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**ABSTRACT**

of the dissertation for the degree of Doctor of Philosophy

**STUDY OF PHASE TRANSITIONS IN  $\text{Ln}_2\text{Ti}_2\text{O}_7$  ( $\text{Ln}=\text{La}$ ,  $\text{Nd}$ ,  
 $\text{Pr}$ ) CERAMIC MATERIALS WITH PEROVSKITE  
STRUCTURE UNDER HIGH PRESSURES**

Speciality: 2223.01 – “Crystallography, physics of  
crystals”

Field of science: Physics

Applicant: **Asif Hamdulla Asadov**

**Baku – 2026**

The work was performed at the “Institute of Physics” PLE of the Ministry of Science and Education of the Republic of Azerbaijan in the Laboratory of Crystallography and crystallophysics.

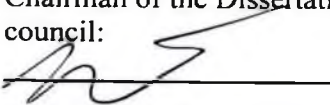
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## GENERAL CHARACTERISTICS OF THE WORK

**Actuality of the topic and degree of elaboration:** The study of materials under extreme conditions forms the cornerstone of condensed matter physics and materials science, creating fundamental concepts about the structural, electronic and thermodynamic properties of solids. New stages of research under high pressures reveal exotic states of matter and unique physical phenomena that are inaccessible under ambient conditions. Among various classes of materials, complex-structure oxides have attracted considerable attention due to their rich chemical structure, tunable electronic properties, and potential applications in catalysis, energy storage and digital devices. The study of layered perovskite  $\text{Ln}_2\text{Ti}_2\text{O}_7$  ( $\text{Ln} = \text{La}, \text{Nd}, \text{Pr}$ ) materials under high pressures is of particular interest, since pressure can cause significant structural changes, electronic transitions and even amorphization<sup>1</sup>, which in turn leads to drastic changes in the properties of the material, examples of which include high conductivity, modified optical properties or a new magnetic state of the substance. Understanding the phase transition of  $\text{Ln}_2\text{Ti}_2\text{O}_7$  ( $\text{Ln}=\text{La}, \text{Nd}, \text{Pr}$ ) under high pressures is essential not only for developing our knowledge of solid state physics, but also for the application of these materials in the preparation of special technologies. Perovskite-like materials such as  $\text{Ln}_2\text{Ti}_2\text{O}_7$  ( $\text{Ln} = \text{La}, \text{Nd}, \text{Pr}$ ) are materials possessing a special crystal structure known as the perovskite structure. Owing to unique properties such as high thermal stability<sup>2</sup>, electrical conductivity and strong magnetism<sup>3</sup>, these materials have broad application potential.

Perovskite-like materials can also be used to create electronic devices with a high efficiency factor, such as field-effect transistors,

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<sup>1</sup> B. Winkler, A. Friedrich, W. Morgenroth, E. Haussühl, et al. Chinese Science Bulletin, 2014. vol.59, No.36, pp. 5278–5282.

<sup>2</sup> S.J. Patwe, V. Katari, N.P. Salke, S.K. Deshpande, et al. Journal of Materials Chemistry C, 2015. vol.3, No.17, pp.4570–4584.

<sup>3</sup> H. Man, A. Ghasemi, M. Adnani, M.A. Siegler, et al. Physical Review Materials, 2023. vol.7, No.6.

which have wide applications in electronics<sup>4</sup>. At the same time, interest in these materials is growing in the aerospace industry. Due to their high thermal and electrical conductivity and strong magnetism, they are considered favorable for catalysts in engine systems, radiation-resistant electronics, thermal management systems and thermoelectric devices. Moreover, they are capable of improving the quality of aerospace optical instruments by being used as high-performance optical coatings and filters<sup>5</sup>.

Overall, the mechanism of the phase transition of  $\text{Ln}_2\text{Ti}_2\text{O}_7$  ( $\text{Ln} = \text{La, Nd, Pr}$ ) systems under high pressure is still insufficiently studied. Since previous scientific studies were mainly carried out under ordinary conditions or on different members of the pyrochlore/perovskite family, gaps concerning the effect of pressure on the structural and electronic properties across different lanthanides still remain. This dissertation was aimed precisely at eliminating that gap by combining experimental methods with theoretical modeling, with the goal of systematically investigating the behavior of  $\text{Ln}_2\text{Ti}_2\text{O}_7$  ( $\text{Ln} = \text{La, Nd, Pr}$ ) materials at high pressure.

**Object and subject of the research:** The object of the research is the layered perovskite materials  $\text{La}_2\text{Ti}_2\text{O}_7$ ,  $\text{Nd}_2\text{Ti}_2\text{O}_7$  and  $\text{Pr}_2\text{Ti}_2\text{O}_7$ , and its subject is their structural phase transitions under high pressure (from normal pressure up to 30.0GPa), structural deformation mechanisms such as the displacement of atoms and ions, the tilting and rotation (distortion) of  $\text{TiO}_6$  octahedra, as well as the effect of these changes on the electrical, dielectric and vibrational properties of the material.

**Goal and objectives of the research:** The main goal of the dissertation work is to elucidate the mechanism of the structural changes occurring as a result of high pressure in  $\text{Ln}_2\text{Ti}_2\text{O}_7$  ( $\text{Ln} = \text{La, Nd, Pr}$ ) compounds and of the phase transitions associated with them. To achieve this goal, the following objectives were solved:

<sup>4</sup> H. Zhu, A. Liu, H. Kim, J. Hong, et al. Chemistry of Materials, 2020. vol.33, No.4, pp.1174–1181.

<sup>5</sup> W. J. Lee, H. J. Kim, J. Kang, D.H. Jang, et al. Annual Review of Materials Research, 2017. vol.47 pp.391–423.

- Investigation of the structural stability and of the sequence of phase transitions of  $\text{Ln}_2\text{Ti}_2\text{O}_7$  ( $\text{Ln} = \text{La}, \text{Nd}, \text{Pr}$ ) compounds under high pressure;

- Correlation of the observed structural changes with changes in the electronic and mechanical properties; study of the distribution of  $\text{La}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Pr}^{3+}$ ,  $\text{Ti}^{4+}$  and  $\text{O}^{2-}$  ions in the crystal lattice and of the mechanism of formation of the crystal structure;

- Determination of the effect of the structure of  $\text{MO}_6$  ( $\text{M} = \text{metal}$ ) octahedra in the  $\text{A}_2\text{B}_2\text{O}_7$  family on the physical properties of the material;

- Study of the vibrational spectra (Raman modes) of the materials depending on high pressure.

**Research methods:** The complex crystal structure of  $\text{Ln}_2\text{Ti}_2\text{O}_7$  ( $\text{Ln} = \text{La}, \text{Nd}, \text{Pr}$ ) compounds requires a comprehensive approach for the accurate determination of their structural, chemical and physical properties. For this purpose, the methods of X-ray diffraction, neutron diffraction and Raman spectroscopy were applied in the work in a mutually complementary manner:

1. X-ray diffraction (XRD): was applied for the determination of the crystal structure, lattice parameters and phase composition of  $\text{Ln}_2\text{Ti}_2\text{O}_7$  ( $\text{Ln} = \text{La}, \text{Nd}, \text{Pr}$ ) compounds. By providing information about the arrangement of atoms in the crystal lattice, this method allows the comparison of the structural features of different compounds;

2. Neutron diffraction (ND): was used for the precise determination of the positions of the atoms in the material, especially of the light oxygen atoms which are difficult to observe by X-rays. This method allows a deeper study of the chemical bonds and the local environment of the elements.

3. Raman spectroscopy: was applied for the analysis of the vibrational motion regimes of atoms and of the strength and nature of chemical bonds. The change of Raman modes under high pressure allows confirmation of phase transitions at the dynamic level.

4. Comparative analysis: The fourth method of this research is the comparison of the structural, chemical and physical properties of  $\text{Ln}_2\text{Ti}_2\text{O}_7$  ( $\text{Ln} = \text{La}, \text{Nd}, \text{Pr}$ ) compounds with other related

compounds. This comparative analysis allows a comprehensive understanding of the similarities and differences between various

compounds, as well as of the advantages and disadvantages of each of them.

The combination of these four methods created conditions for a comprehensive analysis of the structural changes of the studied compounds in both the static and the dynamic aspect.

**Main provisions submitted for defence:**

1. Determination of the transition from the non-centrosymmetric monoclinic  $P2_1$  space group to the higher-symmetry monoclinic  $P2_1/m$  space group in the layered perovskites  $\text{La}_2\text{Ti}_2\text{O}_7$ ,  $\text{Nd}_2\text{Ti}_2\text{O}_7$  and  $\text{Pr}_2\text{Ti}_2\text{O}_7$  under the effect of high pressure (0.0 – 30.0 GPa), of the corresponding critical pressure limits (16.3 GPa for  $\text{La}_2\text{Ti}_2\text{O}_7$ , 19.2 GPa for  $\text{Nd}_2\text{Ti}_2\text{O}_7$ , 13.8 GPa for  $\text{Pr}_2\text{Ti}_2\text{O}_7$ ) and of the character of these transitions.

2. Determination that the main mechanism of the phase transition is the cooperative tilting and rotation of  $\text{TiO}_6$  octahedra, as well as the characteristic displacement of  $\text{Ln}^{3+}$  (La, Nd, Pr) ions along the crystallographic axes.

3. Determination, on the basis of neutron diffraction data, that with increasing pressure the average tilt angle of the octahedra increases sharply, the Ln ions move toward the symmetry plane and the lattice is compressed anisotropically ( $a:b:c \approx 1:2:3$ ).

4. Determination of the symmetry violations for  $\text{La}_2\text{Ti}_2\text{O}_7$ ,  $\text{Nd}_2\text{Ti}_2\text{O}_7$  and  $\text{Pr}_2\text{Ti}_2\text{O}_7$  crystals and of the dependence of the critical pressure required for the phase transition on the radius of the  $\text{Ln}^{3+}$  ion.

5. Determination, by means of Raman spectroscopy under high pressures, of the shift of phonon modes, of the change of their width and of the emergence of new modes; confirmation of the phase transitions at the dynamic level on the basis of the calculation of Grüneisen parameters.

6. Provision of a comprehensive analysis of the structural, static and dynamic changes in layered perovskites on the basis of the application of a complementary combination of X-ray diffraction, neutron diffraction and Raman spectroscopy.

**Scientific novelty of the research:**

1. For the first time, in the layered perovskites  $\text{La}_2\text{Ti}_2\text{O}_7$ ,  $\text{Nd}_2\text{Ti}_2\text{O}_7$  and  $\text{Pr}_2\text{Ti}_2\text{O}_7$ , a transition from the non-centrosymmetric

monoclinic  $P2_1$  space group to the highersymmetry  $P2_1/m$  space group under the effect of high pressure (0–30.0 GPa) was detected, and the critical pressure limits were determined for all three compounds (16.3, 19.2 and 13.8 GPa, respectively).

2. For the first time, the main mechanism of these phase transitions the cooperative tilting and rotation of  $\text{TiO}_6$  octahedra, as well as the characteristic displacement of  $\text{Ln}^{3+}$  (La, Nd, Pr) ions along the crystallographic axes was substantiated by experimental data and density functional theory (DFT) calculations.

3. Newly, on the basis of neutron diffraction data, it was determined that with increasing pressure the average tilt angle of the octahedra increases sharply, the Ln ions move toward the symmetry plane and the lattice is compressed anisotropically ( $a:b:c \approx 1:2:3$ ); this provides an explanation at the atomic level of the increase in crystal symmetry.

4. For the first time, the dependence of the critical pressure required for the phase transition on the radius of the  $\text{Ln}^{3+}$  ion was revealed, and this dependence was explained on the basis of the concept of internal «chemical pressure» that increases as the ionic radius decreases.

5. For the first time, the high-pressure dependence of the phonon modes of  $\text{Ln}_2\text{Ti}_2\text{O}_7$  (Ln = La, Nd, Pr) compounds was studied, it was found that new vibrational modes arise during the phase transition, and Grüneisen parameters were calculated for selected modes.

