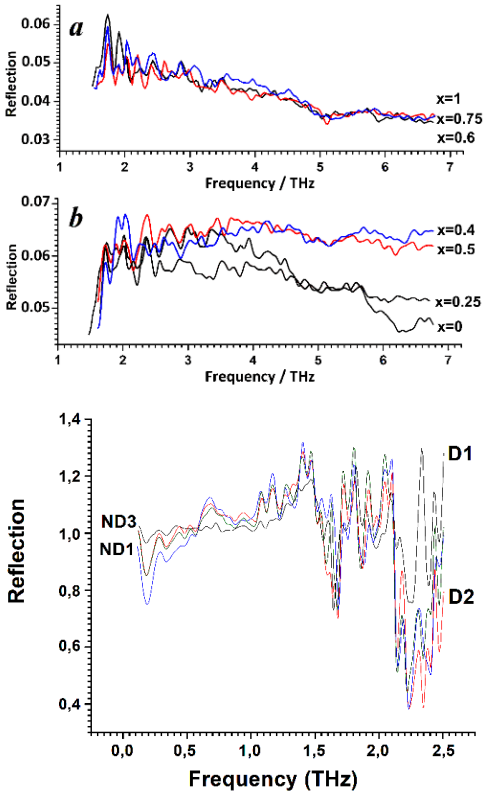


Figure 8. Terahertz reflection spectra: a,b - $Ni_{1-x}Zn_xFe_2O_4$ ferrite nanopowders in the 1-7 THz region and c - $Ni_{0.4}Zn_{0.6}Fe_2O_4$ granular film (sections which selected in Figure 3) in the 0-2.5 THz region

In this work, a split sequence of acoustic modes also observed in the THz spectra of the granular $Ni_{0.4}Zn_{0.6}Fe_2O_4$ ferrite film: (0.34 and 0.48, 0.57 and 0.73, 0.81 and 0.96, 1.05 and 1.21, 1.29 and 1.44, 1.52 and 1.68, 1.76 and 1.96, 2.01 and 2.13 THz). Further, another sequence found: (0.88, 1.12, 1.36, 1.6, 1.87, 2.14 THz). Both sequences of acoustic modes have the interval ~0.24 THz (0.9 meV), inside the group of split sequence the interval is equal to ~0.15 THz (0.6 meV), between groups it is equal to ~0.08 THz (0.33 meV). Besides, oscillations having similar nature of formation, especially, the sequence of acoustic modes, are easily observed on spectra Figure 9a,b in $Ni_{1-x}Zn_xFe_2O_4$ different compositions. The peak positions in the THz spectra of granular $Ni_{0.4}Zn_{0.6}Fe_2O_4$ films of different thicknesses practically do not change, which, as indicated in [42], can occur due to unlimited acoustic phonon modes.

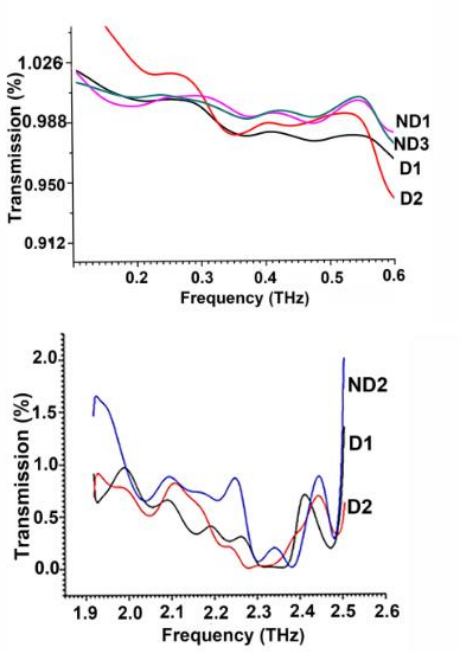


Figure 9. Terahertz transmission spectra of $Ni_{0.4}Zn_{0.6}Fe_2O_4$ films

As noted in [45], in the range from 0.4 to 2 THz, the absorption of electromagnetic radiation in magnetite due to spin ordering is extremely small, since the frequency of the reorientation of spins in the magnetic material does not exceed 0.02 THz [45]. Thus, the absorption process in the THz range is mainly associated with dielectric losses. The transmission spectra of the given sections of $Ni_{0.4}Zn_{0.6}Fe_2O_4$ films in the THz region are shown in Figure 9.

