

ANNOTATION

on the dissertation of Altynai Muratovna Madiyarova on the topic “Development of Physicochemical Foundations for the Synthesis of New Complex Oxide Magnetic Materials,” submitted for the degree of Doctor of Philosophy (PhD) in the educational program “8D05301 – Chemistry”

The dissertation work is presented in accordance with the requirements of subparagraph 2) of paragraph 5-1 of the Rules for Awarding Academic Degrees, approved by Order No. 4 of the Minister of Science and Higher Education of the Republic of Kazakhstan dated January 6, 2025.

In compliance with these requirements, the research findings of the dissertation have been published in peer-reviewed journals ranked in the first and/or second quartiles by impact factor according to the Journal Citation Reports of Clarivate Analytics, within scientific fields relevant to the content of the dissertation. The publication record meets the established criteria and includes at least two research articles, as well as one review article or a series of three publications. In at least one of these publications, the doctoral candidate is the first author or the corresponding author.

Furthermore, in accordance with paragraph 7 of the Regulations on the Dissertation Council of the Non-Commercial Joint Stock Company “Kazakh National Women’s Teacher Training University,” approved by Order No. 09-02-19/277 dated May 25, 2025, specifically subparagraph 7.2.1 “Submission of the Doctoral Dissertation,” the dissertation is submitted for defense in the form of a series of published scientific articles, representing a coherent body of the doctoral candidate’s research publications.

General Description of the Work

The dissertation is devoted to the investigation of the physicochemical foundations for the synthesis of novel complex oxide magnetic materials. In the course of the study, new spinel-structured ferrite materials were synthesized, and their structural, morphological, and electrophysical properties were comprehensively examined.

The sol–gel synthesis method was employed to obtain the samples. The crystal structure of the synthesized compounds was determined by X-ray diffraction (XRD) analysis, while their morphology and elemental composition were studied using scanning electron microscopy (SEM). In addition, the temperature and frequency dependences of their dielectric and electrical properties were investigated.

The results of the study revealed that the newly synthesized complex ferrites possess a single-phase spinel-type structure, and the correlations between their structural parameters and physical properties were established.

Relevance of the Study

In modern materials science, the development of functional magnetic materials and the control of their properties represent one of the key scientific directions. Ferrite materials are widely used in electronics, telecommunications, and energy applications due to their high magnetic permeability, low dielectric losses, and high electrical resistivity.

In recent years, significant scientific interest has been focused on spinel-structured ferrites. The properties of these materials strongly depend on their chemical composition, crystal structure, and synthesis method. In particular, lithium-based ferrites are distinguished by their enhanced magnetic and electrical properties and are considered promising materials for electronic devices and energy storage systems.

Therefore, the synthesis of new complex ferrite compositions and the investigation of their structural and physicochemical properties constitute an important and actual problem in contemporary materials science.

State of Research on the Topic

Numerous scientific studies have been devoted to investigating the structure and properties of ferrite materials. Depending on their crystal structure, ferrites are classified into several groups: spinel ferrites, hexagonal ferrites, garnet ferrites, and orthoferrites.

Among these, spinel-structured ferrites have been extensively studied and attract considerable attention as functional materials. Their general formula is MFe_2O_4 , where metal cations occupy tetrahedral and octahedral sites. The distribution of cations among these sites significantly influences the magnetic and electrical properties of ferrites.

In recent years, particular attention has been paid to lithium-based ferrites due to their structural and electrical characteristics. However, the synthesis and investigation of the structural-functional properties of new complex ferrite compositions remain insufficiently explored. Thus, the development of new ferrite materials and the study of their properties are of both scientific and practical importance.

Research Objective

To develop the physicochemical foundations for the synthesis of novel complex oxide magnetic materials and to investigate their structural, morphological, and electrical properties.

To achieve the stated objective, the following tasks were defined:

- To select effective methods for synthesizing new complex ferrite materials;
- To synthesize complex ferrites using the sol–gel method;
- To determine the crystal structure of the synthesized materials by X-ray diffraction (XRD);
- To investigate the morphology and elemental composition using scanning electron microscopy (SEM);
- To study the dielectric and electrical properties of the new ferrites;
- To determine the influence of synthesis parameters on the structural and physical properties of the materials.

Object of the Research - Novel complex ferrite oxides with a spinel structure.

Subject of the Research - The synthesis of complex ferrites and their structural, morphological, and electrophysical properties.

Research Methods - During the course of the dissertation research, the following advanced physicochemical methods were employed: the sol–gel synthesis

method, X-ray diffraction analysis (XRD, MiniFlex-600), scanning electron microscopy (SEM), Raman spectroscopy, measurements of dielectric and electrical properties, as well as determination of pycnometric density.