6. As a methodological novelty, the behavior of  $\text{Ln}_2\text{Ti}_2\text{O}_7$  (Ln = La, Nd, Pr) layered perovskites at high pressure was studied by a complementary combination of X-ray diffraction, neutron diffraction and Raman spectroscopy, and an experimental basis was formed which allows the analysis of structural, static and dynamic changes within the framework of a unified approach.

### **Theoretical and practical significance of the research:**

**Theoretical significance:** The study of the behavior of layered perovskites under high pressure is of great importance in terms of predicting their performance in extreme environments (for

example, high-pressure industrial conditions), obtaining information about their structural and electronic properties, and designing new materials adapted for specific applications on that basis. At the same

time, the study of pressure-induced phase transitions sheds light on the main mechanisms of structural instability in complex oxides.

**Practical significance:** High-pressure synthesis enables the production of new layered perovskites with unique properties that cannot be obtained by ordinary methods, while the control of the crystal structure and of phase transitions by means of pressure enables the development of new functional materials for electronics, optics and energy conversion. In addition, the results obtained can be applied in the design of devices such as high-pressure sensors and activators.

**Personal contribution of the applicant:** All stages of the research, with the exception of the formulation and scientific substantiation of the problem, namely the analytical review of the scientific literature, the planning and execution of experimental and theoretical work, the interpretation and generalization of the obtained results, as well as the writing and preparation for publication of scientific articles, were carried out personally by the author.

With the direct personal participation of the author:

1. Under diamond anvil cell (DAC) conditions, X-ray diffraction (XRD) and Raman spectroscopy measurements were carried out in the pressure range of 0–30 GPa, and neutron diffraction (ND) experiments were also performed under room conditions.

2. A complete structural analysis of the diffraction data was performed using the Rietveld method; lattice parameters, atomic coordinates and the distortion (tilting and rotation) indicators of  $\text{TiO}_6$  octahedra were determined.

3. The pressure dependence of the Raman modes was analyzed, Grüneisen parameters were calculated and Bond-Valence Sum (BVS) analyses were carried out.

4. A comparison of the experimental results with density functional theory (DFT) calculations was carried out, and the critical pressure values of the phase transitions (16.3 GPa for  $\text{La}_2\text{Ti}_2\text{O}_7$ , 19.2 GPa for  $\text{Nd}_2\text{Ti}_2\text{O}_7$ , 13.8 GPa for  $\text{Pr}_2\text{Ti}_2\text{O}_7$ ) were determined.

The scientific interpretation of the obtained results, the formulation of the main provisions submitted for defence and the preparation of the texts of the scientific articles published on the topic of the dissertation were carried out personally by the author.

**Approbation and application:**

On the topic of the dissertation work, 5 scientific articles 4 of them in reputable foreign journals and 1 in a local journal and 7 conference materials have been published.

The articles submitted on the topic of the dissertation were published in the following journals:

1. A structural phase transition in  $\text{La}_2\text{Ti}_2\text{O}_7$  at high pressure - Physica B: Condensed Matter (2023) [https://doi.org/ 10.1016/j.physb.2023.414753](https://doi.org/10.1016/j.physb.2023.414753)

2. The Effects of High Pressure on the Crystal Structure and Vibration Spectra of Layered Perovskite-Like  $\text{Nd}_2\text{Ti}_2\text{O}_7$  - Solid State Ionics (2024) [https://doi.org/ 10.1016/j.ssi.2023.116447](https://doi.org/10.1016/j.ssi.2023.116447)

3. VIBRATIONAL AND X-RAY MEASUREMENTS OF  $\text{La}_2\text{Ti}_2\text{O}_7$  UNDER HIGH PRESSURE CONDITION” Advanced Physical Research (2024) [https://doi.org/ 10.62476/apr62113](https://doi.org/10.62476/apr62113)

4. A search for pressure-induced phase transition in the layered perovskite-like  $\text{Pr}_2\text{Ti}_2\text{O}_7$  - Journal of Alloys and Compounds, 2024

5. The structural mechanisms of pressure-induced phase transitions in the Carpy-Galy phase layered perovskites - Solid State Sciences, 2024 [https://doi.org/10.1016/j.solidstatesciences. 2024. 107676](https://doi.org/10.1016/j.solidstatesciences.2024.107676)

**Participation was taken in the following scientific conferences submitted on the topic of the dissertation:**

1. The XXVI International Scientific Conference of Young Scientists and Specialists (AYSS-2022)

2. 57th meeting of the PAC for Condensed Matter Physics – (Dubna 2023)

3. Conference on the use of neutron scattering in condensed matter research (RNIKS-2023) Neutron Studies of Condensed Matter (2023)

4. Нейтронные Исследования Конденсированного Состояния (2023)

5. 135th session of the Scientific Council-2024

6. Youth School on Condensed Matter Physics (School FKS-2024) 11th

7. International Conference on Superconductivity and Magnetism - ICSM2026 & 4th International Conference on Quantum Materials and Technologies - ICQMT2026 - Muğla, Türkiye.

**Name of the organization where the dissertation work was carried out:** The dissertation work was carried out at the “Crystallography and crystallophysics” laboratory of the Institute of Physics of Azerbaijan Republic.

**Structure and volume of the dissertation:** The dissertation work includes an introduction, four chapters, main results and a list of literature. The content of the work is described on 176 pages, including 60 figures, 11 tables and a list of literature of 165 titles. The volume of the dissertation (excluding spaces in the text and figures, tables, graphs and the list of literature) is 215955 characters (Introduction – 21733, Chapter I – 52587, Chapter II – 70214, Chapter III – 53498, Chapter IV – 15490, conclusion – 2433 characters).

## **MAIN CONTENT OF THE DISSERTATION**

The introductory part covers the conceptual framework and the scientific substantiation of the research. The scientific novelty of the research lies in its dedication to the systematic study of the mechanisms of phase transitions of these materials under high pressure and in its focus on the comparative analysis of the differences in structural behavior depending on the ionic radius of various lanthanide elements (La, Nd, Pr). The main targets of the research, the specific objectives and the main scientific provisions submitted for defence are formulated and substantiated in detail.

In the first chapter of the dissertation, a broad literature review is presented on the general characteristics of ferroelectric crystals, their physical essence and crystallographic foundations, as well as on how the layered perovskite-type lanthanide compounds  $\text{Ln}_2\text{Ti}_2\text{O}_7$  (Ln = La, Nd, Pr) have been studied in existing scientific research. This chapter provided the theoretical basis for formulating the scientific foundations of the topic and the actuality of the dissertation work.

First of all, the phenomenon of spontaneous polarization as a specific feature of ferroelectric crystals is discussed. In ferroelectrics, spontaneous polarization arises as a result of the ordered displacement of cations and anions in the crystal lattice, and this

phenomenon forms the basis of their electrophysical properties<sup>6</sup>. This feature also causes the observation of the hysteresis effect, which distinguishes ferroelectrics from other dielectric materials. The hysteresis effect makes the response of ferroelectrics to an external electric field nonlinear and enables their use in practical applications, particularly in memory devices and sensor technologies<sup>7</sup>.

The structural lability of perovskite-type crystals is particularly emphasized in the chapter. One of the main features of perovskites is their ability to form a stable structure with various ions. Almost all elements of the lanthanide family can participate in the perovskite structure under certain conditions. This is one of the main reasons why perovskites are widely studied both from the theoretical point of view and in applied fields<sup>8</sup>.

In the first chapter, the main families of layered perovskites the Dion–Jacobson<sup>9</sup>, Ruddlesden–Popper<sup>10</sup> and Carpy–Galy<sup>11</sup> structures are presented in a comparative manner (Figure 1). In each of these families,

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<sup>6</sup> C. Moure, O. Peña. Progress in Solid State Chemistry, 2015. vol. 43 pp. 123–148.

<sup>7</sup> S.A. Basun, G. Cook, V.Y. Reshetnyak, A. V. Glushchenko, et al. Physical Review B, - 2011. vol.84, No.2, - p.024105

<sup>8</sup> T. Saha-Dasgupta. Journal of Physics: Condensed Matter, 2014. vol.26, No.19, p.193201.

<sup>9</sup> M. Dion, M. Ganne, M. Tournoux. Materials Research Bulletin, 1981. vol. 16, No.11, pp.1429–1435.

<sup>10</sup> S.N. Ruddlesden, P. Popper 1958. Acta Crystallographica vol.11, No.1, pp. 54–55.

<sup>11</sup> R. Portier, A. Carpy, M. Fayard, J. Galy. Physica Status Solidi (a), 1975. vol. 30, No.2, pp.683–697.

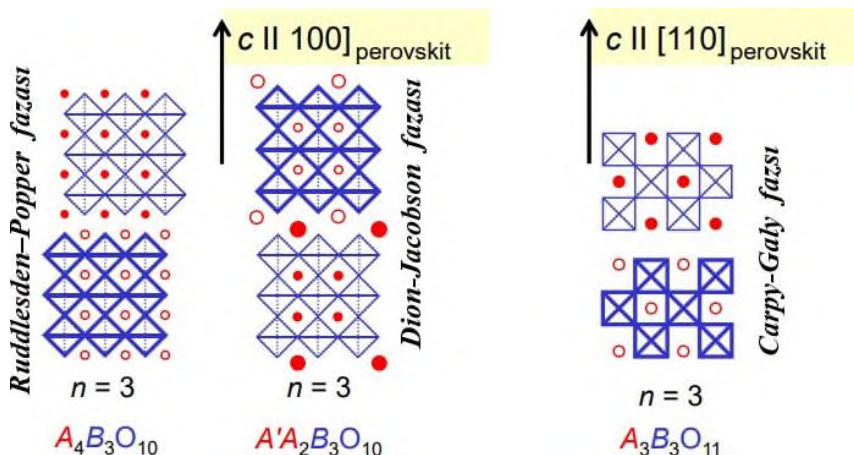


**Figure 1. Schematic representation of the Dion-Jacobson, Ruddlesden-Popper and Carpy-Galy perovskite families<sup>12</sup>.**

In each of these families, the relationship between the form of arrangement of the perovskite blocks, the placement of the intermediate layers and the resulting physical properties is explained in detail. In particular, in  $A_2B_2O_7$ -type perovskites, the placement of Ln ( $\text{La}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Pr}^{3+}$ ) and  $\text{Ti}^{4+}$  ions in the crystal lattice and the distortion forms of  $\text{TiO}_6$  octahedra form the basis of their ferroelectric and dielectric properties<sup>13</sup>. The chapter separately discusses the main causes of the structural instability of perovskites. Three important mechanisms (Figure 2) octahedral tilting, Jahn–Teller distortions (Figure 3) and cation displacements (Figure 4) are comprehensively interpreted. Glazer's notation<sup>14</sup> is analyzed for the classification of octahedral tilts, and Goldschmidt's tolerance factor theory<sup>15</sup> for evaluating the compatibility of the crystal lattice. The application of these models shows that even small differences in the ratio of ionic radii have a serious effect on the change of crystal symmetry and, consequently, on the stability of the ferroelectric properties.

<sup>12</sup> N. Valdez, N.A. Spaldin. Polyhedron, 2019. vol.171, pp.181–192.

<sup>13</sup> Y.A. Titov, N.M. Belyavina, V.Y. Markiv, M.S. Slobodyanik, et al. Journal of Alloys and Compounds, 2005. vol.387, No.1–2, pp.82–85.

<sup>14</sup> A.M. Glazer, *Acta Crystallographica B*, 1972. vol.28, No.11, pp.3384–3392.

<sup>15</sup> V.M. Goldschmidt. *Die Naturwissenschaften*, 1926. vol.14, No.21, pp.477–485.

