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Nanoscale semiconductor and dielectric films and magnetic nanocrystals – new directions of development of the scientific school of Ya. A. Ugai “Solid state chemistry and semiconductors”. Review

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Abstract

New directions of development of the scientific school of Yakov Aleksandrovich Ugai “Solid state chemistry and semiconductors” were considered for the direction “Study of semiconductors and nanostructured functional films based on them”, supervised by I. Ya. Mittova. The study of students and followers of the scientific school of Ya. A. Ugai cover materials science topics in the field of solid-state chemistry and inorganic and physical chemistry. At the present stage of research, the emphasis is being placed precisely on nanoscale objects, since in these objects the main mechanisms of modern solid-state chemistry are most clearly revealed: the methods of synthesis - composition - structure (degree of dispersion) - properties. Under the guidance of Professor I. Ya. Mittova DSc (Chem.), research in two key areas is conducted: “Nanoscale semiconductor and dielectric films” and “Doped and undoped nanocrystalline ferrites”. In the first area, the problem of creating high-quality semiconductor and dielectric nanoscale films on A^{III}B^V by the effect reasonably selected chemostimulators on the process of thermal oxidation of semiconductors and/or directed modification of the composition and properties of the films. They present the specific results achieved to date, reflecting the positive effect of chemostimulators and modifiers on the rate of formation of dielectric and semiconductor films of the nanoscale thickness range and their functional characteristics, which are promising for practical applications.

Nanomaterials based on yttrium and lanthanum orthoferrites with a perovskite structure have unique magnetic, optical, and catalytic properties. The use of various approaches to their synthesis and doping allowing to control the structure and properties in a wide range. In the field of magnetic nanocrystals under the supervision of Prof. I. Ya. Mittova studies of the effect of a doping impurity on the composition, structure, and properties of nanoparticles of yttrium and lanthanum orthoferrites by replacing the Y(La)³⁺ and Fe³⁺ cations are carried out. In the Socialist Republic of Vietnam one of the talented students of Prof. I. Ya. Mittova, Nguyen Anh Tien, performs studies in this area. To date, new methods for the synthesis of nanocrystals of doped and undoped ferrites, including ferrites of neodymium, praseodymium, holmium, etc. have been developed.

Keywords: Semiconductors, Dielectrics, Magnetic nanocrystals, Ferrites, Nanoscale films, Nanocrystals

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1. Introduction

New research of the scientific school of Ya. A. Ugai “Solid state chemistry and semiconductors” [1] in the subdivision “Study of semiconductors and nanostructured functional films based on them”, supervised by I. Ya. Mittova, are developing in a number of directions “in breadth and depth”. They are performed by both the followers of Yakov Aleksandrovich’s work and by the “students of followers”, which is reflected in Table 1. In fact, we can talk about a deeper scientific continuity, since Yakov Aleksandrovich defended his Ph.D. thesis on the physical and chemical analysis of salt systems under the

guidance of Prof. A. P. Palkin, who, in turn, was a student of Full Member of the Russian Academy of Sciences N. S. Kurnakov. The coverage of modern materials science topics in the field of solid-state chemistry and inorganic and physical chemistry as developed by students and followers of the scientific school of Ya. A. Ugai, his “scientific children, grandchildren, and great-grandchildren” can be seen in Table 1. Here one cannot fail to mention one of the most talented, beloved, and successful students of Ya. A. Ugai, Evelina Domashevskaya. For many years she was the Head of the Department of Solid-State Physics and Nanostructures of Voronezh State

Table 1. Defence of thesis

No.	Thesis	Full name of the applicant	Title of dissertation	Year of defence
1	2	3	4	5
Scientific advisor/consultant Prof. I. Ya. Mittova				
1	Doctorate	Natalia Ivanovna Ponomareva	Formation of functional layers on semiconductors by chemical vapour deposition from organoelement compounds	2004
2	Doctorate	Alexander Mikhailovich Samoilo	Directed synthesis of lead telluride films doped with gallium and indium with the controlled content of impurity atoms and deviation from stoichiometry	2006
3	Doctorate	Viktor Fedorovich Kostryukov	Combined effect of chemostimulants on the thermal oxidation of gallium arsenide	2011
4	Doctorate	Elena Viktorovna Tomina	Chemically stimulated oxidation of GaAs and InP under the action of d-metals (Ni, Co, V), their oxides and oxide compositions	2017
5	PhD	Tatiana Alexandrovna Gadebskaya	Growth kinetics and some properties of doped oxide films on silicon	1983
6	PhD	Natalia Ivanovna Ponomareva	Interaction of chlorides of elements of III, IV and V groups with the surface of silicon and gallium arsenide in an oxidizing atmosphere	1984
7	PhD	Victoria Vladimirovna Pukhova	Interactions in Si-E _x S _y structures (E = In, Ge, Pb, Sb, Bi) and GaAs-E _x S _y (E = In, Pb, Sb) during their thermal oxidation	1986
8	PhD	Vera Vasilievna Sviridova	Thermal oxidation of gallium arsenide and indium phosphide in the presence of impurity oxides	1995
9	PhD	Irina Vladimirovna Kuznetsova	Phase formation processes in alumina ceramics modified with oxides of copper, nickel and boron	1995
10.	PhD	Elena Viktorovna Tomina	Thermal oxidation of gallium arsenide and indium phosphide with the participation of chlorides and oxochlorides of elements of groups IV - VI	1997
11	PhD	Viktor Fedorovich Kostryukov	Nonlinearity of the combined effect of lead, antimony and bismuth oxides on the thermal oxidation of gallium arsenide	2000
12	PhD	Olga Anatolyevna Pinyaeva	Chemostimulating effect of chromium derivatives on thermal oxidation of gallium arsenide	2001