We can see the presence of oscillations associated with acoustic modes. In these intervals, the change in transmission shows a weak dependence on the frequency of the terahertz field. Comparing the obtained results of terahertz investigations with work data [46] in which the soft modes of trimeron order in magnetite, one can easily note their closeness, proving the observation possibility of similar order in $Ni_{0.4}Zn_{0.6}Fe_2O_4$ and in all compositions of Ni,Zn-ferrites, caused by the existence of super-exchange interaction of $Fe^{2+}$-$O^2$-$Fe^{3+}$ type in them.

## 5. CONCLUSIONS

The granular ferrite films are obtained by the influence of impulse laser radiation (laser Spectra–Physics Tsunami, radiation parameters: radiation wavelength 1.064 μm, impulse duration 10 ns, energy density 480 mJ/cm$^2$) on $Ni_{0.4}Zn_{0.6}Fe_2O_4$ powder submicron particles marked on the glass substrate. The conglomerate melting of submicron particles and their combining into drop-shaped structures proving on the wetting process of the glassy substrate by ferrite occurs in an external magnetic field at the influence of laser with duration ~10 ns. The role of mutual orientation of domain and external magnetic fields is established. It is obvious that formed ferrite microstructures will have the specifically space-modulated magnetic and electric profiles due to the chosen macrostructure geometry.

The luminescence of modified thin film Ni-Zn ferrite with a maximum near 600 nm is observed at the two-photon excitation. The comparison of obtained results of terahertz investigations with work data [47] show the possibility of observation of trimeron order in all compositions of Ni-Zn ferrites as a result of the existence of super-exchange interaction of $Fe^{2+}$-$O^{2}$-$Fe^{3+}$ type in them.

It was found that in the THz optical spectra of nanogranular $Ni_{0.4}Zn_{0.6}Fe_2O_4$ films, resonance vibrations due to low-frequency acoustic phonon modes of nanostructures are observed.

The effect of generation with optical pumping in non-epitaxial, polycrystalline, nano-thin $Ni_{1-x}Zn_xFe_2O_4$ ferrite films has been discovered. Generation was recorded both in the visible (1.8 eV) and in the far infrared (880 $cm^{-1}$) spectral regions (Figures 4-6) at an exciting laser radiation power of more than 4 mW and at a temperature $T$ = 300 K.

## ACKNOWLEDGEMENTS

The work is carried out in limits within the framework of Azerbaijan-Belorussian project at financial support of Belorussian and Azerbaijan Republican Funds of fundamental investigations, project: Ф18А3-003 Belarus and projects: EIF-2013-9(15)-46/05/1-M-12 and EIF-BGM-3-BRFTF-$2^{+}$/2017 Azerbaijan.

## REFERENCES

[1] A.A. Habibzadeh, N.R. Babayeva, A.M. Hashimov, T.R. Mehdiyev, "Magnetoelectric and Magnetoelasic Properties of Ferromagnetic Shell of Frequency Dependent Resistor", 6th International Conference on Technical and Physical Problems of Power Engineering (ICTPE-2010), pp. 617-621, Tabriz, Iran, 14-16 September 2010.

[2] Sh. Aliyeva, S. Aliyeva, T. Mehdiyev, "SHF-Magnetic Properties of FD-Resistor Shell", International Journal on Technical and Physical Problems of Engineering (IJTPE), Issue 14, Vol. 5, No. 1, 2013, pp. 119-126, March 2013.

[3] C.L. Chien, "Magnetism and Giant Magneto-Transport Properties in Granular Solids", Ann. Rev. Mater. Sci., Vol. 25, pp. 129-160, 1995.

[4] A.S. De Albuquerque, J.D. Ardisson, E. Bittencourt, W.A. De Almeida Macedo, "Structure and Magnetic Properties of Granular NiZn-Ferrite - $SiO_2$", Mater. Res, Vol. 2, pp. 235, 1992.

[5] A.V. Agashkov, B.A. Bushuk, A.M. Varaneckiy, T.R. Mehdiyev, "Method for Obtaining Ferrite Microstructures with Spatially Modulated Magnetic and Electric Profiles", Proc. XII ISTC, pp. 244-245, Minsk, Belarus, 2019.

[6] A.B. Rinkevich, A.V. Korolev, M.I. Samoylovich, S.M. Klshcheva, D.V. Perov, "Magnetic Properties of 3D Nanocomposites Consisting of an Opal Matrix with Embedded Spinel Ferrite Particles", Tech. Phys., Vol. 61, pp. 194-201, 2016.