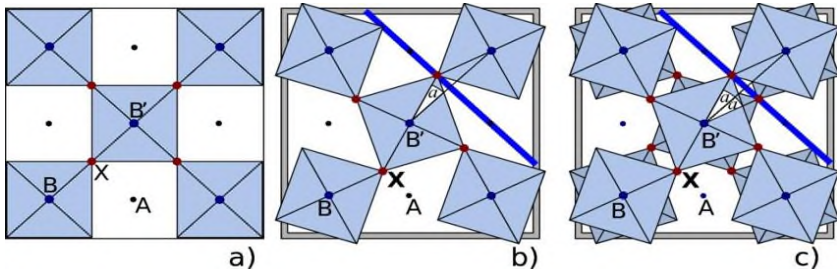


**Figure 2. a) In the ideal perovskite structure the octahedra are untilted, b) octahedral tilts occur in the same phase, and c) octahedral tilts occur in opposite phases**

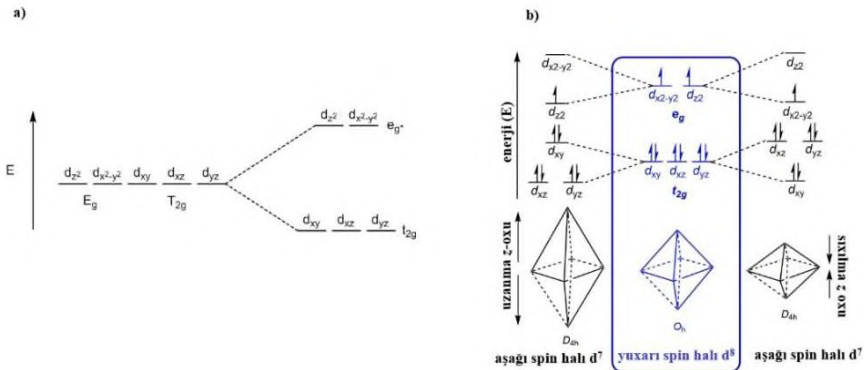


**Figure 3. Elongation and compression of the octahedra as a result of the Jahn-Teller effect.**

For example, the large radius of the  $\text{La}^{3+}$  ion (1.16 Å) causes the monoclinic  $\text{P2}_1$  phase to remain stable in  $\text{La}_2\text{Ti}_2\text{O}_7$ , whereas the  $\text{Nd}^{3+}$  (1.109 Å) and  $\text{Pr}^{3+}$  (1.126 Å) ions with smaller radii create stronger distortions in the structure and lead to the predominance of orthorhombic symmetry<sup>16,17,18</sup>. The results obtained by neutron

<sup>16</sup> A.G. Asadov, D.P. Kozlenko, A. Mammadov, R. Mehdiyeva, et al. Physica B: Condensed Matter, 2023. vol.655 p.414753.

<sup>17</sup> A.G. Asadov, A. Mammadov, D.P. Kozlenko, R. Mehdiyeva, et al. Journal of Alloys and Compounds, 2024. vol.1003 p.175461.

<sup>18</sup> A.G. Asadov, R. Mehdiyeva, A. Mammadov, D.P. Kozlenko, et al. Solid State Ionics, - 2024. vol.406 - p.116447.

diffraction methods show that the tilting patterns of  $\text{TiO}_6$  octahedra and the displacements of Ln ions are the main indicators of structural instability<sup>19</sup>.

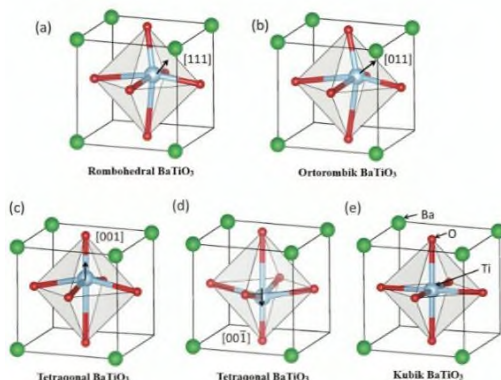


**Figure 4. Displacements of the  $\text{Ti}^{3+}$  cation in the  $\text{ABO}_3$  crystal in different phases<sup>20</sup>.**

In addition, it is noted that Jahn–Teller distortions create more stable, but lowersymmetry structures by removing electron degeneracy in ferroelectric materials. These distortions are related in particular to the unequal distribution of the d-orbital electrons of the B-cations and, as a result, create local deformation in the crystal lattice.

In the second chapter of the dissertation, the experimental-methodological basis of the research is formed and the methods ensuring the scientific reliability of the future results are substantiated in detail. This chapter is not limited to the description of technical procedures, but also analytically evaluates the advantages of the chosen methods, their conformity with the scientific goals set and their role in the interpretation of the results.

At the first stage, the chemical and technological features of the Mineralization Polymerizing Complex (MPC) synthesis method used

<sup>19</sup> C.J. Howard, H.T. Stokes. Acta Crystallographia Section B, - 2005. vol.61 pp.93–111.

<sup>20</sup> S. A. Hayward, E. K. H. Salje. Journal of Physics: Condensed Matter, 2002.



for the preparation of the research objects the  $\text{La}_2\text{Ti}_2\text{O}_7$ ,  $\text{Nd}_2\text{Ti}_2\text{O}_7$  and  $\text{Pr}_2\text{Ti}_2\text{O}_7$  samples are explained. The main reason for choosing the MPC method is that it ensures the obtaining of a homogeneous mixture, a high degree of purity and the stable formation of the monoclinic  $\text{P}2_1$  phase<sup>21</sup>. It was observed that in samples synthesized by this method the phase composition and morphological structure are more stable, which increased the accuracy of the subsequent high-pressure experiments.

The chapter broadly describes the technology of obtaining high pressure. Here, the construction and operating principles of diamond anvil cells (DAC) and the pressure range of their application are explained in detail<sup>22</sup>. Thanks to DAC technology, it became possible to carry out research on the samples in the pressure range up to 30 GPa. For the accurate measurement of pressure, the ruby luminescence method was applied, and the calibration principles and the degree of reliability of this method were widely interpreted. The analysis showed that the ruby luminescence method allows the pressure to be measured accurately even in nanometer-sized areas and ensures the correctness of the results.

An important part of the methodological foundations is the thermodynamic analysis of the phases. Here, on the basis of the concept of Gibbs free energy, the pressure-dependent behavior of phase transitions is explained. The classification of phase transitions by types I, II and III was carried out, and the crystallographic and thermodynamic indicators of each of them were systematized. This approach showed that pressure is not limited to changing the structural parameters only, but can also transform the symmetry of the material by redistributing its internal energy.

The theoretical foundations of the X-ray diffraction (XRD) applied for the study of the structure and of the neutron diffraction (ND) by means of the DN-6 neutron diffractometer at the IBR-2 reactor (Figure 5) are explained extensively in the chapter. X-ray diffraction allows the study of the arrangement of atoms in the crystal lattice, the calculation of lattice parameters and the determination of the phase composition. Neutron diffraction, on the other hand, is considered

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<sup>21</sup> F. A. Lichtenberg, A. Herrnberger, K. Wiedenmann, J. Mannhart. Progress in

Solid State Chemistry, 2001. vol.29, No.1– 2, pp.1–70.

<sup>22</sup> C. E. Weir, E. R. Lippincott, A. Van Valkenburg, E.N. Bunting. Journal of research of the National Bureau of Standards.

superior in terms of more accurately tracking the positions of light elements, especially oxygen atoms<sup>23</sup>. Thanks to the combination of these methods, it became possible to track structural changes at both the cation and the anion level.

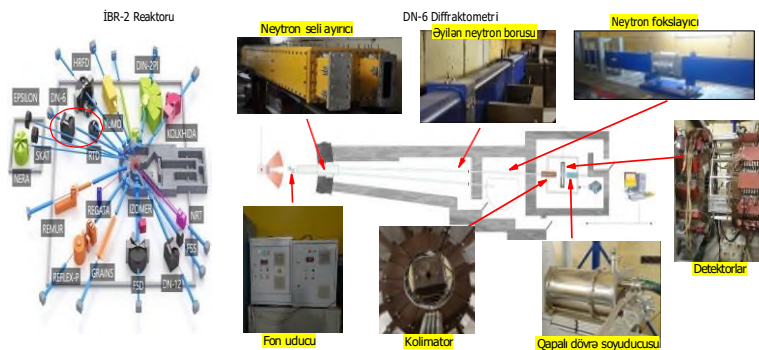


**Figure 5. Schematic representation of the IBR-2 reactor and the DN-6 diffractometer.**

Particular attention in the chapter is paid to Rietveld analysis. This method was used in the processing of polycrystalline diffraction data and enabled the determination of structural parameters with their smallest details. The application of the Rietveld method was necessary both in terms of statistical reliability criteria and of the optimization of structural models.

Another important methodological approach is related to Raman spectroscopy. The analysis of Raman spectra with the Confotec® Duo Raman spectrometer (Figure 6) made it possible to track the vibrational motion modes of the atoms in the materials.

<sup>23</sup> D.P. Kozlenko, S. Kichanov, E. Lukin, B. Savenko. Crystals 2018, vol.8, p.331, 2018.

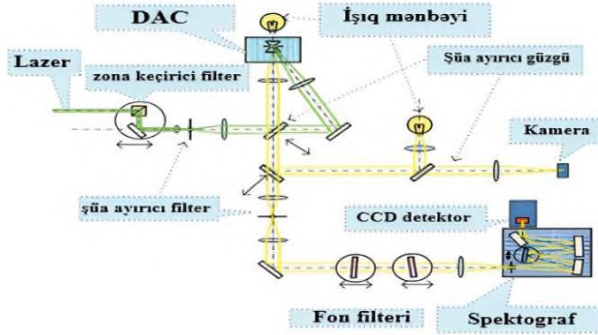
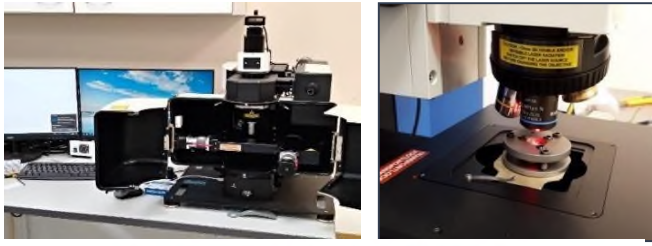


**Figure 6. General view and technical scheme of the Confotec® Duo Raman spectrometer.**

With the application of this method, the change of the vibrational modes under pressure was observed, and Grüneisen parameters were also calculated.

This made it possible to obtain fundamental results in terms of understanding the response of the dynamic properties of the materials to pressure. Raman spectroscopy also made it possible to detect the emergence of new vibrational modes, which created conditions for a deeper understanding of the microscopic mechanism of phase transitions.

The analytical result of Chapter II is that the integrative application of various experimental methods X-ray diffraction, neutron diffraction and Raman spectroscopy allows a comprehensive study of both the static and the dynamic aspects of the structural changes of  $\text{Ln}_2\text{Ti}_2\text{O}_7$  ( $\text{Ln} = \text{La}, \text{Nd}, \text{Pr}$ ) compounds. Thanks to this methodological approach, not only the pressure ranges in which phase transitions occur, but also the mechanisms of these transitions at the atomic level can be determined. Thus, the main scientific contribution of Chapter II is that the experimental basis necessary for the reliability of the results of

studies conducted at high pressure was formed and its advantages were analytically substantiated.

In the third chapter of the dissertation, the results of the main experimental studies carried out and their analysis are presented in detail. This chapter is devoted both to tracking the behavior of the individual  $\text{Ln}_2\text{Ti}_2\text{O}_7$  ( $\text{Ln} = \text{La}, \text{Nd}, \text{Pr}$ ) compounds under high pressure and to carrying out their comparative analysis in order to reveal general regularities.

First, the behavior of the  $\text{La}_2\text{Ti}_2\text{O}_7$  crystal at high pressure was studied. The results of X-ray diffraction showed that as pressure increases, the lattice parameters decrease monotonically, as given in Figure 7.