End of Table 1

1	2	3	4	5
13	PhD	Olga Vladimirovna Artamonova	Synthesis of nanoceramic materials based on zirconium dioxide stabilized with indium oxide	2004
14	PhD	Alexey Sergeevich Sukhochev	Solid-phase interactions during the thermal oxidation of Me/GaAs and MeO/GaAs structures (Me = Fe, Co, Ni)	2006
15	PhD	Irina Alexandrovna Donkareva	Localization regions of interactions between activator oxides during the thermal oxidation of gallium arsenide	2006
16	PhD	Petr Konstantinovich Penskoj	Thermal oxidation of GaAs under the influence of Sb ₂ O ₃ , Bi ₂ O ₃ , MnO, MnO ₂ chemostimulant compositions with inert components Ga ₂ O ₃ , Al ₂ O ₃ , Y ₂ O ₃	2009
17	PhD	Nguyen Anh Tien	Synthesis, structure and properties of La(Y) _{1-x} Sr(Ca) _x FeO ₃ (x = 0.0; 0.1; 0.2; 0.3) nanopowders	2009
18	PhD	Alexander Alexandrovich Lapenko	Evolution of nanoscale film and island structures Me/InP (GaAs) and Me _x O _y /InP (GaAs) (Me = V, Co) during thermal oxidation	2010
19	PhD	Dinh Van Tac	Sol-gel synthesis and properties of nanocrystalline ferrites based on Y ₂ O ₃ -Fe ₂ O ₃ system	2012
20	PhD	Boris Valdimirovich Sladkopezhev	Influence of the methods for the formation of V _x O _y /InP structures on the features of their thermal oxidation and the composition of the films	2013
21	PhD	Alexey Alekseevich Samsonov	Thermal oxidation of InP modified by deposited compositions of NiO+PbO, V ₂ O ₅ +PbO oxides	2013
22	PhD	Maria Viktorovna Berezhnaya	Effect of zinc and barium on the structure and properties of YFeO ₃ and LaFeO ₃ -based nanopowders synthesized by the sol-gel method	2019
Scientific adviser prof. N. I. Ponomareva				
23	PhD	Pavel Ivanovich Manelyak	Influence of an anolyte disinfectant solution on the stability of geometric shapes of silicone imprints (joint supervision with DSc in Medical Sciences, Professor Edward Sarkisovich Kalivrajian, now deceased)	2009
24	PhD	Elena Viktorovna Budakova	Clinical and experimental substantiation of the use of an isoprene-styrene thermoplastic elastomer for basic removable laminar dentures (joint supervision with DSc in Medical Sciences, Professor Edward Sarkisovich Kalivrajian, now deceased)	2009
25	PhD	Tatiana Dmitrievna Poprygina	Synthesis, structure, and properties of hydroxyapatite and the composites and coatings based on it	2012
Scientific adviser Prof. A. M. Samoilov				
26	PhD	Mikhail Konstantinovich Sharov	Synthesis and properties of lead telluride films doped with gallium on silicon substrates	2000
27	PhD	Sergey Vladimirovich Belenko	One-step synthesis of gallium-doped PbTe/Si films with a specified composition and optimized functional parameters	2013

University, and now she is a professor of this department. The scientific school created by her “Atomic and electronic structure of solid state and nanostructures” is widely known not only in Russia, but also around the world. Undoubtedly, a great contribution in the formation of our scientific school was made by such outstanding students of Yakov Aleksandrovich as Associate Professor E. M. Averbakh (his first graduate student), professor V. Z. Anokhin, Associate Professors V. R. Pshestanchik and V. L. Gordin, who have unfortunately passed away. All of them laid the foundations for the study of objects that were new for that time, thin films of various functional purposes on semiconductors. New objects of research are mainly nanoscale, since in this area the main regularity of modern solid-state chemistry is most visibly and clearly manifested: synthesis method – composition – structure (degree of dispersion) – properties. This choice was due to the need to establish new fundamental laws of solid-state chemistry, the requirements of modern materials science, reflected in the current List of Critical Technologies (Technologies for the Production and Processing of Functional Nanomaterials) and the List of Priority Areas for the Development of Science, Technology and Engineering in the Russian Federation (Industry of Nanosystems).

2. Nanoscale semiconductors and dielectric films

Prospects for the development of all spheres of human activity are unambiguously associated with the improvement of microelectronic and nanoelectronic element bases. A variety of properties of $A^{III}B^V$ type semiconductors determines their widespread use in devices for various technical purposes: for the production of the variety of optoelectronic devices in the infrared and visible ranges, high-speed electronic and powerful microwave devices [2].

One of the main tasks of the targeted formation of heterostructures on $A^{III}B^V$ with the desired properties is the production of high-quality dielectric and semiconductor films of nanometer thickness and the improvement of the properties of the interfaces. The creation of high-quality heterostructures on $A^{III}B^V$ by thermal oxidation is complicated by the mechanisms of

ongoing processes, due to the implementation of a negative communication channel between the stages of component-wise oxidation in the case of InP, the enrichment of films with unoxidized indium, and the segregation of arsenic in the elementary state at the inner interface of the heterostructure for GaAs [3]. Thermal oxidation of $A^{III}B^V$ with the simultaneous action of interface modifiers and growing films, allowing to control their composition, nanostructure and properties, and chemostimulating agents promoting the accelerated formation of films with a decrease in the operating parameters of the process and blocking the negative communication channel of the intrinsic thermal oxidation of $A^{III}B^V$, allows achieving acceptable optical and electrophysical characteristics and to control the nanostructure of films, which is one of the factors determining their properties.

High-quality thermal oxide films on InP can be used in the development of highly efficient and cheap photoconverters of natural and linearly polarized radiation based on InP. Gallium arsenide, along with indium phosphide, is the most promising material for the production of next generation microwave integrated circuits [4].

The emergence of gallium arsenide microelectronics resulted in the creation of efficient and high-power injection lasers and LEDs in the wavelength range of 600-900 nm based on GaAs/GaAlAs heterostructures. Indium phosphide turned out to be a necessary component of more complex heteroepitaxial structures. As a result of these studies, InP technology arose and was rapidly developed, which currently constitutes a significant portion of micro- and optoelectronics. Laser diodes based on InP/InGaPAs/InP are a key element of optoelectronics for fiber-optic communication, processing, data storage, etc., since they cover the ranges of the highest optical fibre transparency (wavelengths 1.3 and 1.55 μm) [5]. In modern commercial and technical cable communications (intercomputer communications, long-distance telephony, local networks, etc.), these heterolasers are mainly used.

The energy parameters of the single-crystal phase of InP and GaAs are very close to the parameters of single-crystal silicon, which allows the manufacture of hybrid integrated electronics

devices compatible with silicon [6]. In addition to the production technology of microwave integrated circuits [4, 7, 8], heterostructures based on indium phosphide and gallium arsenide find many other applications, for example, as photodetectors [9, 10], in field-effect transistors based on Gatestacktechnology [11], memory cells [12], optoelectronic devices [13], in solar cells [14].

Wide-gap and optically transparent gallium phosphide is the main material for the creation of light-emitting diodes, photodetectors, photodetectors; it is promising for the development of high-temperature electronics devices capable of operating at temperatures significantly exceeding the reached limits of modern temperature sensors [15–17]. The unique optical properties of GaP single crystals are used to manufacture optical lenses and lenses for lasers [13]. However, any practical application of GaP requires the formation of various functional films (conductive, dielectric, antireflection, etc.) on its surface, which is undoubtedly associated with a number of technical difficulties. The use of gallium phosphide as waveguides and optical lenses for lasers is usually associated with the encapsulation of GaP single crystals in layers of a material with a lower refractive index ($n_{\text{GaP}} < 3.3$), i.e., antireflection. Usually, AlGaP is used as the deposited material, which is well matched in lattice size with GaP [18].

Separately, it is necessary to highlight the areas of research associated with the formation of $A^{\text{III}}B^{\text{V}}$ metal oxide semiconductor heterostructures by various methods. Among them are ZnO/InP heterostructures used to create optoelectronic devices and acoustic sensors [19, 20]; SnO_2/InP with certain electrophysical properties, allowing their use as gas-sensitive sensors [21, 22]; multilayer heterostructures with a manganese dioxide layer with promising magnetic characteristics [23]. The range of synthesis methods used for such heterostructures is extremely wide: aerosol pyrolysis, molecular beam epitaxy, magnetron sputtering, CVD processes, etc. However, now, the idea of multipurpose control of the formation of functional nanoscale films on the surface of $A^{\text{III}}B^{\text{V}}$ semiconductors by dopants remains practically unrealized. This approach allows fine adjustment of the kinetics and mechanism of the synthesis processes of these objects and the variation of their

composition, nanostructure, and, consequently, their properties within wide limits.