The application of these methods enabled a comprehensive investigation of the structural and physicochemical properties of the synthesized materials.

Scientific Novelty of the Dissertation Research

As a result of the study:

- For the first time, new complex ferrites with compositions $\text{Li}_{0.5}\text{MnFe}_{1.5}\text{O}_4$ and $\text{LiCr}_{3.4}\text{Fe}_{1.6}\text{O}_8$ were synthesized;
- It was established that the synthesized compounds are single-phase complex oxides with a spinel structure;
- Their crystal structure, morphology, and elemental composition were determined;
- The influence on the electrical and dielectric properties of the newly synthesized complex oxides was investigated.

The scientific novelty of the dissertation is substantiated by the following key provisions proposed for defense:

- A scientifically grounded methodology for synthesizing novel complex ferrites using the sol–gel method has been developed;
- The spinel-type crystal structure of the synthesized ferrites has been confirmed;
- The structural and morphological features of the new ferrites have been identified;
- The temperature and frequency dependences of the electrical and dielectric properties of complex ferrites have been established.

Scientific Results

1. Scientific Results of the First Article

In this study, the sol–gel method was employed to synthesize a new complex ferrite with the composition $\text{Li}_{0.5}\text{MnFe}_{1.5}\text{O}_4$, and its physicochemical nature was investigated. The structure and composition of the synthesized ferrite were determined using X-ray phase analysis. The results showed that the sample crystallizes in the $Fd3m$ space group, which is characteristic of the spinel structure and indicates a highly symmetric atomic arrangement.

The lattice parameters were found to be $a = b = c = 8.3677 \text{ \AA}$, corresponding to a face-centered cubic crystal lattice. The unit cell volume was $585.90 \text{ \AA}^3$. Furthermore, the close agreement between the X-ray density (4.678 g/cm^3) and the pycnometric density (4.675 g/cm^3) confirms the high structural density of the material and indicates a minimal presence of defects and voids.

The microstructure and elemental composition were analyzed using scanning electron microscopy (SEM). The SEM images reveal a fine-grained surface morphology consisting of interconnected particles. Most particles are agglomerated, forming larger structures composed of nanosized primary particles. According to the scale, the agglomerates are in the micrometer range, while the individual particles are nanoscale in size. This morphology can be explained by particle growth and

agglomeration due to high surface energy during synthesis. Additionally, the particles exhibit a relatively porous and uniformly distributed structure, which contributes to enhanced reactivity.

The study confirmed that the synthesized complex ferrite corresponds to the stoichiometric composition $\text{Li}_{0.5}\text{MnFe}_{1.5}\text{O}_4$. The particle sizes were observed to be relatively large, approximately 50.0 μm , 20.0 μm , and 10.0 μm . The EDS spectrum clearly shows the energy distribution of elements: oxygen (O) and lithium (Li) appear in the low-energy region, while manganese (Mn) and iron (Fe) are detected in the high-energy region.

Electrophysical measurements were carried out using an LCR-800 instrument over a temperature range of 293–483 K and frequencies from 1.5 kHz to 10 kHz. The results indicate that electrical conductivity gradually increases with temperature from 300 K to approximately 380–390 K, which is attributed to the enhanced activity of charge carriers. As temperature increases, electron mobility within the crystal lattice improves, leading to higher conductivity.

However, in the temperature range of 390–400 K, the conductivity reaches its maximum value, after which it sharply decreases. This behavior is associated with a transition in the material's state, specifically from a ferrimagnetic to a paramagnetic phase.

2. Scientific Results of the Second Article

A new complex ferrite material with the composition $\text{LiCr}_{3.4}\text{Fe}_{1.6}\text{O}_8$ was synthesized using the sol–gel method, and its physicochemical properties were investigated. X-ray diffraction (XRD) analysis showed that the compound has lattice parameters $a = b = c = 8.279 \text{ \AA}$, indicating a face-centered cubic crystal structure. The material was confirmed to be single-phase with a spinel-type structure. The low R-factor value (0.036 or 3.6%) confirms the reliability of the structural model.

The close agreement between the X-ray density (4.694 g/cm^3) and pycnometric density (4.695 g/cm^3) indicates high phase purity and uniform incorporation of chromium ions into the lattice.

According to the Williamson–Hall analysis, the clustering of data points suggests uniform diffraction peak parameters, indicating structural homogeneity and similar crystallite sizes. The slope of the fitted line corresponds to lattice microstrain, while the intercept provides the average crystallite size. The crystallite size was estimated to be approximately 9.12 nm, and the microstrain was 1.71×10^{-3} .