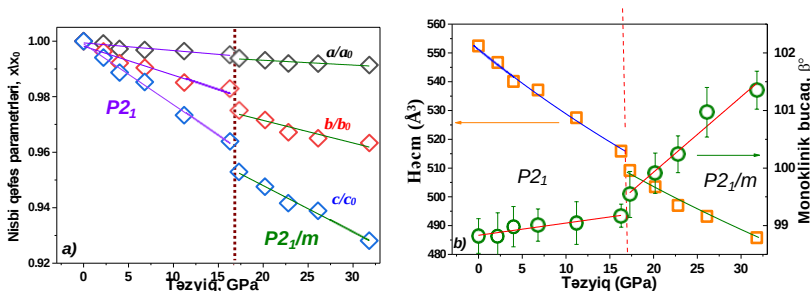


**Figure 7. a) Pressure dependence of the relative lattice parameters for the low-pressure and highpressure phases of the  $\text{La}_2\text{Ti}_2\text{O}_7$  compound. b) Pressure dependence of the unit cell volume for the low-pressure and high-pressure phases of the  $\text{La}_2\text{Ti}_2\text{O}_7$  compound.**

As a result of the fitting for the low-pressure  $P2_1$  phase, the values  $B_0 = 183(4)$  GPa and  $B' = 5(1)$  were obtained. For the high-pressure  $P2_1/m$  phase, the volume compression analysis resulted in  $B_0 = 201(1)$  GPa and a fixed value of  $B' = 4$ . These values reflect a certain stiffening of the structure under compression and are significantly higher than the results  $B_0 = 121(23)$  GPa and  $B' = 18(5)$  given in previous studies<sup>24</sup>.

At pressures above approximately 16.3 GPa, significant

changes are observed in the diffraction patterns. At this threshold,

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<sup>24</sup> F.X. Zhang, J. Lian, U. Becker, et al. *Journal of Solid State Chemistry*. vol.180, pp.571–576, 2007

several new diffraction lines appear; clear reflections are observed at positions of approximately  $2\theta = 6.4^\circ$ ,  $7.5^\circ$  and  $9.4^\circ$ , while at the same time the reflections belonging to the low-pressure monoclinic phase, located at approximately  $8.0^\circ$ ,  $9.7^\circ$  and  $21.0^\circ$ , disappear completely. Along with this, changes also occur in the relative intensities of the remaining diffraction lines, which indicates the existence of important rearrangements in the main crystal structure. These observations are clear indicators of a phase transition induced by the effect of pressure in  $\text{La}_2\text{Ti}_2\text{O}_7$ .

The phase transition is accompanied by clear changes in the lattice parameters. Thus, the  $b$  and  $c$  parameters decrease noticeably, while the monoclinic  $\beta$  angle shows a sharp increase, which can also be considered a sign of a reconstructive or strongly displacive transformation. Conversely, the  $a$  parameter is almost unaffected and does not exhibit particular anomalies around the transition point. This behavior demonstrates the anisotropic compression properties of the lattice. The directional compressions of the lattice parameters were calculated according to the expression  $\kappa_{ai} = -(1/a_{i0})(da_i/dP)|_T$ , where  $a_i = a, b, c$ . The values obtained for the low-pressure  $P2_1$  phase were  $\kappa_{a1} = 0.00022(1) \text{ GPa}^{-1}$ ,  $\kappa_{b1} = 0.0010(1) \text{ GPa}^{-1}$  and  $\kappa_{c1} = 0.0022(1) \text{ GPa}^{-1}$ . As a result of the transition to the  $P2_1/m$  phase at high pressure, these values decreased:  $\kappa_{a2} = 0.00017(1) \text{ GPa}^{-1}$ ,  $\kappa_{b2} = 0.0008(1) \text{ GPa}^{-1}$  and  $\kappa_{c2} = 0.0017(2) \text{ GPa}^{-1}$ . These results show that in the high-pressure phase the compression decreases relatively, but the anisotropic compression character of the lattice is preserved. In both phases, the  $b$  axis remains the least compressible and the  $c$  axis the most compressible direction, which corresponds to the features of the layered perovskite-like structure, that is, to the tilting of  $\text{TiO}_6$  octahedra and to the interlayer interactions.

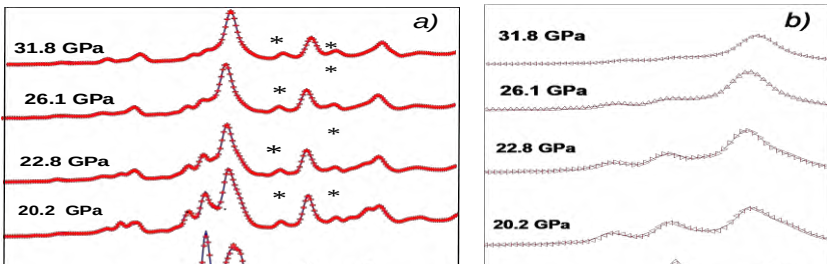




**Figure 8. a) X-ray diffraction patterns of the  $\text{La}_2\text{Ti}_2\text{O}_7$  compound measured at selected pressures and at room temperature. b) Enlarged region of the X-ray diffraction patterns of the  $\text{La}_2\text{Ti}_2\text{O}_7$  compound measured at selected pressures and at room temperature. Experimental points and calculated profiles are shown. The ‘\*’ marks indicate additional lines belonging to the Re gasket of the high-pressure cell.**

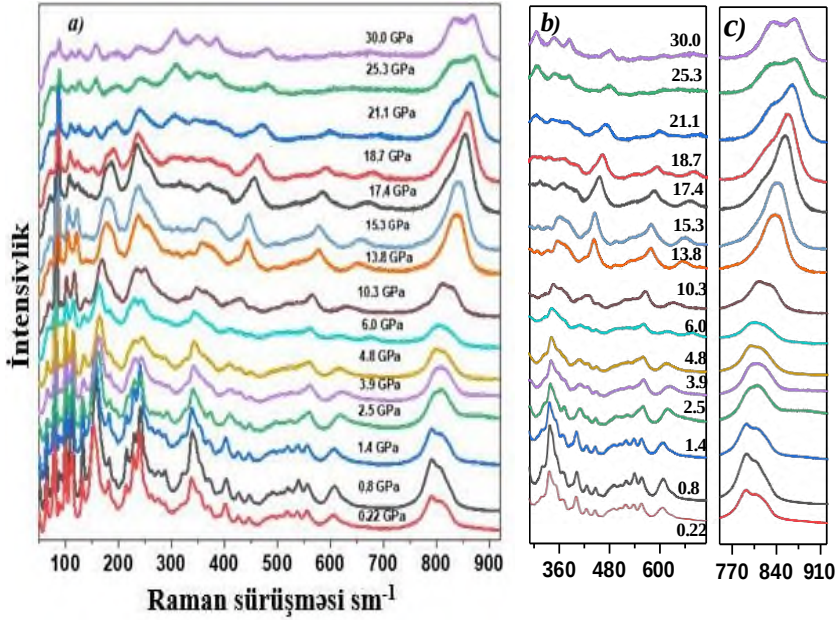


**Figure 9. a) Raman spectra of the  $\text{La}_2\text{Ti}_2\text{O}_7$  compound at different pressures. b) Enlarged part of the Raman spectra of  $\text{La}_2\text{Ti}_2\text{O}_7$  in the  $370\text{--}680\text{ cm}^{-1}$  range. c) Enlarged part of the Raman spectra of  $\text{La}_2\text{Ti}_2\text{O}_7$  in the  $760\text{--}920\text{ cm}^{-1}$  range.**

A sharp change is observed in the X-ray spectrum of the lattice at a pressure of 16.3 GPa (Figure 8). This change is related to the transition from the monoclinic  $\text{P2}_1$  phase to the more symmetric  $\text{P2}_1/\text{m}$  phase. The results of Raman spectroscopy (Figure 9) and the violation of the continuity of the spectra of some Raman modes (Figure 10) also confirmed this phase transition: at a pressure of 16.3 GPa, part of the existing vibrational modes disappeared and new modes appeared. These changes prove that a serious symmetry transformation occurred in the structure of the material. The Rietveld analysis of the X-ray diffraction data showed that the tilt angles of the  $\text{TiO}_6$  octahedra changed, and also that the positions of the La ions in the crystal lattice were redistributed. As a result of the analysis, it

was determined that this transition is accompanied by a

transformation from the ferroelectric state to the paraelectric state, that is, spontaneous polarization in  $\text{La}_2\text{Ti}_2\text{O}_7$  is completely lost.

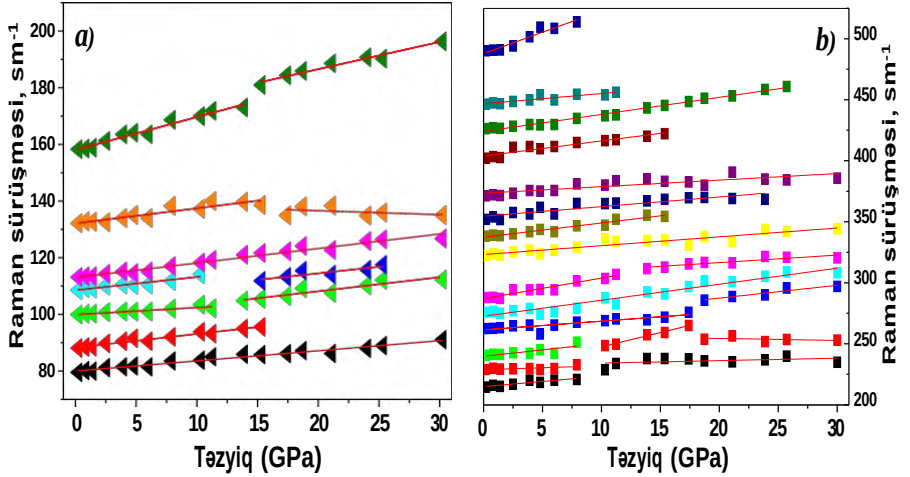


**Figure 10. Pressure dependence of the Raman modes of the  $\text{La}_2\text{Ti}_2\text{O}_7$  compound. The range of the calculated errors is within the size of the symbols. The solid lines show the linear interpolation of the experimental data.**

In the layered crystal structure of  $\text{La}_2\text{Ti}_2\text{O}_7$ , the lanthanum ions form a somewhat distorted plane of octahedral layers as a result of the displacement of the ions relative to each other (Figure 11b). In a complex crystal structure, it is quite difficult to determine the precise positions of light atoms such as oxygen on the basis of X-ray diffraction data. Nevertheless, in the studies carried out, the positions of the lanthanum atoms were determined; although these values should be considered approximate, they are informative enough to show the trends of the structural changes. In our work, the dependence of the relative displacements of the  $\text{La}^{3+}$  ions is presented in Figure 11a. The observations show that the relative distance  $\Delta$  between lanthanum ions located at different crystallographic positions undergoes sharp changes. In particular, after the phase transition occurs at pressures above 16.3 GPa, a significant increase in the amount of displacement of the rare-earth elements was

recorded, which indicates a further strengthening of the disorder in the crystal structure of the  $\text{La}_2\text{Ti}_2\text{O}_7$  compound under high pressure.