In the modern world, the demand for portable gas sensors is increasing due to the need for their widespread use in various branches of technology (for the prevention of explosions, fires) and for the control of environmental pollution. All these circumstances stimulated the development of research in the field of semiconductor gas sensors around the world. However, the study of the physical and chemical processes underlying the operation of sensors is still far from complete. Namely, the understanding of these processes allowed creating a new generation of highly efficient, reliable, and economical devices based on sensor elements. Among the materials studied, nanocrystalline tin dioxide has found the greatest practical application [24–27]. In addition to tin dioxide materials, other oxide materials are also studied (In_2O_3 , ZnO, MoO_3 , Ga_2O_3), which may be of interest for creating chemical sensors. Indium oxide is characterized by its high sensitivity, fast response, a convenient range of resistance variation, and a sufficiently low temperature for detecting oxidizing and reducing gases in air [24]. The data [28, 29] and the results of studies [30] suggest that the decisive role in the exceptional sensory properties of In_2O_3 belongs to the high mobility of surface oxygen, which is characteristic for this oxide. There is an adsorption-competitive mechanism of the sensory response, which is associated with the displacement of oxygen from the surface with the subsequent adsorption of the detected gas molecules on the active sites of indium oxide. However, the low-dimensional structure of a single semiconducting metal oxide obtained by various methods does not solve the problem of selectivity and stability of the sensor material.

Therefore, it becomes necessary to alloy the oxide. It was shown in the study [24] that $\text{Fe}_2\text{O}_3 \cdot \text{In}_2\text{O}_3$ thin films exhibit maximum sensitivity to ozone at an operating temperature of 370 °C. In addition, the number of studies in which it was proposed to use multicomponent systems based on indium oxide with additives of other metal oxides ZnO – In_2O_3 , MgO – In_2O_3 , In_2O_3 – SnO_2 for the detection of chlorine in air is currently increasing [31, 32]. Attention is also paid to sensors based on copper oxide [33–35].

A significant disadvantage of the materials presented in the literature by various authors for the production of sensors is the high operating temperature (above 200 °C). This disadvantage can be offset by creating materials of mixed compositions [35].

The main direction of the development of our ideas, continuing the development of the considered section of the scientific school, is the use of chemostimulators and modifiers of the interface and growing films in the process of $A^{III}B^V$ oxidation for the control of the rate of their formation, composition, nanostructure, and properties [36–39]. The solution to the problem of creating high-quality semiconductor and dielectric films of nanometer scale thickness on $A^{III}B^V$ is possible when changing the mechanism of thermal oxidation of these semiconductors from intrinsic to chemostimulated by influencing the process using reasonably selected chemostimulators and/or directed modification of the composition and properties of the films. The participation of chemostimulators in the oxidation process ensures the occurrence of new interface reactions with kinetically coupled and heterogeneous catalytic stages. In this case, the kinetic blocking of negative communication channels between the stages of oxidation of components A^{III} and B^V due to the creation of new, positive channels with the participation of chemostimulators, the temperature and time of the synthesis process are reduced with a simultaneous modification of the composition and properties of functional films of nanometer thickness in the case of a chemostimulator with a modifying effect. We have previously shown [40–42] that the use of only modifiers of the inner interface and the films themselves already prevents the evaporation of the volatile component and degradation of the inner interface, reduce the density of surface states at the inner interface of the heterostructure, and control the structure and surface relief at the nanoscale. Naturally, the use of the combined action of a chemostimulator and a modifier is the most effective approach to solving this scientific problem. Based on many years of research, we have developed 2 methods for introducing a chemostimulator (modifier) into an oxidizing environment: directly in the process of thermal

oxidation of a semiconductor through the gas phase (method 1) and preliminary application to the surface, after which thermal oxidation of an already formed heterostructure occurs (method 2). At the same time, depending on the effect on the semiconductor surface, is the process of applying a chemostimulator (modifier), in the framework of method 2 we used two methods: method 1 (hard method) magnetron or vacuum-thermal deposition on the semiconductor surface and method 2 (soft method) of aerosol deposition or centrifugation. There is no noticeable effect on the semiconductor surface during the creation of the heterostructure using method 2 [43, 44].

The use of modifiers in combination with chemostimulators, in addition to blocking the diffusion of component A into the film in the unoxidized state and chemical bonding of component B at the inner interface, provides control over the growth rate, nanostructure, and properties of thermal oxide films and allows the development of new processes for the formation of functional nanosized dielectric and semiconductor films on $A^{III}B^V$ semiconductors. The combined use of growth chemostimulators and modifiers is especially important in the formation of nanoscale films of a given thickness, when in the process of oxidation using only a chemostimulating agent due to the small thickness of the synthesized samples, the positive effect of the chemostimulator may not be fully realized [45, 46]. Chemostimulating and modifying agents can be introduced during the oxidation of semiconductors in one compound. In particular, with the chemical deposition of sulphides (PbS , Sb_2S_3 , etc.) on the surface of semiconductors, during the oxidation of the formed heterostructures, the cation-forming element capable of the transit transfer of oxygen to the substrate components provides the rapid formation of the film by the catalytic or transit mechanism, partially performing the modifying function during its doping. The main modifying role is played by the anionic agent, influencing the characteristics of the internal interface, the composition, and, consequently, the characteristics of the films. The change in the composition of the films in the processes of oxidation of sulphide/semiconductor heterostructures according to the sulphide –

sulphate – oxosulphate – oxide scheme allows obtaining a whole spectrum of their different characteristics. The effectiveness of the effect of sulphur on the properties of the internal interface of a thermal oxide film with a semiconductor was demonstrated by preliminary treatment of the substrate surface in sulphur vapour [47, 48].

The use of complex compounds such as manganese and bismuth vanadate phosphates in the processes of chemically stimulated $A^{III}B^V$ oxidation demonstrated a positive effect [49, 50], since manganese and bismuth oxides previously were demonstrated as effective chemostimulators of thermal oxidation of $A^{III}B^V$, in which the cation has a pronounced chemo-stimulating activity, and the anion can provide ready-made fragments of growing oxide films such as PO_4^{3-} groups or groups that are isostructural to them.

The use of chemostimulators and/or modifiers is promising for the stepwise synthesis of nanoscale films on $A^{III}B^V$ in combination with different types of activation of their action, heat treatment or pulsed photonic treatment, which expands the possibilities of controlling the rate of formation of films, their composition, structure, and properties [43, 44, 51].

Some of the specific results achieved to date reflecting the positive effect of chemostimulators and modifiers on the rate of formation of dielectric and semiconductor films of the nanoscale thickness range and their functional characteristics that have prospects for practical application are summarized in Table 2.