[7] V.V. Dobrovickiy, A.K. Zvezdin, A.F. Popov, "Giant Magnetoresistance, Spin-Reorientation Transitions and Macroscopic Quantum Phenomena in Magnetic Nanostructures", Physics-Uspekhi, Vol. 166, pp. 439-447, 1996.

[8] I.A. Sherstnev, "Electronic Transport and Magnetic Structure of Nanosland Ferromagnetic Materials Systems", Ph.D. Dissertation, P.N. Lebedev Physical Institute of the Russian Academy of Sciences, 2014.

[9] L. Neel, "Saturation of Some Rendered Ferrites", Vol. 230, pp. 190-192, 1950 (in French).

[10] E.W. Gorter, "Philips Research Reports 9", Eindhoven, Netherland, 1954.

[11] K.P. Belov, "Ferrimagnets with a 'Weak' Magnetic Sublattice", Phys. Usp., Vol. 39, pp. 623-634, 1996.

[12] A.S. Komlev, "Radiation-Thermal Sintering in a Beam of Fast Electrons of Polycrystalline Ferrospinels", Ph.D. Dissertation, University of Moscow, 2018.

[13] D. Stauffer, A. Aharany, "Introduction to Percolation Theory", Taylor & Francis, London, 2018.

[14] A.V. Neimark, "Electrophysicsl Properties of a Percolation Layer of Finite Thickness", Sov. Phys. JETP, Vol. 71, pp. 341-349, 1990.

[15] S.P. Malyukov, "Physico-Technological Foundations of Creating Magnetic Heads for High-Density Information Recording", Dissertation Doctor of Technical Sciences, Taganrog, 2003.

[16] A.E. Muslimov, A.V. Butashin, V.M. Kanevskiy, "The Influence of Mechanical Stresses on the Magnetic Properties of $NiFe_2O_4$ and $CoFe_2O_4$ Films", Technical Physics Letters, Vol. 44, pp. 730-734, 2018.

[17] A.P. Klishin, S.V. Rudnev, V.I. Vereshagin, O.S. Andrienko, "Features of the Formation of Nano- and Microstructures of Powders and Monolithic Samples of $Al_2o_3$ When Firing without Imposing and with Imposing an Electromagnetic Field", Letters of Higher Educational Institutions, Physics, Vol. 58, pp. 106-110, 2015.

[18] B.K. Argymbek, S.E. Kichanov, D.P. Kozlenko et al., "Crystal and Magnetic Structures of Granular Powder Spinel Mn-Zn and Ni-Zn Ferrites", Phys. Solid State, Vol. 60, pp. 1727-1732, 2018.

[19] Sh. Aliyeva, S. Babayev, T. Mehdiyev, "Raman Spectra of $Ni_{1-X}Zn_XFe_2O_4$ Nanopowders", JRS, Vol. 49, pp. 271-278, 2018.

[20] A.V. Agashkov, "Laser Microscope with Submicron Resolution", Non-Destructive Testing and Diagnostics, Vol. 1, pp. 17-24, 2015.

[21] T.R. Mehdiyev, Sh.A. Ahmadova, A.A. Sadigova, Sh.N. Aliyeva, X.A. Gasanova "Investigation of Photoluminescence Properties of Ni-Zn Ferrites", 16th International Conference on Technical and Physical Problems of Power Engineering (ICTPE-2020), No. 14, Code 02ELC03, pp. 66-69, Istanbul, Turkey, 12-13 October 2020.

[22] Sh. Aliyeva, T. Mehdiyev, "Peculiarites of Magnetic Interaction in $Ni_{1-x}Zn_xFe_2O_4$", European Conference on Innovations in Technical and Natural Sciences, pp. 76-82, 2017.