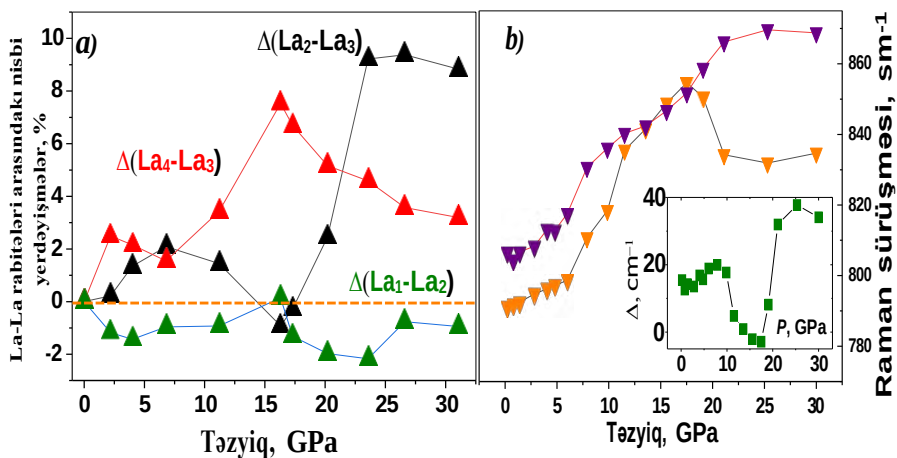


**Figure 11. a) Pressure dependence of the relative distance between lanthanum ions in the crystal structure of the  $\text{La}_2\text{Ti}_2\text{O}_7$  compound. b) Positions of the doublet lines in the Raman spectrum of the  $\text{La}_2\text{Ti}_2\text{O}_7$  compound. The range of the calculated errors is within the size of the symbols. The splitting of the doublet depending on pressure is shown in the additional graph.**

The neutron diffraction pattern of the  $\text{La}_2\text{Ti}_2\text{O}_7$  compound was measured under room conditions and the corresponding diffraction pattern is presented in Figure 12. For the correct analysis of the neutron diffraction data, a number of structural models proposed in previous studies were tested. Among these models were the monoclinic  $P2_1$ ,  $P2$ ,  $Pm$ ,  $P2/m$  and orthorhombic  $\text{Cmc}2_1$  phases. As previously expected, the monoclinic structural model with  $P2_1$  symmetry provided the best description of the experimental data.

This result shows that there are no additional impurities or foreign phases in the  $\text{La}_2\text{Ti}_2\text{O}_7$  sample and that the measured sample has a high purity level. The calculated lattice parameters were determined as  $a = 7.752(4) \text{ \AA}$ ,  $b = 5.510(2) \text{ \AA}$ ,  $c = 12.962(3) \text{ \AA}$  and  $\beta$

= 98.7(2)°, and these values show good agreement with the results obtained in recent studies. These indicators allow an accurate description of the initial geometry of the crystal lattice of the  $\text{La}_2\text{Ti}_2\text{O}_7$  compound, as well as of the arrangement of the atoms. The

details and precise numerical values of these structural parameters are given in Table 1.

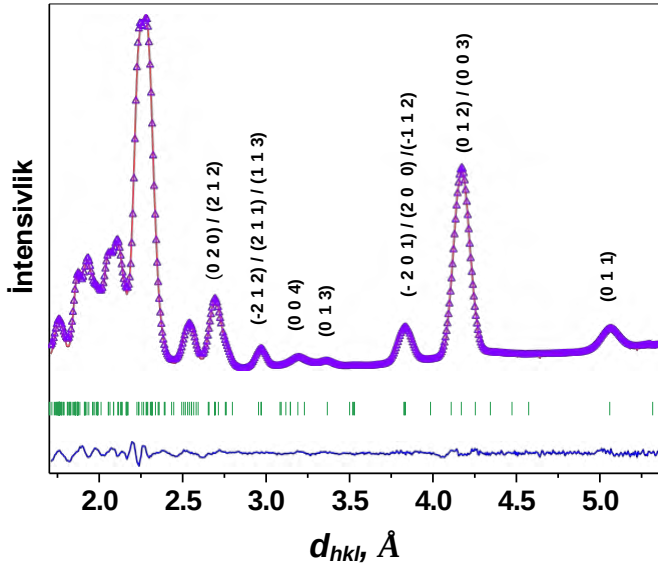


**Figure 12.** Neutron diffraction patterns of the  $\text{La}_2\text{Ti}_2\text{O}_7$  compound, measured under room conditions and refined by the Rietveld method. Experimental points, calculated profiles and the difference curve are shown. The lines indicate the calculated positions of the diffraction peaks corresponding to the monoclinic phase with  $\text{P2}_1$  symmetry. The indices of several diffraction peaks are also presented.

**Table 1.**

**Atomic coordinates of the monoclinic phase of the  $\text{La}_2\text{Ti}_2\text{O}_7$  compound based on neutron diffraction data.**

| <i>Atom</i> | <i>x</i>  | <i>y</i>  | <i>z</i>  |
|-------------|-----------|-----------|-----------|
| <i>La1</i>  | 0.2615(8) | 0.2992(8) | 0.1067(5) |
| <i>La2</i>  | 0.7877(7) | 0.293(4)  | 0.1086(7) |
| <i>La3</i>  | 0.3211(3) | 0.8386(4) | 0.388(1)  |
| <i>La4</i>  | 0.8647(2) | 0.8520(5) | 0.3820(9) |
| <i>Ti1</i>  | 0.0653(3) | 0.7370(9) | 0.1288(7) |
| <i>Ti2</i>  | 0.5129(7) | 0.7598(9) | 0.1272(4) |
| <i>Ti3</i>  | 0.0883(6) | 0.2480(1) | 0.3152(1) |
| <i>Ti4</i>  | 0.5761(9) | 0.2735(1) | 0.3141(3) |
| <i>O1</i>   | 0.7714(6) | 0.7866(6) | 0.0930(5) |
| <i>O2</i>   | 0.2697(3) | 0.7152(4) | 0.0784(8) |
| <i>O3</i>   | 0.0166(4) | 0.0243(4) | 0.0160(6) |
| <i>O4</i>   | 0.4744(7) | 0.0366(7) | 0.0154(2) |
| <i>O5</i>   | 0.0856(3) | 1.0057(3) | 0.2338(3) |
| <i>O6</i>   | 0.5254(4) | 0.9684(1) | 0.2353(2) |
| <i>O7</i>   | 0.0325(3) | 0.4843(2) | 0.2041(9) |
| <i>O8</i>   | 0.5661(3) | 0.443(9)  | 0.1856(6) |
| <i>O9</i>   | 0.1001(4) | 0.5517(3) | 0.4119(1) |
| <i>O10</i>  | 0.6070(8) | 0.5721(7) | 0.4001(9) |
| <i>O11</i>  | 0.1209(7) | 0.063(3)  | 0.4401(3) |
| <i>O12</i>  | 0.6002(2) | 0.0763(4) | 0.4347(1) |
| <i>O13</i>  | 0.3252(1) | 0.3023(4) | 0.3052(8) |
| <i>O14</i>  | 0.8110(9) | 0.2315(1) | 0.2995(1) |

The X-ray diffraction patterns of the  $\text{Nd}_2\text{Ti}_2\text{O}_7$  compound were measured at room temperature and at selected pressures from 0 GPa to 30.2 GPa, and the results are presented in Figure 13.

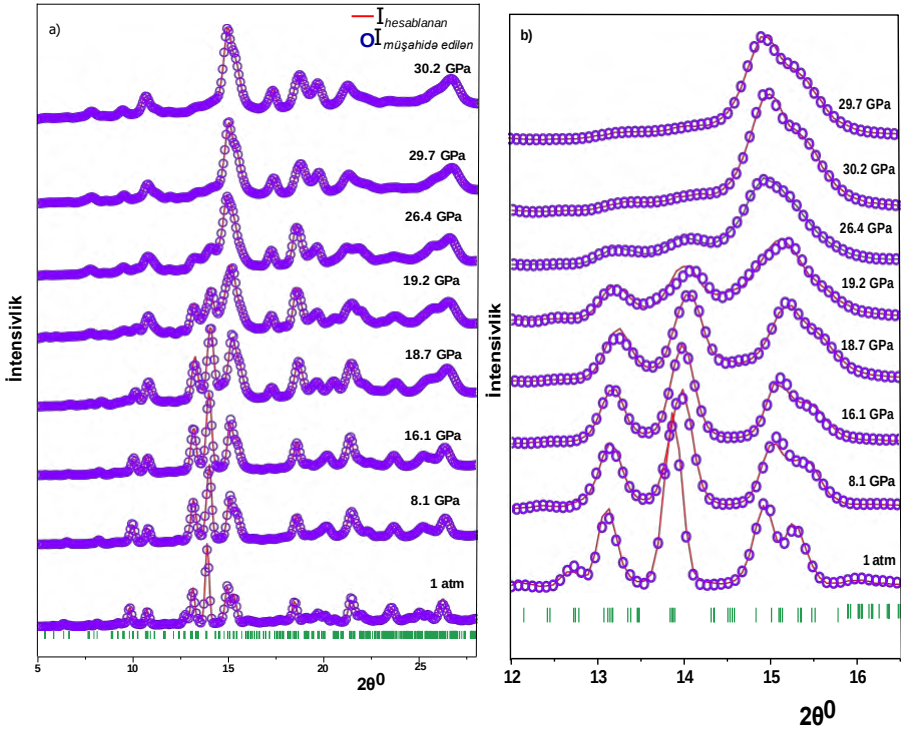


**Figure 13. X-ray diffraction patterns of the  $\text{Nd}_2\text{Ti}_2\text{O}_7$  compound, obtained at room temperature and at selected pressures from 1 atm to 30.2 GPa. a) Full spectrum of  $\text{Nd}_2\text{Ti}_2\text{O}_7$  at different pressures. b) The “fingerprint” region of the spectrum of  $\text{Nd}_2\text{Ti}_2\text{O}_7$  at different pressures. The vertical lines below show the calculated positions of the nuclear peaks. The spectral line shapes presented here allow a comparison between the observed spectrum and the spectrum obtained as a result of the calculations. The results were refined by the profile fitting method by means of the Fullprof program.**

The analysis of the experimental data obtained at normal pressure showed that the crystal structure of the  $\text{Nd}_2\text{Ti}_2\text{O}_7$  sample is monoclinic, has the  $P2_1$  ( $C_2^2$ ) symmetry group, and the lattice parameters were determined as  $a=7.763(4)$  Å,  $b=5.503(2)$  Å,

$c=25.962(3)$  Å and  $\beta=98.4(2)^\circ$ . These results agree both with our neutron diffraction data and with the results obtained in previous

studies. When the pressure became  $P > 19.2$  GPa, a second-order phase transition occurred. This manifested itself in the appearance of additional diffraction peaks at positions of approximately  $7.70^\circ$ ,  $9.50^\circ$  and  $17.20^\circ$  (Figure 13). Significant changes in the intensity of the diffraction peaks were observed over the entire region of the  $2\theta$  interval. Our studies showed that the peak at approximately  $9.70^\circ$  was clearly split and a new peak appeared near  $10.70^\circ$ , while at the same time a separate peak around  $8.10^\circ$  became invisible. This significant phenomenon is closely related to the compression of the unit cell. In addition, four clear peaks existed in the main spectral region ( $2\theta = 12.0^\circ\text{--}16.0^\circ$ ), and during the analysis a new peak at the position of  $14.90^\circ$ , which had not been observed before in this interval, was detected. This particular spectral change can be explained by the emergence of a new and different phase in the initial monoclinic phase. During the analysis of the diffraction data, a number of structural models were tested: the  $P2_1(C_2^2)$ ,  $P2(C_2^1)$ ,  $Pm(Cs^1)$ ,  $P2/m(C_2h^1)$ ,  $Cmc2_1(C_2v^{12})$  and  $Pna2_1(C_2v^9)$  symmetries. As a result of these checks, the monoclinic  $P2 (C_2^1)$  structural model was selected for the high-pressure phase and a satisfactory fitting of the experimental data was obtained. The lattice parameters calculated for the high-pressure monoclinic  $P2 (C_2^1)$  phase were determined as  $a=7.62(5)$ ,  $b=5.37(2)$ ,  $c=24.45(9)$  Å and  $\beta=99.56(1)^\circ$ . The observed structural phase transition shows similarity with the phase transition induced by pressure in the  $La_2Ti_2O_7$  sample. We encountered certain difficulties in the analysis of the phase transition. The scattering of X-rays from the electron cloud made it difficult to accurately determine the positions of the oxygen atoms at high pressure. As a result, alternative methods were applied in order to investigate the arrangement of the  $TiO_6$  octahedra. Due to this limitation, the position of the oxygen atoms can only be estimated on the basis of the known positions of the Ti atoms in the unit cell.