The main fundamental results achieved by the scientific group under the supervision of DSc in Chemistry, Professor I. Ya. Mittova, which includes DSc in Chemistry E. V. Tomina and V. F. Kostryukov, PhD in Chemistry B. V. Sladko-pevtsev and A. A. Samsonov, PhD students and students, are as follows:

1. The concept of the multifunctional effect of chemostimulators-modifiers, often in one compound and in a single process, was proposed. Schemes were also proposed for the mechanisms of thermal oxidation processes of $A^{III}B^V$ under the influence of simple and complex compounds and their compositions as a physicochemical basis for the development of new processes for the formation of semiconductor and dielectric films on $A^{III}B^V$ with a given growth rate and

target characteristics. The specificity of catalytic processes in new nonequilibrium systems with solid-phase thin-film catalysts, reagents, and products has been revealed. The nature of the synergistic effects of the joint action of the chemostimulators deposited on the surface of $A^{III}B^V$ semiconductors and modifiers of the processes of oxidation of heterostructures was established [36–38, 52–55].

2. The nonlinear effects of the influence of binary compositions of oxide-chemostimulators on the formation of thin films on GaAs and InP were established and quantitatively interpreted using the concept of relative partial and integral thicknesses [39, 56–64].

3. The dependence of the nonlinear effect of the combined action of chemostimulators on the oxidation state of the element forming one of the oxides of the composition was revealed, both paired with the oxide of another element, and with the oxide of the same element, but in a different oxidation state [59, 65, 66].

4. The nature and spatial localization of binding stages under the combined action of chemostimulators on the thermal oxidation of GaAs and InP, responsible for the observed nonlinear effects, have been established [67–71].

5. The fundamental possibility of the additive effect of a composition of oxides, one of which is an inert component, on the process of thermal oxidation of GaAs has been proved [72–78].

6. The presence of a sensor signal for the presence of reducing gases in the atmosphere for thin films synthesized on the surface of GaAs and InP by chemically stimulated thermal oxidation under the influence of both individual chemostimulating oxides and their compositions was established [79–82].

7. Methods for precision doping of thin films on the surface of GaAs and InP have been developed [81, 83, 84].

8. Methods were developed for the synthesis of nano-sized nanostructured oxide films on InP and GaAs using a V_2O_5 gel allowing to modify the surface of semiconductors under mild conditions, characterized by their efficiency and ease of implementation, variability of the composition, the thickness and morphology of deposited layers of oxide dopants over a wide range [43, 51, 85, 86].

Table 2. Multifunctionality of the action of chemostimulants and modifiers in the processes of synthesis of nanoscale films on A^{III}B^V

Characteristics of the object		Oxidation mode, T, °C / t, min	EAE, kJ/mol Stage 1 / Stage 2	Oxidation mechanism	Relative increase in film thickness compared to intrinsic oxidation (% or times)	The composition of the films	The result of the impact	Resistivity (ρ), breakdown voltage (E)	Properties of the synthesized films
Chemo-stimulant	Semiconductor								
Modifiers									
Method - introduction through the gas phase									
AlPO ₄	InP	475–550/10–60	153	intrinsic	120%	AlPO ₄ , InPO ₄	modification		
Method – surface application – hard methods									
SnO ₂	InP	475–550/10–60	48	intrinsic	–	In(PO ₃) ₃ , P ₂ O ₅ , In ₂ O ₃ , SnO ₂ , Sn ₃ (PO ₄) ₂	modification	ρ = 9.0·10 ⁶ Ohm·cm	semiconductor
Superposition modifier + modifier									
SnO ₂ /InP + AlPO ₄	InP	530/10–60		intrinsic	–	AlPO ₄ , InPO ₄ , Sn ₃ (PO ₄) ₂	modification	ρ = 8.5·10 ⁷ Ohm·cm	semiconductor
Chemostimulants									
Method – surface application – hard methods									
MnO ₂	GaAs	450–550/10–60	95	transit	up to 7.5 times	Ga ₂ O ₃ , As ₂ O ₃ , MnO ₂	chemo-stimulation	ρ = 1.2' 10 ¹⁰ Ohm·cm; E = 5.2·10 ⁶ V/cm	dielectric
	InP	450–550/10–60	180	transit	up to 2.1 times	In ₂ O ₃ , InPO ₄ , Mn ₂ O ₃ , MnO ₂	chemo-stimulation	ρ = 6.3·10 ⁸ Ohm·cm; E = 7·10 ⁶ V/cm	dielectric
Superposition chemostimulant + modifier									
Method – surface application – soft methods									
BiP _x V _{1-x} O ₄	InP	490–570/5–60	51	transit-catalytic	62 – 248%	BiVO ₄ , InPO ₄ , BiPO ₄ , V ₂ O ₅	chemo-stimulation and modification		
Mn ₃ (P _x V _{1-x} O ₄) ₂	GaAs	490–550/5–60	156	transit	up to 220%	MnAsO ₄ , Mn ₃ (VO ₄) ₂ , Mn ₃ (PO ₄) ₂ , GaAs, GaAsO ₄	chemo-stimulation and modification		

Method – application to the surface and simultaneous introduction from the gas phase									
	InP	450–550/10–60	110	transit	up to 240%	In(PO ₃) ₃ , Mn ₂ P ₂ O ₇ , MnO, Mn ₂ O ₃ , Mn ₃ (PO ₄) ₂ , MnPO ₄	chemo- stimulation and modification	ρ = 1.5·10 ¹⁰ Ohm·cm	dielectric
Superposition of chemostimulant + inert component									
Sb ₂ O ₃ +Y ₂ O ₃	GaAs	530/10–40		transit	2–6 times	Ga ₂ O ₃ , As ₂ O ₃ , Sb ₂ O ₃	chemo- stimulation	ρ = 1.5·10 ⁶ Ohm×cm	Semiconductor with gas sensitivity
PbO + Y ₂ O ₃	InP	560/10–60		transit	2–4 times	In ₂ O ₃ , InPO ₄ , PbO	chemo- stimulation	ρ = 1.5·10 ⁶ Ohm×cm	Semiconductor with gas sensitivity
Superposition chemostimulant + chemostimulant									
PbO + Bi ₂ O ₃	GaAs	530/10–40		transit	2–4 times	Ga ₂ O ₃ , As ₂ O ₃ , PbO, Bi ₂ O ₃	chemo- stimulation	ρ = 1·10 ⁶ Ohm×cm	Semiconductor with gas sensitivity
Sb ₂ O ₃ + V ₂ O ₅	GaAs	530/10–40		transit	3–6 times	Ga ₂ O ₃ , As ₂ O ₃ , Sb ₂ O ₃ , V ₂ O ₅	chemo- stimulation	ρ = 1·10 ⁶ Ohm×cm	Semiconductor with gas sensitivity
PbO + V ₂ O ₅	InP	560/10–60		transit	2–4 times	In ₂ O ₃ , InPO ₄ , PbO, V ₂ O ₅	chemo- stimulation	ρ = 1·10 ⁶ Ohm×cm	Semiconductor with gas sensitivity
Standards									
GaAs, standard-1		450–550/10–60	110	intrinsic	–	As, Ga ₂ O ₃ , As ₂ O ₃	–	ρ = 1·10 ⁵ Ohm×cm	Semiconductor
InP, standard-2		450–550/10–60	270	intrinsic	–	In, In ₂ O ₃ , InPO ₄	–	Ohmic conductivity	Conductive

9. Studies of the chemically stimulated thermal oxidation of GaAs and InP have established the decisive influence of the physicochemical nature of the chemostimulator, the procedure and the method of its introduction into the system on the mechanism of the process. It was shown that the introduction of an oxide chemostimulator through the gas phase and its application by soft methods on the semiconductor surface causes the transit mechanism of oxidation. The application of compounds providing a renewable cyclicity of the process by rigid methods provides a synchronous catalytic mechanism for the process. Data on the dependence of the composition, thickness, and rate of formation of films, their morphology on the procedure and method of introducing various chemostimulators-modifiers into the system were obtained [46, 51, 86–90].