Raman spectroscopy was used to investigate vibrational properties. The observed peaks corresponding to Fe–O and Cr–O bonds further confirm the spinel structure. In the first spectrum, bands were observed at 195–206 cm^{-1} , 509–516 cm^{-1} , 597–618 cm^{-1} , and 650–720 cm^{-1} , corresponding to lattice vibrations of metal–oxygen bonds. The intense band in the 650–720 cm^{-1} region is attributed to symmetric vibrations of metal–oxygen bonds in tetrahedral sites. Slight shifts in band positions are associated with chromium ion incorporation.

In the second spectrum, prominent bands were observed at 348 cm^{-1} , 400 cm^{-1} , 851 cm^{-1} , 892 cm^{-1} , and 930 cm^{-1} , with the strongest band near 851 cm^{-1} , corresponding to symmetric metal–oxygen vibrations.

SEM analysis revealed that the material consists of agglomerated particles with sizes ranging from approximately 5 μm to 200 μm . The particles are predominantly semi-spherical and polyhedral in shape. Nanoscale primary particles combine to form micrometer-sized agglomerates. EDS analysis confirmed the elemental composition, with Li and O peaks in the low-energy region and Cr and Fe peaks in the high-energy region.

Electrophysical measurements showed that electrical resistivity decreases with increasing temperature in the range of 300–400 K, due to enhanced charge carrier mobility and electron hopping between Fe^{2+} and Fe^{3+} ions. Around 390–400 K, resistivity reaches a minimum and then increases again with further temperature rise, indicating a transition from ferrimagnetic to paramagnetic behavior.

The AC conductivity remains relatively constant at low frequencies, indicating strong insulating properties, making the material suitable for applications in resistors and capacitors. With increasing temperature and frequency, resistivity decreases due to enhanced charge carrier mobility.

3. Scientific Results of the Third Article

The review article systematically analyzes the synthesis methods, structural features, and functional properties of spinel ferrite nanoparticles (MFe_2O_4). Various synthesis techniques—including co-precipitation, combustion, sol–gel, thermal decomposition, hydrothermal, solvothermal, microwave-assisted, sonochemical, electrochemical, and solid-state reaction methods—are comparatively discussed in terms of their physicochemical principles, advantages, and limitations.

The influence of synthesis parameters on crystal structure, morphology, cation distribution between tetrahedral and octahedral sites, as well as magnetic, dielectric, and optical properties, is comprehensively examined. In addition, the capabilities of characterization techniques such as X-ray diffraction (XRD), scanning electron microscopy combined with energy-dispersive spectroscopy (SEM/EDS), Fourier-transform infrared spectroscopy (FTIR), FT-Raman spectroscopy, and dielectric and magnetic measurements are thoroughly summarized.

The conclusion highlights the high application potential of spinel ferrite nanoparticles in electronics, microwave devices, water purification, catalysis, sensors, and biomedical fields.

Theoretical and Practical Significance of the Work

The results of the study make it possible to establish the physicochemical principles underlying the synthesis of new complex ferrite materials.

The obtained results can be applied in the development of functional magnetic materials, the production of electronic devices, sensor technologies, and energy storage systems.

Approbation of Practical Results

The main results of the dissertation research were presented at international scientific conferences and discussed within the scientific community.

1. International Conference “Fundamental and Applied Aspects of the Development of Chemistry and Innovative Technologies,” dedicated to the 90th anniversary of Academician Kakina Sulaymankulov, National Academy of Sciences of the Kyrgyz Republic. Bishkek, Kyrgyzstan, 2023.

2. Kazakh-Uzbek Symposium “Contemporary Issues in Polymer Science,” aimed at discussing the current state and development trends in the chemistry of high-molecular compounds, integrating prospective scientific directions, the production of natural and synthetic polymers, composite materials, and the integration of chemical science and education. Almaty, Kazakhstan, 2023.

Publications and Author’s Contribution

The main results of the dissertation research are reflected in 6 publications, including: 3 articles published in journals indexed in the Clarivate Analytics Web of Science database, belonging to the first and/or second quartiles by impact factor; 2 articles published in scientific journals included in the list recommended by the Committee for Quality Assurance in Science and Higher Education of the Republic of Kazakhstan; 1 article published in the Russian Science Citation Index (RSCI).

1. Mataev M., Madiyarova A., Patrin G., Abdraimova M., Nurbekova M., Durmenbayeva Z. Synthesis of New Complex Ferrite $\text{Li}_{0.5}\text{MnFe}_{1.5}\text{O}_4$: Chemical–Physical and Electrophysical Research.