The lattice parameters of both monoclinic phases of  $\text{Nd}_2\text{Ti}_2\text{O}_7$  and the pressure dependence of the unit cell volume are shown in Figure 14. Anomalies in the pressure dependence of the lattice parameters were observed at approximately  $P \sim 19.2$  GPa and the structural phase transition was confirmed. The compression of the lattice is anisotropic, and in the monoclinic phases the  $c$  axis was determined to be the most compressible direction. The average compression indicators were fixed as  $k_{ai} = -(1/a_{i0})(da_i/dP)|_T$ , ( $a_i = a, b, c$ ) and for the  $c$  axis it was determined as  $k_c = 0.0026(1) \text{ GPa}^{-1}$ , which is approximately three times more compared with the  $a$  and  $b$  parameters ( $k_a = 0.0009 \text{ GPa}^{-1}$  and  $k_b = 0.0008 \text{ GPa}^{-1}$ ). After the structural phase transition, a strong compression anisotropy was also preserved:  $k_a = 0.00084(2) \text{ GPa}^{-1}$ ,  $k_b = 0.0015(6) \text{ GPa}^{-1}$  and  $k_c = 0.0040(2) \text{ GPa}^{-1}$ . A sharp increase of the monoclinic  $\beta$  angle occurred near the phase transition (Figure 14c).

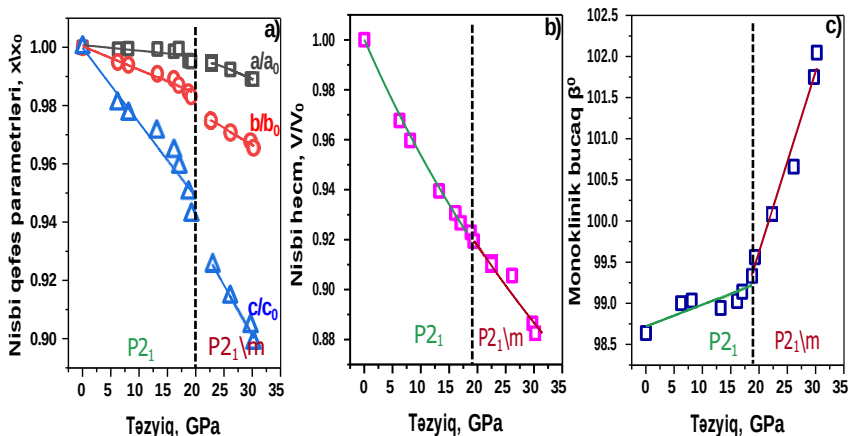


**Figure 14.** The relative lattice parameters (a) and the relative crystal lattice volume (b) of the  $\text{Nd}_2\text{Ti}_2\text{O}_7$  compound are presented as functions of pressure. The pressure dependence of the monoclinic  $\beta$  angle for both monoclinic phases is shown in panel (c).

The analysis of the Raman spectra of the  $\text{Nd}_2\text{Ti}_2\text{O}_7$  compound at high pressure shows that as pressure increases, the wavenumbers of the Raman modes mainly exhibit an increasing tendency. The spectrum obtained under normal conditions shows similarity with the results observed for  $\text{La}_2\text{Ti}_2\text{O}_7$  (Figure 15), and the existence of 132 Raman-active modes in the crystal structure with monoclinic  $\text{P2}_1$  symmetry is confirmed theoretically.

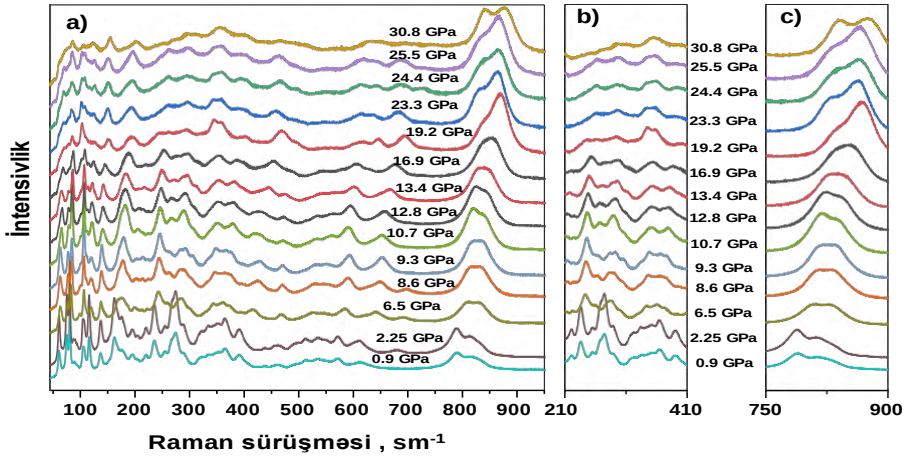


**Figure 15. Raman spectra of the  $\text{Nd}_2\text{Ti}_2\text{O}_7$  compound (a) and their expanded parts (b and c), measured in the pressure range from 0.9 GPa to 30.8 GPa and at room temperature.**

Although a regular increase in the wavenumbers was recorded in the pressure range  $P < 19.2$  GPa (Figure 16), the intensity of some Nd-O related modes decreases and they are lost at the background level. This situation is explained by the change in the interaction of the Nd atoms with the  $\text{TiO}_6$  octahedra and by the shortening of the bond lengths. When the pressure reaches the level of 19.2 GPa, the emergence of new Raman modes indicates that a structural phase transition has occurred. These modes are associated with changes in the coordination environment of the Nd atoms and with the removal of degeneracy.

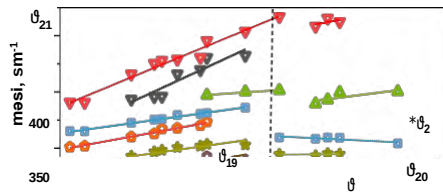
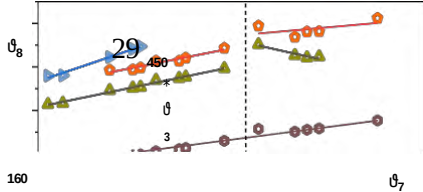


**Figure 16. Pressure dependence of the vibrational modes of the  $\text{Nd}_2\text{Ti}_2\text{O}_7$  compound and their linear interpolation.**

The emergence of negative Grüneisen parameters of the Raman modes in the highpressure environment (Table 2) indicates the formation of a new structural phase. In this phase, the angular distortions of the  $\text{TiO}_6$  octahedra and the displacement of the Nd atoms along the  $c$  axis cause the elongation of the Nd-O bonds and the weakening of the vibrational modes. The splitting observed in the intensity of the doublet located near  $\sim 800 \text{ cm}^{-1}$  in the Raman spectra as a result of the increase in pressure is related to the symmetrization of the  $\text{TiO}_6$  octahedra. Overall, the changes recorded in the Raman spectra indicate the structural instability of the  $\text{Nd}_2\text{Ti}_2\text{O}_7$  compound in the low-pressure phase and the weakening of the ferroelectric

phase. These results are explained by the distortions of the  $\text{TiO}_6$

octahedra, the anisotropic deformation properties of the Nd-O bonds and the continuous character of the phase transition.

**Table 2.**

**Observed Raman vibrational modes of the Nd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> compound for the low-pressure and high-pressure phases; their values measured at normal pressure and at high pressure (P = 20.0 GPa) are given.**

|            |                                                 |                                                  | Aşağı təzyiq fazası<br>(0GPa–20.0GPa)                                                       |               | Yüksək təzyiq fazası<br>(20.0GPa–30.8GPa)                                                   |               |
|------------|-------------------------------------------------|--------------------------------------------------|---------------------------------------------------------------------------------------------|---------------|---------------------------------------------------------------------------------------------|---------------|
| Mod        | $\nu_i$ (sm <sup>-1</sup> )<br><i>P=0.9 GPa</i> | $\nu_i$ (sm <sup>-1</sup> )<br><i>P=20.0 GPa</i> | $\left(\frac{\partial \nu_i}{\partial P}\right)_T$<br>(sm <sup>-1</sup> GPa <sup>-1</sup> ) | $\gamma_{iT}$ | $\left(\frac{\partial \nu_i}{\partial P}\right)_T$<br>(sm <sup>-1</sup> GPa <sup>-1</sup> ) | $\gamma_{iT}$ |
| $\nu_8$    | 162.7(2)                                        | 190.2(6)                                         | 1.28(3)                                                                                     | 1.51(1)       | -1.12(6)                                                                                    | -1.19(7)      |
| $\nu_{24}$ | 512.6(2)                                        | 615.8(6)                                         | 4.89(8)                                                                                     | 1.83(1)       | -0.13(2)                                                                                    | -0.04(3)      |
| $\nu_{25}$ | 571.3(1)                                        | 645.4(8)                                         | 3.13(7)                                                                                     | 1.05(2)       | -0.79(1)                                                                                    | -0.24(8)      |

The X-ray diffraction analysis of the Pr<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> compound at high pressure (Figure 17) shows that the crystal structure of this material undergoes significant structural changes with increasing pressure. Under normal conditions, a layered perovskite-type structure is observed in Pr<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> with the P2<sub>1</sub> symmetry group, and the arrangement of the Pr ions with the distorted TiO<sub>6</sub> octahedra determines the crystal symmetry. As pressure increases, the intensities and angles of the diffraction peaks change, and some peaks merge to form new reflections. In particular, the emergence of new peaks at the angles of  $2\theta=17.0^\circ$  and  $2\theta=20.43^\circ$  is associated with the symmetrization of the TiO<sub>6</sub> octahedra and with the formation of a new phase. These changes are related to displacements in the arrangement of the Pr ions and to the reorganization of the perovskite layers.

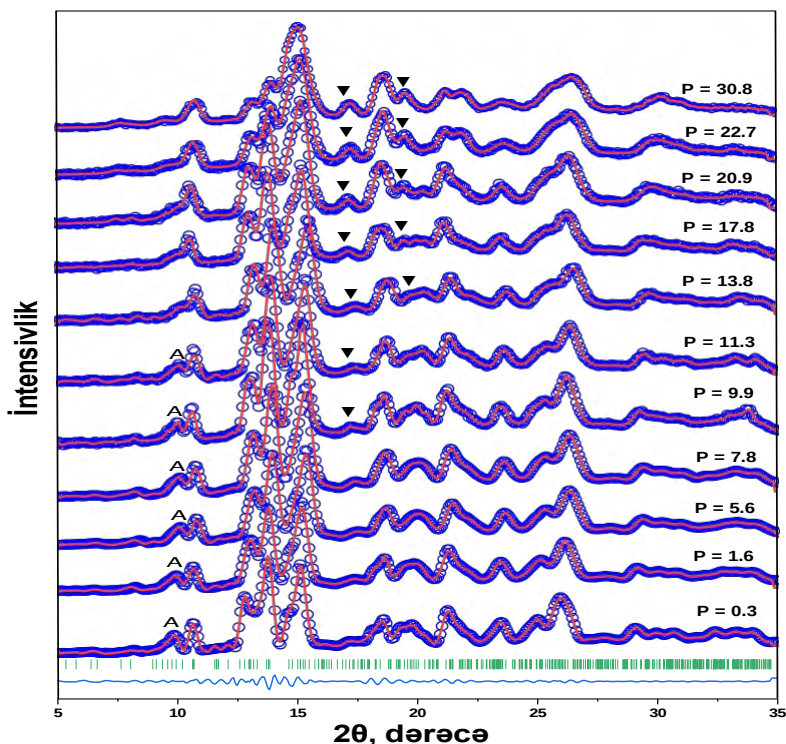


**Figure 17.** X-ray diffraction patterns of the  $\text{Pr}_2\text{Ti}_2\text{O}_7$  compound at different pressures and the results processed by the Rietveld method. The experimental points, calculated profiles and the difference curve are shown. The marks below indicate the calculated positions of the Bragg reflections. The peaks that disappear during the phase transition caused by pressure are indicated by the  $\square$  symbol, and the newly emerging diffraction peaks by the  $\blacktriangledown$  symbol.