10. The high efficiency of the application of the spectral ellipsometry method for determination of the thickness and optical constants of nanoscale films of complex compositions, grown as a result of thermal oxidation of InP and GaAs under the influence of chemostimulators-modifiers was proved [81, 91–94].

11. It was found that magnetron sputtering is the optimal method for the formation of oxide heterostructures (V_2O_5 , MnO_2 , etc.)/ semiconductor efficiently blocking the diffusion of unoxidised indium into the film during thermal oxidation in comparison with mild methods of modifying the semiconductor surface. Weakly absorbing films with a low content of unoxidised indium, no more than 1–2%, have been synthesized [89, 93].

12. Chemically stimulated oxidation of indium phosphide with a nanosized layer of bismuth vanadate phosphate on the surface led to a significant decrease in EAE (~ 50 kJ/mol) as compared to the intrinsic oxidation of InP (~ 270 kJ/mol), which indicates a significant chemostimulating effect of a complex chemostimulators on the thermal oxidation process of InP due to the decomposition of a complex chemostimulator-modifier with the formation of oxides-chemostimulators, as well as isostructural phosphate and vanadate fragments embedding in the forming film. The presence of V_2O_5 in films with a significant decrease in EAE and a large relative increase in the thickness of

the films throughout the entire process suggest the presence of the catalytic component of the oxidation mechanism [95]. The composition and optical properties of the films confirm the effective blocking of the diffusion of unoxidised indium into the forming films, which favourably affects their functional properties. The chemically stimulated oxidation of gallium arsenide with a nanosized layer of manganese vanadate phosphate on the surface proceeds by a transit mechanism as was evidenced by the EAE value of the process (about 150 kJ/mol), comparable by an order of magnitude with that of the reference oxidation of InP (~ 270 kJ/mol). According to the XRD results, a chemostimulator with a pronounced catalytic mechanism of action (V_2O_5), originally present in vanadate-phosphate was not revealed in films, which indicates the absence of a catalyst regeneration cycle: $V_2O_5 \leftrightarrow VO_2$. Vanadate-phosphates of bismuth and manganese act simultaneously as both chemostimulators and modifiers of the thermal oxidation process, acting according to the transit mechanism for heterostructures on GaAs and according to transit-catalytic mechanism for heterostructures on InP, and leading to an acceleration of the process up to 220–248% (see Table 2). Thermal oxidation of InP with magnetron deposited nanoscale layers of the MnO_2 chemostimulator and the simultaneous introduction of a chemostimulator-modifier $Mn_3(PO_4)_2$ through the gas phase led to an increase in the growth rate of the films up to 240% compared with the intrinsic oxidation of InP, the absence of under-oxidized indium in the films, the high content of a whole spectrum of phosphates (XRD, IRS, AES, USXES, SE), and, as a consequence, their dielectric characteristics (resistivity up to 10^{10} Ohm-cm, see Table 2).

The traditions established by the scientific school of Professor Yakov Aleksandrovich Ugai are continued by DSc in Chemistry, Professor A. M. Samoilov [96–101].

The main objectives of these studies are the investigation of the fundamental physicochemical properties of semiconductor systems with sensor properties and the improvement of methods for the directed synthesis of hetero- and nanostructures based on these materials for the achievement of optimal values of their functional parameters.

The focus of studies is on multicomponent narrow-bandgap A^{IV}B^{VI} semiconductors capable of efficiently detecting electromagnetic radiation in the terahertz and infrared regions of the spectrum [102–115], as well as wide-bandgap transparent metal oxides, which are promising for the creation of gas sensors and ultraviolet radiation sensors [116–129]. The study of these materials is currently carried out in several directions: the investigation of fundamental physicochemical properties, which are fundamental for the functioning of these systems as sensor materials [102, 103, 105, 109–112]; methods for the synthesis of PbTe thin films were optimized based on the data on the solubility of Ga and In in PbTe<Ga> and PbTe<In> with high sensitivity to IR radiation [104, 106, 111, 124, 125].

The obtained experimental data on the thermal stability and crystal structure of palladium (II) oxide allowed developing methods for the synthesis of nanostructures with different morphological organization, which demonstrated high sensitivity to toxic gases with oxidizing properties as well as good speed and stability of the sensory response over time [120–123]. The results of calculating the region of nonstoichiometry of nanocrystalline PdO films [127–129] in the future will allow finding the optimal conditions for the synthesis of nanostructures with high selectivity for detecting poisonous and explosive gases with oxidizing and reducing properties in atmospheric air [126].

The materials science traditions of the school were developed somewhat unexpectedly in the studies of DSc in Chemistry, Professor N. I. Ponomareva by the development of new methods for the synthesis of hydroxyapatite (HA) composites, allowing to obtain particles included in a biopolymer matrix. Since the properties of both HA itself and composites based on it depend on the particle size, the research task was to obtain nano-HA. It was shown that with the dropwise mixing of the reagents and the addition of alizarin red, promoting the formation of centres of induced crystallization, the rate of formation of stoichiometric HA in an aqueous solution increased by more than 100 times in comparison with the reference process. Synthesis of GA in a model body fluid (SBF) leads to the formation of type A carbonate hydroxyapatite corresponding

to the formula $\text{Ca}_{10}(\text{PO}_4)_6(\text{CO}_3)_{0.5x}(\text{OH})_{2-x}$, where $x < 2$ (EPXMA, IRS), which was explained by the presence of a bicarbonate ion in SBF and carbon dioxide in the air [130, 131]. A method for the synthesis of nano-HA in drops of microemulsions prepared on the basis of toluene/octane and water with the addition of AOT as a surfactant has been developed, and it was shown that the particles had needle shape (length 10–20 nm and width 2–4 nm) and were covered with an amorphous shell. It was found that in the formation of HA composites with biopolymers, the determining factors are the presence of carboxyl, hydroxyl, and sulpho groups in the used biopolymers and the negative surface charge of the polymers. An excess of calcium ions increased the degree of binding of these organic components with HA and significantly increased the hardness of composites (up to 260 MN/m²) [132–134]. N. I. Ponomareva et al. Proposed a new economically viable method for the formation of bioactive coatings on the surface of titanium by the deposition of carbonate films from the solution with their subsequent transformation into phosphate and hydroxyapatite films [133–137]. The authors provided recommendations for the impregnation of HA with carbon implants [138, 139].

3. Doped and undoped nanocrystalline yttrium and lanthanum ferrites

The development of research in the field of semiconductor and dielectric films of the nanoscale thickness range by the followers of the scientific school of Ya. A. Ugai naturally spread to the area of magnetic nanocrystals. The increased interest in nanomaterials based on yttrium and lanthanum orthoferrites with a perovskite structure was caused by their unique magnetic, optical, and catalytic properties [140, 141] and the ability to control their structure and properties through doping over a wide range.