[23] Sh. Aliyeva, T. Mehdiyev, "Peculiarities of Magnetic Interaction in $Ni_{1-x}Zn_xFe_2O_4$ Nanodimensional

Ferrites", Smart Nanocomposites, Vol. 8, pp. 149-153, 2017.
[24] M.M. Sushinskiy, "Resonant Inelastic Light Scattering in Crystals", Physics-Uspekhi, Vol. 154, pp. 353-379, 1988.
[25] T.P. Mehdiyev, A.M. Gashimov, N.R. Babayeva, A.A. Habibzade, "Electric and Magnetic Properties of Frequency-Dependent Resistor Shell", AJP Fizika, , Vol. XIV, No. 3, pp. 207-217, 2008.
[26] A.A. Habibzadeh, T.R. Mehdiyev, A.M. Hashimov, E.V. Dmitriyev, N.R. Babayeva, "Influence of Concentration and the Sizes of Ferromagnetic Granules on Electrical and Magnetic Properties of FD-Resistor Shell," International Journal for Knowledge, Science and Technology, Vol. 1, No. 1, pp. 49-56, 2009.
[27] G. Dixit, J.P. Singh, R.C. Srivastava, H.M. Agrawal, R.J. Chaudhary, "Structural, Magnetic and Optical Studies of nickel Ferrite Thin Films", Adv. Mat. Lett., Vol. 3, pp. 21-28, 2012.
[28] V.G. Baryaxtar, B.A. Ivanov, O.N. Golubeva, "Phenomenological Theory of Relaxation in Two-Sublattice Ferrite", Ukrainian Journal of Physics, Vol. 58, pp. 1149-1155, 2013.
[29] V.V. Ustinov, A.B. Rinkevich, D.V. Perov, A.M. Burkhanov, M.I. Samoylovich, S.M. Klshcheva, E.A. Kuznetsovc, "Giant Antiresonance in Electromagnetic Wave Reflection from a 3D Structure with Ferrite Spinel Nanoparticles", Technical Physics, Vol. 83, pp. 104-112, 2013.
[30] M. Moskovits, "Surface-Enhanced Spectroscopy", Rev. Mod. Phys., Vol. 57, pp. 783, 1985.
[31] F. Brouers, S. Blacher, A.N. Lagarkov, A.K. Sarychev, P. Gadenne, V.M. Shalaev, "Theory of Giant Raman Scattering from Semicontinuous Metal Films", Phys. Rev. B., Vol. 55, p. 13234, 1997.
[32] M.A. Noginov, G. Dewar, M.W. McCall, N.I. Zheludev, "Tutorials in Complex Photonic Media", SPIE Publications, Washington, 2009.
[33] A.K. Sarychev, V.M. Shalaev, "Electrodynamics of Metamaterials", World Scientific Publisher, Singapore, 2007.
[34] T. Englert, G. Abstreiter, I. Pontcharra, "Determination of Existing Stress in Silicon Films on Sapphire Substrate Using Raman Spectroscopy", Sol. State Electron, Vol. 23, pp. 31-33, 1980.
[35] H.Y. Huang, Chen Z.Y., R.P. Wang, et al., "Jahn-Teller Distortion Driven Magnetic Polarons in Magnetite", Nat. Commun., Vol. 8, p. 15929, 2017.
[36] M.S. Senn, J.P. Wright, J.P. Attfield, "Charge Order and Three-Site Distortions in the Verwey Structure of Magnetite", Nature, Vol. 481, pp. 173-176, 2012.
[37] M.S. Senn, J.P. Wright, J. Cumby, J.P. Attfield, "Charge Localization in the Verwey Structure of Magnetite", Phys. Rev. B, Vol. 92, pp. 024104, 2015.
[38] L.V. Gasparov, et al., "Infrared and Raman studies of the Verwey Transition in Magnetite", Phys. Rev. B, Vol. 62, pp. 7939-7944, 2000.
[39] L.V. Gasparov, D. Arenas, "Magnetite: Raman Study of the High-Pressure and Low Temperature Effects", J. Appl. Phys., Vol. 97, p. 10A922, 2005.
[40] R.J. McQueeney, M. Yethiraj, W. Montfrooij, et al., "Investigation of the Presence of Charge Order in Magnetite by Measurement of the Spin Wave Spectrum", Phys. Rev. B, Vol. 73, p. 174409, 2006.
[41] G. Subias, J. Garcia, J. Blasco, "EXAFS Spectroscopic Analysis of the Verwey Transition in $Fe_3O_4$", Phys. Rev. B, Vol. 71, p. 155103, 2005.
[42] E.J. Samuelsen, O. Steinsvoll, "Low-Energy Phonons in Magnetite", Phys. Status Solidi b, Vol. 61, pp. 615-620, 1974.
[43] W.E. Baker, "Axisymmetric Modes of Vibration of Thin Spherical Shell", J. Acoust. Soc. Am., Vol. 33**,** pp. 1749-1758, 1961.
[44] R. Rakshit, D. Sarkar, M. Pal, et al., "Acoustic Vibration Induced High Electromagnetic Responses of $Fe_3O_4$ Nano-Hollow Spheres in the THz Regime", J. Phys. D: Appl. Phys., Vol. 48, pp. 245301-24538, 2015.
[45] B.T. Draine, A. Lazarian, "Magnetic Dipole Microwave Emission from Dust Grains", Astrophys. J., Vol. 512, pp. 740-754, 1999.
[46] E. Baldini, C.A. Belvin, M. Rodriguez-Vega, et al., "Discovery of the Soft Electronic Modes of the Trimeron Order in Magnetite", Nature Physics, Vol. 16, pp. 541-545, 2020.
[47] Sh.N. Alieva, A.M. Kerimova, R.B. Abdullaev, T.R. Mekhtiev, "Infrared Diffuse Reflectance Spectra of Micropowders of $Ni_{1-x}Zn_xFe_2O_4$ Ferrites", Physics of the Solid State, Vol. 59, pp. 543-549, 2017.