The Rietveld analyses carried out under high pressure show that a transition from the ferroelectric  $\text{P2}_1$  phase to the paraelectric  $\text{P2}_1/\text{m}$  phase occurs in  $\text{Pr}_2\text{Ti}_2\text{O}_7$ . This result was confirmed both by empirical X-ray diffraction observations and by density functional theory 18 (DFT) calculations. The structural analyses show that as pressure increases, the crystal lattice parameters decrease, the

monoclinic angle  $\beta$  changes sharply (Figure 18) and the unit cell

volume exhibits a nonlinear dependence corresponding to the Birch–Murnaghan equation. For the low-pressure phase, the bulk modulus was determined as  $B_0 = 194.9 \pm 6.4$  GPa, and for the high-pressure phase as  $B_0 = 210.8 \pm 8.1$  GPa.

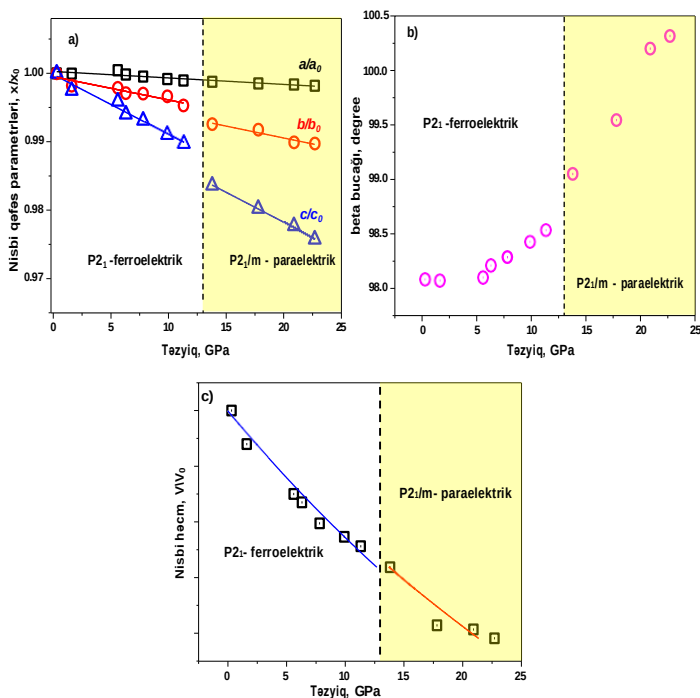


**Figure 18. a) Changes occurring in the relative crystal parameters at different pressures for the lowpressure and high-pressure phases of  $\text{Pr}_2\text{Ti}_2\text{O}_7$ . b) Changes of the monoclinic angle ( $\beta$ ) at different pressures for both phases. c) Changes of the unit cell volume of both phases depending on pressure.**

The movement of the Pr ions along the c axis (Figure 19) shows the anisotropic behavior of the structure and causes the initiation of the phase transition.

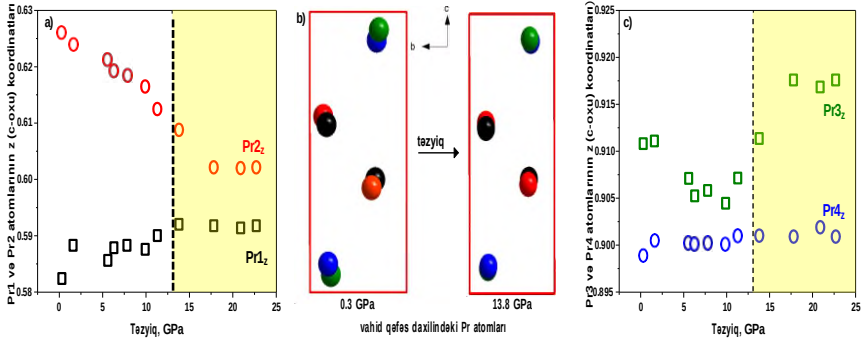


**Figure 19. a) Pressure dependence of the coordinates of the Pr1 and Pr2, c) Pr3 and Pr4 atoms along the z axis. In the schematic representations in the middle (b), the positions of the Pr atoms at pressures of 0.3 and 13.8 GPa are shown.**

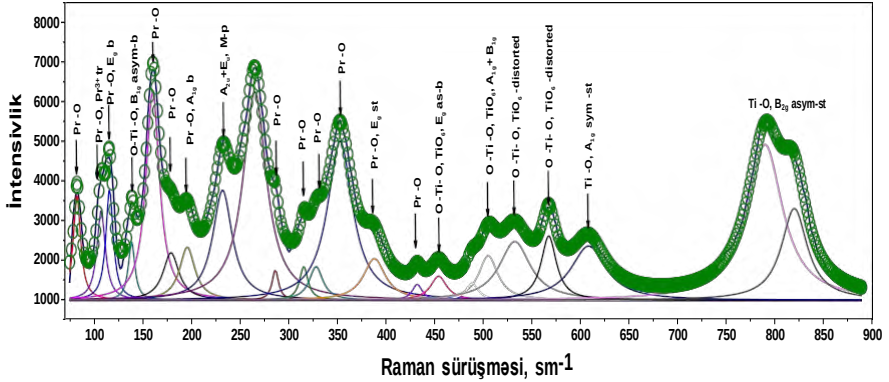


**Figure 20. Raman spectrum of the Pr<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> compound under normal conditions. Peak fitting curves and preliminary assignments of the detected Raman modes.**

The approach of the Pr1 and Pr2 ions, and the initial approach followed by the separation of the Pr3 and Pr4 ions, affect the orientation of the TiO<sub>6</sub> octahedra, leading to a change in the structural

symmetry. As a result, under high-pressure conditions, the

paraelectric  $P2_1/m$  phase was determined as the most stable and energetically superior model for  $\text{Pr}_2\text{Ti}_2\text{O}_7$ . These results form an important scientific basis for understanding the effect of pressure on the crystal structure and the mechanism of phase transitions in  $\text{Pr}_2\text{Ti}_2\text{O}_7$ .

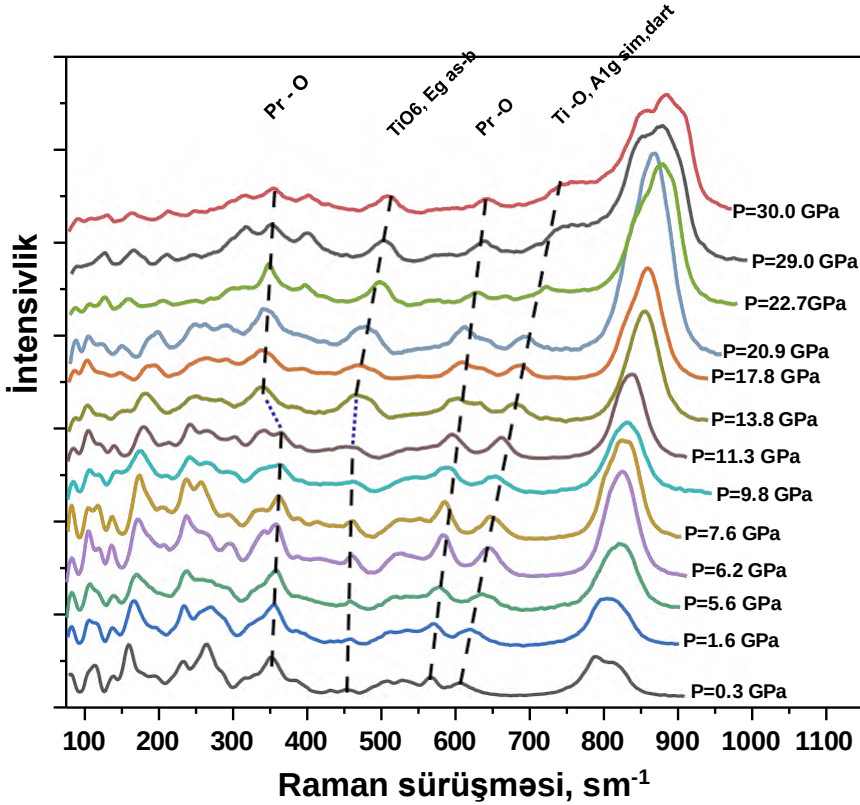


**Figure 21. Raman spectra of the  $\text{Pr}_2\text{Ti}_2\text{O}_7$  compound at different pressures. The positions of some Raman modes are shown depending on pressure.**

In the experimental stage, the Raman spectra of the  $\text{Pr}_2\text{Ti}_2\text{O}_7$  sample were recorded under ordinary conditions (Figure 20) and in the pressure interval from 0.3 GPa to 30.0 GPa (Figure 21). Based on the factor group analysis, it was predicted that the material has 132

normal vibrational modes. With the gradual increase of pressure, linear changes were observed in the wavenumbers of the vibrational

modes. In particular, at the pressure level of 13.8 GPa, unusual anomalies were detected in the behavior of the vibrational modes.

Under the influence of the phase transition, the formation of a new Raman mode with a wavenumber of  $320.13 \text{ cm}^{-1}$  was observed, which was attributed to the vibrational properties of the Pr-O bonds.

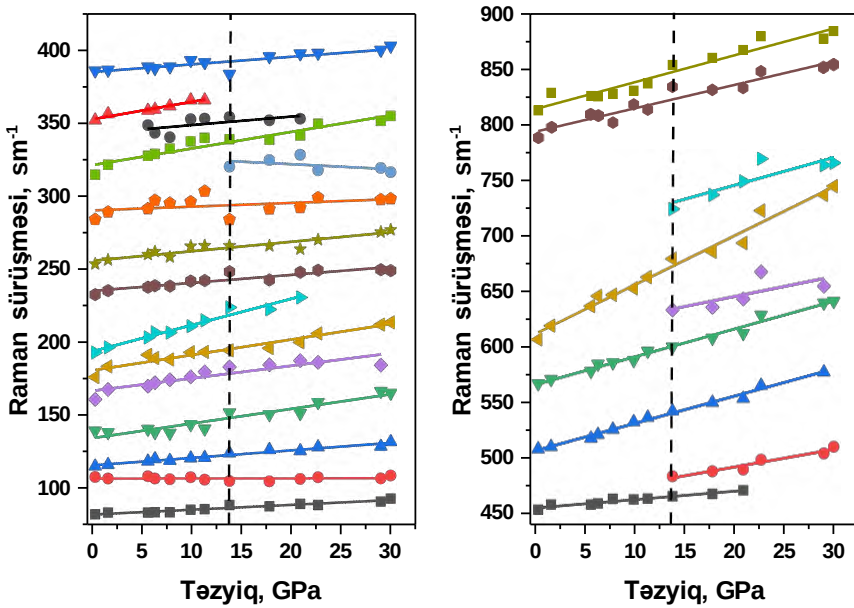


**Figure 22. Changes created by pressure in the positions of the Raman modes of the  $\text{Pr}_2\text{Ti}_2\text{O}_7$  compound. The thick straight lines show the linear fitting of the experimental data. The pressure point at which the phase transition occurs is marked with dotted lines.**

At the same time, the modes at the wavenumbers of 483.46  $\text{cm}^{-1}$  and 634.23  $\text{cm}^{-1}$  corresponding to the  $\text{TiO}_6$  octahedra became more noticeable, and also the particular Raman peak observed at the wavenumber of 724.87  $\text{cm}^{-1}$  reflected the vibrational properties of the Pr-Ti-O bonds (Figure 22). The emergence of new Raman peaks was also noted. These observations clearly showed that a pressure-induced phase transition occurs in the material.