Among the methods for obtaining nanosized REE ferrites, the sol-gel method is widely used, allowing nanopowders with a narrow particle size distribution to be formed at relatively low temperatures using simple and inexpensive equipment. Variations of the sol-gel method include the polymer-gel process, in which the formation of a gel is achieved by introducing a water-soluble polymer into the initial solution followed by

evaporation, and the Pechini method (citrate-gel), which uses citric acid, ethylene glycol, or polyvinyl alcohol [142–144]. Hydrothermal treatment of precipitated yttrium and iron (III) hydroxides makes it possible to obtain single crystals of yttrium ferrite [145, 146], microcrystalline [147, 148] and nanocrystalline powders [147, 149, 150] by selecting the appropriate precursors, pH of the medium, and conditions of hydrothermal treatment. The mechanism of the formation of yttrium ferrite nanopowders under the conditions of glycine-nitrate combustion is described in [151, 152]. The synthesized particles are characterized by a rhombic and hexagonal structure with a particle size of 30 to 53 nm and 6 to 14 nm, respectively. It was found that the phase composition and average crystallite size are significantly influenced by the glycine/nitrate ratio, which determines the combustion temperature.

By the method of decomposition of alkoxide complexes, yttrium orthoferrite nanopowders are formed at a temperature of 680 °C and exhibit weak ferromagnetism [153]. One of the modern methods for the synthesis of ferrite nanocrystals is microwave synthesis. The method for the synthesis of vanadate and ferrite precipitation from a solution of precursors under the influence of microwave radiation is characterized by the simplicity of implementation, economy, and high synthesis rate. Microwave radiation stimulates the decomposition of salt precursors, the dehydration and synthesis of target products is due to the uniformity and high rate of microwave heating and acceleration of the processes of “nucleation” under the influence of “non-thermal” effects [154].

Effective absorption of microwave radiation requires the presence in the substance of either dipoles that can reorient and rotate under microwave action, or free charge carriers that can move when the microwave field is applied. Water molecules located in the crystal lattice of crystalline hydrates-precursors have a significant dipole moment. The decomposition of the used crystalline hydrates in a microwave field proceed to oxides, since the formation of an oxide product begins before the removal of all water contained in the system.

Compared to traditional heating methods, microwave heating has several undoubted

advantages: during microwave heating, the walls of the vessel are not heated, only the reaction mixture is heated. As a result of this: the reaction time was reduced (by 10-1000 times); directed activation of reacting molecules was carried out; there were no side processes of destruction on the walls of the vessel, the overheating of the solvent above the boiling point was absent; the flow of energy stopped after the termination of the reaction [155, 156].

Microwave exposure followed by ultrasonic treatment of synthesized YFeO_3 and BiFeO_3 samples using sodium hydroxide as a precipitant allowed synthesizing chemically homogeneous nanopowders with a significant decrease in the energy intensity of the process. The resulting YFeO_3 and BiFeO_3 particles had a nearly spherical shape, they were characterized by a small size dispersion in the range of 20–100 nm [157, 158].

The change in the magnetic properties of doped ferrites was caused by several reasons: a change in the size and shape of particles, a distortion of the crystal lattice due to the difference in ionic radii, a change in the valence state of iron upon the introduction of a dopant, and the appearance of oxygen nonstoichiometry.

Studies of the effect of a doping impurity on the composition, structure, and properties of yttrium orthoferrite nanoparticles can be divided into two directions: substitution of the Y^{3+} and Fe^{3+} cation. We are working in both directions.

During the first stage of research, it was shown that the substitution of Y^{3+} by La^{3+} in yttrium ferrite nanopowders synthesized by coprecipitation led to an increase in magnetization from 0.041 A·m²/ kg for $x = 0$ to 0.231 A·m²/ kg for $x = 0.4$ and a decrease in the coercive force, which indicates a significant contribution of crystal lattice distortion in the formation of the magnetic properties of the material [159]. This effect was found even in the case of isovalent substitution, and in this case, it was due to the size factor.

The change in the magnetic properties in the case of heterovalent substitution was due not only to size factors, but also due to a change in the valence state of iron for compensation of the charge and the appearance of oxygen nonstoichiometry.

Data obtained by doping yttrium ferrite with some doubly charged cations are presented by

us in [160–162]. Sol-gel synthesis of $Y_{1-x}A_xFeO_3$ samples (where $A = Ca^{2+}, Sr^{2+}, Cd^{2+}$) is based on the processes of co-deposition of cations and annealing in a muffle furnace at a temperature of 750 °C for 1 h. Doping with Ca^{2+} and Cd^{2+} cations with ionic radius slightly exceeding the ionic radius of Y^{3+} , led to a decrease in the particle size, specific magnetization, and coercive force. Decrease in D_{av} was explained by the appearance of internal stresses, limiting the growth of crystals [163]. Despite the deviation from Goldschmidt's rule [164], the substitution of Y^{3+} with strontium cations is possible and causes a significant increase in the coercive force from 3.98 kA/m ($x = 0$) up to 409.94 kA/m ($x = 0.3$), i.e. the formation of a new type of magnetic material, a hard magnetic ferromagnet.

It could be assumed that the doping of yttrium ferrite with barium cations would lead to a strong increase in the magnetic characteristics due to the incorporation of Ba^{2+} into position of Y^{3+} (since $r(Ba^{2+}) > r(Y^{3+})$ [165]), and the introduction of Zn^{2+} can change the magnetic properties both in the direction of decreasing (since zinc cations have a small radius) and increasing their value in the case of substitution of iron cations with Zn^{2+} ions. Indeed, in the studies of our team it was shown [165, 166] that the substitution of La^{3+} or Y^{3+} cations in orthoferrites by doubly charged Zn^{2+} and Ba^{2+} caused the distortion of the crystal lattice, a change in the valence state of iron, which, in turn, affects the strength of the exchange interaction and leads to a change in physicochemical properties, which expands the scope of the synthesized materials. Thus, nanocrystalline powders $(1-x)YFeO_{3-d} : xZn^{2+}$ and $(1-x)LaFeO_{3-d} : xZn^{2+}$, which are characterized by weak ferromagnetism, are promising materials for the production of devices requiring rapid re-magnetization of the sample with minimal energy consumption, for example, when creating transformer coils, and, nanopowders $(1-x)YFeO_{3-d} : xBa^{2+}$ and $(1-x)LaFeO_{3-d} : xBa^{2+}$ can be used to solve the problem of increasing the density of media for the magnetic recording of information, since they are magnetically hard materials. It was shown that the doping of nanocrystalline yttrium ferrite powders with zinc by coprecipitation followed by heat treatment causes a nonmonotonic

decrease in the crystallite size from 60 ± 6 nm $x = 0$ to 50 ± 4 nm $x = 0.2$ (XRD), contributes to an increase in the specific magnetization from 0.242 A m²/kg for $x = 0$ to 0.556 A m²/kg for $x = 0.2$ (in the field 1250 kA/m). The presence of $ZnFe_2O_4$ impurities in the samples led to an increase in the ferromagnetic character of the samples.