## BIOGRAPHIES

**Talat Rzaqulu Mehdiyev** was born in Baku, Azerbaijan, in June 1944. He is head of "Reception, saving and processing of information" Department at the Institute of Physics, Azerbaijan National Academy of Sciences (Baku Azerbaijan, Doctor of Physics-Mathematical Sciences. His experience is 55 years, and he has a specialty in physics of semiconductors and dielectrics (optics, roentgen diffractometer, magnetic and electric properties and etc); applied and system programming, electronics, calculative technique. At the same time, he is editor of Azerbaijan Journal of Physics. He has authored or coauthored several papers (over to 150) local and international conference proceedings.

**Arif Mamed Hashimov** was born in Shahbuz, Nakhchivan, Azerbaijan on September 28, 1949. He is a Professor of Power Engineering (1993); Chief Editor of Scientific Journal of "Power Engineering Problems" from 2000; Director of Institute of Physics of Azerbaijan National Academy of Sciences (Baku, Azerbaijan) from 2002 up to 2009; and Academician and the First Vice-President of Azerbaijan National Academy of Sciences from 2007 up to 2013. He is laureate of Azerbaijan State Prize (1978); Honored Scientist of Azerbaijan (2005); Cochairman of International

Conferences on "Technical and Physical Problems of Power Engineering" (ICTPE) and Editor in Chief of International Journal on "Technical and Physical Problems of Engineering" (IJTPE). Now he is a High Consultant in "Azerenerji" JSC, Baku, Azerbaijan and Director of Institute of Physics, Azerbaijan National Academy of Sciences, Baku, Azerbaijan. His research areas are theory of non-linear electrical Networks with distributed parameters, neutral earthing and ferroresonant processes, alternative energy sources, high voltage physics and techniques, electrical physics. His publications are 350 articles and patents and 5 monographs.

**Shahla N. Aliyeva** was born in Baku, Azerbaijan, in May 1985. She received the M.Sc. degree from Baku State University (Baku, Azerbaijan) in 2007 and Ph.D. degree in Physics-Electronics in the field of "Magnetic properties of $Ni_{1-x}Zn_xFe_2O_4$ micropowders and thin films" in 2016. She is a leading scientific researcher, Doctor of Philosophy on Physics. She has authored or coauthored of several papers (more than 35) in journals and international conference proceedings. Her research interests are electronics, magnetic, electric and optic properties of ferrites.

**A.V. Agashkov** was born in Grodno, Belarus, on April 20, 1951. He graduated from the Physical Faculty of the Belarusian State University, and defended the Ph.D. thesis in 1973 (Minsk, Belarus). Now he is a leading scientific researcher at the Institute of Physics of the National Academy of Sciences of Belarus. His fields of scientific activity are the investigation of the propagation of laser radiation in inhomogeneous media, including metamaterials and liquid crystals, polarization effects upon reflection of laser radiation from submicron metal structures, development of optical control methods in technological processes of manufacturing nano.

**Boris Anatolyevich Bushuk** was born in 1946. He is the Belarusian Physicist, Doctor of Physical and Mathematical sciences (1992). He is a chief scientific researcher at the Institute of Physics, National Academy of Sciences of Belarus. He is laureate of the State Prize of Belarus in 1994. He is author of scientific works on laser physics and photonics of molecules. He developed a method of studying the mechanisms of super-fast intermolecular processes of complex organic structures in condensed environments.