Materials, 2024, 17, 3754. <https://doi.org/10.3390/ma17153754>.

Author’s status: Corresponding author (doctoral candidate).

Journal metrics (2024): Impact Factor – 3.2; Q2 in Metallurgy & Metallurgical Engineering; CiteScore – 6.4 (71st percentile in Materials Science).

Contribution: Conducted experiments, interpreted the results, prepared and formatted the original manuscript, and participated in the full preparation of the article in accordance with journal requirements.

2. Mataev M., Madiyarova A., Abdraimova M., Nurbekova M., Seibekova K., Tursyn Z., Kezdykbayeva A., Ramachandran K., Keskin B. Novel Spinel Li–Cr Nano-Ferrites: Structure, Morphology, and Electrical/Dielectric Properties. International Journal of Molecular Sciences, 2025, 26, 10409. <https://doi.org/10.3390/ijms262110409>.

Author’s status: Corresponding author (doctoral candidate).

Journal metrics (2025): Impact Factor – 4.9; Q1 in Inorganic Chemistry; CiteScore – 9.9 (85th percentile).

Contribution: Conducted experiments, interpreted results, prepared and formatted the original manuscript, and contributed to the complete preparation of the article.

3. Mataev M., Madiyarova A., Abdraimova M., Tursyn Z., Ramachandran K. Structure–Property–Application Relationships of Spinel Ferrite Nanoparticles: From Synthesis to Functional Systems. International Journal of Molecular Sciences, 2026, 27, 2096. <https://doi.org/10.3390/ijms27052096>.

Author’s status: Corresponding author (doctoral candidate).

Journal metrics (2026): Impact Factor – 4.9; Q1 in Inorganic Chemistry; CiteScore – 9.9 (85th percentile).

Contribution: Conducted experiments, interpreted results, prepared the original manuscript, and participated in full article preparation.

4. Mataev M.M., Madiyarova A.M., Patrin G.S., Abdraimova M.R., Nurbekova M.A., Tursunova Zh.I. Synthesis and Physicochemical Characteristics

of Complex Ferrite $\text{CrNaFe}_2\text{O}_5$. Chemical Journal of Kazakhstan, 2024, 1(85), 109–118. <https://doi.org/10.51580/2024-1.2710-1185.11>.

Contribution: Conducted experiments, interpreted results, prepared and formatted the manuscript, and contributed to full article preparation.

5. Mataev M.M., Madiyarova A.M., Patrin G.S., Abdraimova M.R., Nurbekova M.A. Synthesis and Physicochemical Properties of a New Complex Ferrite. Proceedings of the National Academy of Sciences of the Republic of Kazakhstan. Series Chemistry and Technology, 2024, Vol. 3, No. 460, pp. 137–146. <https://doi.org/10.32014/2024.2518-1491.242>.

Contribution: Conducted experiments, interpreted results, prepared the manuscript, and ensured compliance with journal requirements.

6. Mataev M.M., Abdraimova M.R., Madiyarova A.M., Patrin G.S. Synthesis of Complex Ferrite $\text{CrLiFe}_2\text{O}_5$ and Its X-ray and Electron Microscopic Study. Proceedings of the National Academy of Sciences of the Kyrgyz Republic, Bishkek, 2023. ISSN 0002-3221.

Contribution: Conducted experiments, interpreted results, prepared and formatted the manuscript, and contributed to full article preparation.

7. Mataev M.M., Patrin G.S., Madiyarova A.M., Abdraimova M.R. Synthesis and Physicochemical Characteristics of Complex Ferrite $\text{CrNaFe}_2\text{O}_5$. Proceedings of the Kazakh-Uzbek Symposium “Modern Problems of Polymer Science”, Almaty, 2024.

Contribution: Conducted experiments, interpreted results, prepared and formatted the manuscript, and participated in full preparation.

Relationship of work with national research programs

The dissertation work is carried out within the framework of the following state-funded research program:

– Grant funding for scientific and/or scientific-technical projects for 2025–2027 from the Ministry of Science and Higher Education of the Republic of Kazakhstan: ‘Synthesis and study of the properties of multicomponent perovskites for the creation of magnetosensitive media with controlled physicochemical characteristics’ IRN AP26198947;

– Internal funding, in accordance with Order No. 236 of 26 April 2023 of the Kazakh National Girls' Pedagogical University: ‘Synthesis and Physical Fundamentals of New Composite Multiferroics for Spintronics’.

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