It was found that the developed technique for the synthesis [167] of $(1-x)YFeO_{3-d} : xBa^{2+}$ nanopowders led to the formation of particles with a size of 30 ± 2 nm for $x = 0$ to 55 ± 5 for $x = 0.1$ (XRD), characterised by the presence of a soft magnetic and magnetic hard sublattice within the same chemical phase.

In our studies [168], a method for the sol-gel synthesis of $LaFeO_3$ using an aqueous solution of ammonia as a precipitant was demonstrated, lanthanum ferrite was doped with calcium and strontium. It was found that the introduction of Ca^{2+} into the ferrite lattice caused an increase in the average crystallite diameter from 30 nm for $LaFeO_3$ up to 50 nm, in the case of Sr^{2+} it was up to 70 nm. Doping with calcium and strontium cations led to an increase in the coercive force and specific magnetization of the samples. The change in the magnetic properties of lanthanum ferrite upon doping with doubly charged cations was caused by the partial transition of Fe^{5+} in Fe^{4+} , as well as distortion of the crystal lattice due to the difference in the ionic radii of La^{3+} and the dopant. With an equal content of Ca^{2+} and Sr^{2+} cations in the composition of the samples, the magnetic properties were different: $H_c(La_{0.7}Ca_{0.3}FeO_3) < H_c(La_{0.7}Sr_{0.3}FeO_3)$, a $J(La_{0.7}Ca_{0.3}FeO_3) > J(La_{0.7}Sr_{0.3}FeO_3)$.

The complexity of the formation of lanthanum ferrite nanopowders doped with zinc and barium is due to the large difference in the ionic radii of lanthanum and the dopant introduced. However, despite the narrow homogeneity region, single-phase samples with a complex magnetic structure were obtained [169, 170]. The maximum degree of doping of lanthanum ferrite with zinc was $x_{real} = 0.07$. As the amount of the introduced dopant increased, the unit cell volume nonmonotonically increased from 240.634 \AA^3 ($x = 0$) up to 242.245 \AA^3 ($x = 0.2$) and the average crystallite size increased from 58 ($x = 0$) to 123 nm ($x = 0.2$), which was due to the incorporation of Zn ions²⁺ into the position of Fe^{3+} , since $r(Zn^{2+}) > r(Fe^{3+})$. $(1-x)LaFeO_{3-d} : xZn^{2+}$

nanoparticles, depending on the composition, possess different types of magnetic ordering: antiferromagnetic and ferrimagnetic. The doping of YFeO_3 nanopowders with Zn^{2+} cations with a radius of less than Y^{3+} , should negatively affect the magnetization and coercive force. However, the formation of nanocrystals, characterized by a complex distribution of the doping cation was observed. The formation of particles with the structure “crystal core - amorphous shell” led to the arrangement of a part of the dopant ions in the form of an amorphous shell of zinc oxide. The increase in specific magnetization $(1-x)\text{YFeO}_{3-\delta} : x\text{Zn}^{2+}$ with an increase in the amount of Zn^{2+} was due to the reorientation of the magnetic moments of iron ions, as was observed in the study [171]. The distortion of the crystal lattice was insignificant, therefore, in this case, it did not significantly affect the properties. The enhancement of the ferromagnetic character of the material was also due to the presence of zinc ferrite in the spinel phase [166]

The introduction of Ba^{2+} cations into a LaFeO_3 lattice in the position of La^{3+} caused an increase in the parameters of the crystal lattice and the average particle diameter from 25 ($x = 0$) up to 42 nm ($x = 0.1$). The maximum nominal doping level was $x = 0.1$ (XRD). The synthesized particles exhibited the properties of a hard magnetic ferromagnet with a wide hysteresis loop. The non-monotonic change in the magnetic characteristics was due to the formation of a complex magnetic structure combining a hard magnetic and soft magnetic sublattice.

Thus, as in the case of yttrium ferrite, the doping of lanthanum ferrite with doubly charged barium and zinc cations led to the formation of materials exhibiting different magnetic properties, which allows using them for the production of information storage devices [165, 166, 169, 170]

Changes in the magnetic properties of yttrium ferrite upon doping with doubly charged cations were caused by several factors: first, due to the difference in ionic radii of Y^{3+} and dopant, distortion of the crystal lattice occurred and the particle size changed; secondly, such doping refers to heterovalent isomorphic transformations, which resulted in the formation of Fe^{4+} cations, i.e., a double exchange interaction of $\text{Fe}^{3+}-\text{O}^{2-}-$

Fe^{4+} occurred, holes which were charge carriers in the transition from the Fe^{4+} ion to Fe^{3+} ion through the p -orbital of oxygen were generated [172]. It was shown in studies [159, 161] that upon the doping of lanthanum ferrite, an increase in the magnetization can be caused by similar reasons. The absence of such an interaction in perovskite $\text{Y}_{1-x}\text{La}_x\text{FeO}_3$ [159] explains its lower magnetization compared to $\text{Y}_{1-x}\text{Cd}_x\text{FeO}_3$ [161] with the same degree of substitution, since with an increase in the cadmium content, although the size of the resulting particles $\text{Y}_{1-x}\text{Cd}_x\text{FeO}_3$ decreased, their magnetization increased monotonically. Therefore, the compensation described above probably has a stronger effect on the magnetization than a change in particle size.

It should be noted that the data available in the literature on the effect of zinc on the size of nanocrystals and the magnetic properties of LaFeO_3 nanopowders are very controversial. In studies [173, 174], the possibility to substitute La^{3+} cations with Zn^{2+} cations in lanthanum orthoferrite synthesized by the coprecipitation method was shown. A decrease in the crystal lattice volume with an increase in the dopant concentration led to an increase in the orthorhombic distortion of the LaFeO_3 perovskite lattice, which caused an increase in magnetization.

In studies [175, 176], the results of the synthesis of $\text{LaFe}_{1-x}\text{Zn}_x\text{O}_3$ nanopowders by the gel combustion method were presented, the mechanism of incorporation of the dopant and the effect on the magnetic structure of the material were described. The introduction of Zn^{2+} instead of Fe^{3+} led to the transformation of $\text{Fe}^{3+} - \text{Fe}^{4+}$ and the formation of oxygen vacancies in the perovskite structure, which changed the angle and length of the Fe-O bonds. The structural analysis showed that zinc doping causes oxygen nonstoichiometry in the system. This can change the valence state of Fe^{3+} and hence the magnetization [176].

The doping of lanthanum ferrite with zinc, regardless of the preparation method and the position of the dopant in the perovskite lattice (in the position of La^{3+} or Fe^{3+}) led to the formation of particles with a complex magnetic structure: an antiferromagnetic core - a ferromagnetic shell, as was evidenced by the shift of the hysteresis loop towards a negative field strength [174–176].

Due to the fact that the difference between the radii of $\text{La}^{3+} - \text{Zn}^{2+}$ is much higher than that of $\text{Fe}^{3+} - \text{Zn}^{2+}$, the substitution of iron cations by zinc is more likely. This was proved by us for $(1-x)\text{LaFeO}_{3-\delta} : x\text{Zn}^{2+}$ nanopowders synthesized by co-deposition followed by annealing in a muffle furnace [170]. The substitution of some Fe^{3+} ions with Zn^{2+} ions led to the formation of a material with a complex magnetic structure. By controlling the amount of dopant introduced, it was possible to obtain materials with antiferromagnetic (for $x = 0; 0.075; 0.15$) or ferrimagnetic ($x = 0.05; 0.1; 0.2$) properties.

Lower specific magnetization for samples of yttrium ferrite doped with Zn^{2+} , Cd^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} cations compared with $(1-x)\text{LaFeO}_{3-\delta} : x\text{E}^{2+}$, indicates a significant contribution of the effect of double exchange interaction on the magnetic properties of the material. The magnitude of the magnetization and coercive force of lanthanum ferrite nanopowders doped with doubly charged cations depends on the difference in ionic radii, i.e., on the distortion of the crystal lattice. With an increase in the dopant content, the dependence of the magnetization on the particle size has not been established. Consequently, the above compensation and the structure factor seem to have a stronger effect on magnetization than a change in the particle size of the studied yttrium and lanthanum ferrites. The described results can be used to obtain composite materials [177, 178]. In addition, the detected inclusions of the ferromagnetic Fe_2O_3 , BaFe_2O_4 , ZnFe_2O_4 phases show that the synthesized samples are promising for creating granular structures [179, 180].

From the described above information, a complex mechanism for the incorporation of zinc into the lattices of yttrium and lanthanum ferrites can be proposed, and, based on the difference in atomic radii, it is most likely to be incorporated into the place of iron. However, as shown above, this statement is far from clear. Such transition elements as manganese and nickel should occupy positions of iron in the structure, since they are quite similar in their properties. The corresponding studies belong to the above-mentioned second direction. A significant increase in the magnetic parameters of YFeO_3 nanoparticles was observed upon doping with magnetic ions Mn^{3+} , as shown in [181]. It is

believed that the magnetic moment of the Mn^{3+} ion is higher than Fe^{3+} in oxides of the perovskite type, and this should be the reason for the increase in magnetic moments with an increase in the amount of dopant in $\text{YFe}_{1-x}\text{Mn}_x\text{O}_3$ [182]. In addition, the enhancement of antiferromagnetic ordering is due to distortions in the crystal lattice. In studies [183, 184] the results of doping of yttrium and lanthanum ferrite powders with nickel Ni^{2+} by successive precipitation using an aqueous solution of potassium hydroxide are presented [184]. The single-phase of $\text{YFe}_{1-x}\text{Ni}_x\text{O}_3$ ($x = 0-0.25$) samples is achieved at a temperature of 800 °C for 1 h, respectively (XRD). With an increase in the content of the dopant Ni to $x = 0.3$ after annealing at 800 °C for 1 h, in addition to YFeO_3 , NiO and Y_2O_3 impurity phases are formed. With an increase in Ni^{2+} content in the YFeO_3 lattice from $x = 0.1$ to 0.25, a decrease in the coercive force from 1332.6 to 887.9 Oe was observed, while the values of excess magnetization M_r and saturation magnetization M_s increased: from $1.8 \cdot 10^{-1}$ up to $3.2 \cdot 10^{-1}$ emu/g and 0.67 to 1.18 emu/g, respectively.

The introduction of Ni^{2+} cations into the LaFeO_3 lattice in the position of Fe^{3+} causes a decrease in the parameters of the crystal lattice and a decrease in average particle diameter from 28.72 ($x = 0$) to 23.59 nm ($x = 0.25$). For $\text{LaFe}_{1-x}\text{Ni}_x\text{O}_3$ samples with an increase in the content of Ni^{2+} dopant from $x = 0$ to 0.25, an increase in the coercive force from 42.53 Oe to 160.76 Oe was observed, while the values of excess magnetization M_r and saturation magnetization M_s decreased: from $1.0 \cdot 10^{-2}$ up to $3.8 \cdot 10^{-4}$ emu/g and from $0.24 \cdot 10^{-1}$ up to $0.74 \cdot 10^{-4}$ emu/g [183]. It was found that an increase in the content of the dopant Ni^{2+} in YFeO_3 and LaFeO_3 lattices allows varying the value of the coercive force (H_c) and saturation magnetization (M_s), which expands new possibilities of using doped yttrium and lanthanum ferrites in a strong magnetic field.

In the study [185], $\text{YFe}_{1-x}\text{Mn}_x\text{O}_3$ ($x = 0.1; 0.2; 0.3; 0.4$) perovskite nanopowders were synthesized by chemical coprecipitation using 5% KOH as the precipitating reagent. The introduction of manganese ions into the YFeO_3 lattice using the proposed method led to an increase in the parameters of the crystal lattice ($b = 7.7373 \div 7.5194 \text{ \AA}$, $c = 5.3014 \div 5.2592 \text{ \AA}$); unit cell

volume ($V = 229.425 \div 224.4012 \text{ \AA}^3$), average particle size ($D_{\text{XRD}} = 23.6081 \div 22.9449 \text{ nm}$). An increase in the coercive force ($H_c = 56.94 \div 150.95 \text{ Oe}$) and residual magnetization ($M_r = 0.23 \div 0.50 \text{ emu/g}$) with an increase in the dopant content was revealed.

Nanocrystalline $\text{La}_{1-x}\text{Cd}_x\text{FeO}_3$ ($x = 0, 0.05, 0.1, 0.15, 0.2$) powders, characterized by a narrow region of homogeneity $x_{\text{max}} = 0.09$ (EPXMA, XRD) were synthesized by co-deposition followed by thermal annealing at $950 \text{ }^\circ\text{C}$ for 1 h. Introduction of Cd^{2+} cations led to a decrease in the average crystallite size from $10\text{--}70 \text{ nm}$ for $x = 0$ to $5\text{--}60 \text{ nm}$ for $x = 0.1$ (TEM). The synthesized nanocrystals exhibited the properties of ferrimagnets [186].

In this direction, the work related to the section of the scientific school of Ya. A. Ugai, continue abroad. Thus, in the Socialist Republic of Vietnam, Nguyen Anh Tien, who defended his PhD thesis in Russia under the supervision of I. Ya. Mittova, is the Head of the Department of General and Inorganic Chemistry of Ho Chi Minh City University of Education, and with his colleagues and co-authors successfully conducts research into the synthesis and characterization of ferrite nanocrystals. The studies are being carried out in co-authorship with Russian colleagues (a scientific group led by I. Ya. Mittova) in accordance with the Memorandum of Understanding, concerning the program for the development of cooperation in the field of higher education, signed between Voronezh State University and Ho Chi Minh City University of Education. To date, new methods for the synthesis of nanocrystals of doped and undoped ferrites, including REE ferrites (neodymium, praseodymium, holmium, etc.) by solution methods have been developed; the regularities of changes in magnetic properties depending on the synthesis method, particle size, physicochemical nature of the dopant, and the level of doping have been established [187–192]. This research has been repeatedly supported by internal grants from the Socialist Republic of Vietnam.

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17. Government Order for higher education institutions in the area of scientific research for 2014-2016 (projects No. 673, 225).

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Author contributions

All authors made an equivalent contribution to the preparation of the publication.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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