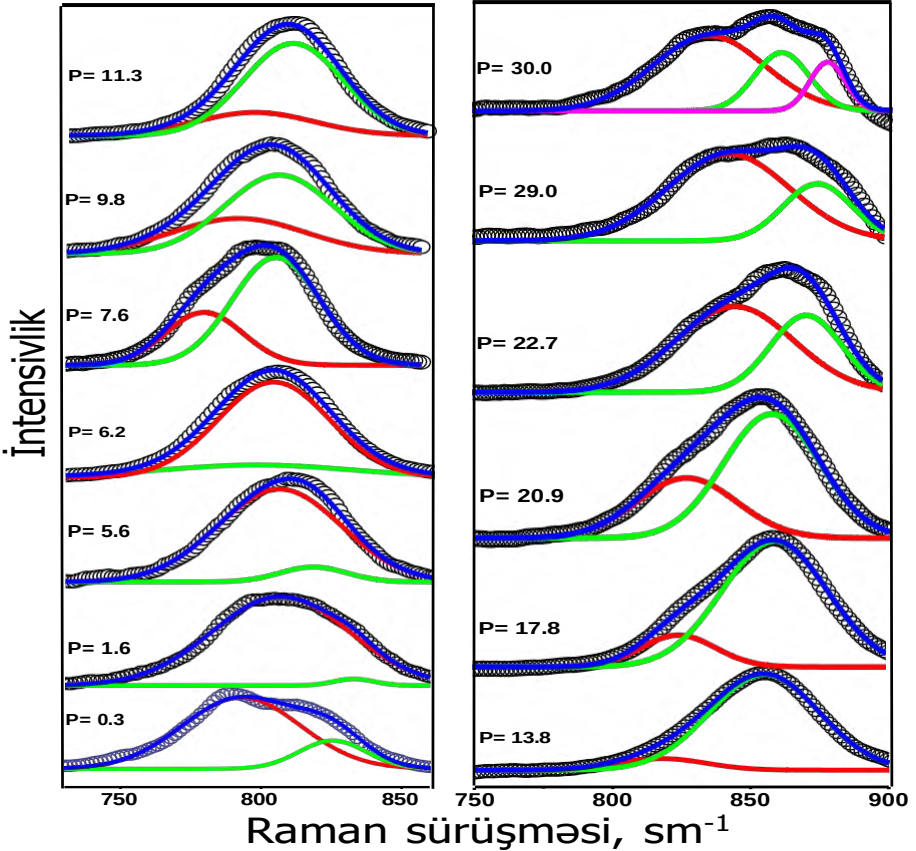


**Figure 23. The effect of pressure on the O-Ti-O asymmetric stretching vibrational modes in the  $\text{Pr}_2\text{Ti}_2\text{O}_7$  compound is shown. The red line at 788  $\text{cm}^{-1}$  and the green line at 813  $\text{cm}^{-1}$  are shown in order to separate the doublet modes.**

Significant changes were recorded in the relative intensities of the modes with the wavenumbers of  $788\text{ cm}^{-1}$  and  $813\text{ cm}^{-1}$  participating in the Raman doublet (Figure 23). After the phase transition, a sharp increase was observed in the intensity of the Raman peak with a wavenumber of  $788\text{ cm}^{-1}$ . This phenomenon was initially explained by the symmetrization of the deformed  $\text{PrO}_6$  and  $\text{TiO}_6$  polyhedra and by the increase in the degeneracy of some Raman modes.

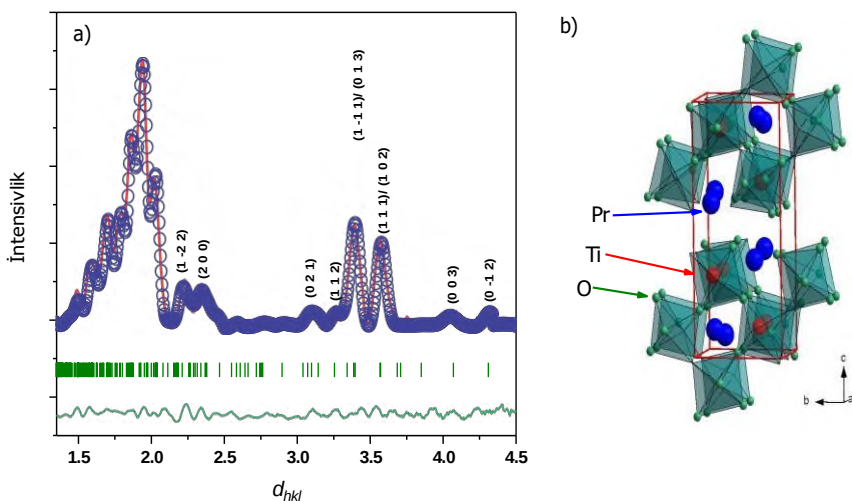


**Figure 24. a) Neutron diffraction patterns of the  $\text{Pr}_2\text{Ti}_2\text{O}_7$  compound under normal conditions, b) schematic representation of the monoclinic crystal structure of  $\text{Pr}_2\text{Ti}_2\text{O}_7$ .**

The structural changes occurring as a result of the application of pressure also affected the electrical properties of the material. In particular, the changes occurring in the  $\text{TiO}_6$  octahedra caused a decrease in the electric dipole moments by changing the charge distribution between the ions. As a result of this process, it was

observed that the initial ferroelectric properties of the  $\text{Pr}_2\text{Ti}_2\text{O}_7$  compound were lost. These observations clearly demonstrated that pressure directly affects both the crystal structure and the electrical properties of the material.

The atomic structure of the  $\text{Pr}_2\text{Ti}_2\text{O}_7$  compound was studied by the neutron diffraction method (Figure 24). As a result of the Rietveld analysis, it was determined that the material is characterized by the P21 monoclinic space group. The crystal lattice parameters were determined as  $a = 7.705(1) \text{ \AA}$ ,  $b = 5.524(1) \text{ \AA}$ ,  $c = 12.873(7) \text{ \AA}$  and  $\beta = 98.7(2)^\circ$ . The structural model precisely described the coordinates of four Pr, four Ti and fourteen O atoms and showed full agreement with the experimental data.

**In the fourth chapter** of the dissertation, the atomic dynamics in  $\text{Ln}_2\text{Ti}_2\text{O}_7$  ( $\text{Ln}=\text{La, Nd, Pr}$ ) layered perovskites under high pressure is characterized by three main deformation mechanisms: the change in the shape of the  $\text{TiO}_6$  octahedra, the collective tilting and rotational motions of the octahedra, and the displacements of the rare-earth ions within the crystal plane.

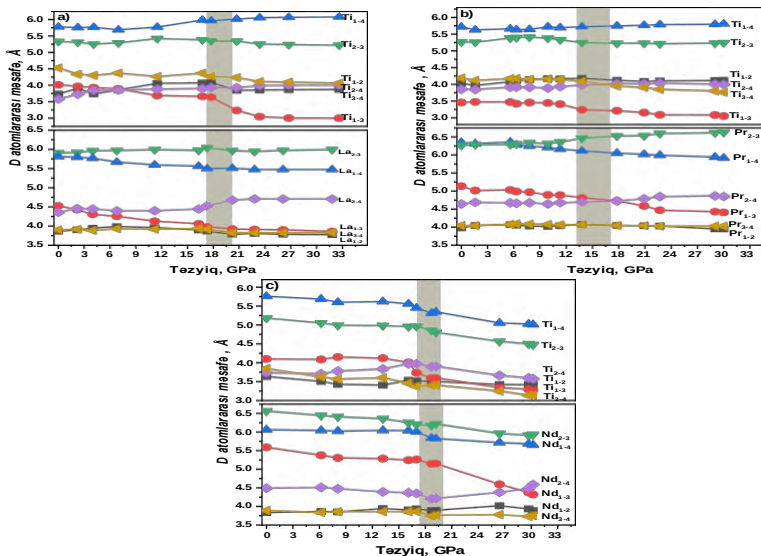


**Figure 25. Change of the interatomic distances with increasing pressure: a)  $\text{La}_2\text{Ti}_2\text{O}_7$ , b)  $\text{Pr}_2\text{Ti}_2\text{O}_7$ , c)  $\text{Nd}_2\text{Ti}_2\text{O}_7$ .**

As pressure increases, the decrease in the distances between the Ti1–Ti3 atoms reflects the compression of the crystal lattice, while the increase in the distances between the Ln2–Ln4 atoms is explained by the mutual repulsive effects of the large-radius cations (Figure 25). The structural changes were quantified by the Bond-Valence-Sum method. The increase in pressure causes a decrease in the Ti–O bond lengths, increasing the BVS values for Ti (Figure 26). At the same time, a decrease in the coordination numbers of the rare-earth cations is observed at the critical pressure points.

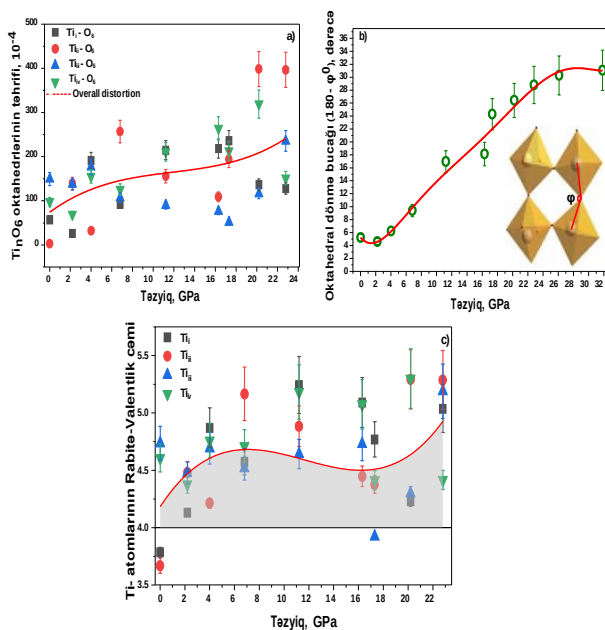


**Figure 26. a) Deformation of the  $\text{TiO}_6$  octahedra in the  $\text{La}_2\text{Ti}_2\text{O}_7$  sample, b) tilt angles of the octahedra, c) Bond-Valence Sum (BVS) values of the Ti atoms in  $\text{La}_2\text{Ti}_2\text{O}_7$ .**

The phase transitions occurring at critical pressures involve the transition from the  $\text{P2}_1$  monoclinic phase to the  $\text{P2}_1/\text{m}$  paraelectric phase. This transition is governed by the increasing tilt angles of the

TiO<sub>6</sub> octahedra and by the displacement of the Ln cations. The

corresponding critical pressures were observed for  $\text{La}_2\text{Ti}_2\text{O}_7$  (16.3 GPa),  $\text{Nd}_2\text{Ti}_2\text{O}_7$  (19.2 GPa) and  $\text{Pr}_2\text{Ti}_2\text{O}_7$  (13.8 GPa).

## MAIN RESULTS

1. For the first time, structural phase transitions accompanied by a transition from the non-centrosymmetric monoclinic  $\text{P2}_1$  space group to the higher-symmetry monoclinic  $\text{P2}_1/\text{m}$  space group under high pressure were experimentally detected in the  $\text{La}_2\text{Ti}_2\text{O}_7$ ,  $\text{Nd}_2\text{Ti}_2\text{O}_7$  and  $\text{Pr}_2\text{Ti}_2\text{O}_7$  compounds. The critical pressure limit was determined for all three compounds:  $\text{La}_2\text{Ti}_2\text{O}_7$  - 16.3 GPa,  $\text{Nd}_2\text{Ti}_2\text{O}_7$

- 19.2 GPa,  $\text{Pr}_2\text{Ti}_2\text{O}_7$  - 13.8 GPa. It was shown that these transitions are of type I character and result in the loss of the ferroelectric properties of the materials (ferroelectricparaelectric transition)<sup>17, 24</sup>.

2. It was determined that the main driving mechanism of the phase transition is the cooperative tilting and rotation of the  $\text{TiO}_6$  octahedra, as well as the characteristic displacement of  $\text{Ln}^{3+}$  (La, Nd, Pr) ions along the crystallographic axes<sup>25</sup>.

3. A comprehensive analysis of the neutron diffraction studies showed that as pressure increases, the average tilt angle of the octahedra increases sharply and the Ln ions move toward the symmetry plane, causing an increase in the overall crystal symmetry. These atomic displacements lead to the anisotropic compression of the lattice ( $a:b:c \approx 1:2:3$ ) and facilitate the decrease of the interlayer distance<sup>18, 24, 26</sup>.

4. The comparative analysis revealed that the critical pressure required for the phase transition depends on the radius of the  $\text{Ln}^{3+}$  ion; the internal «chemical pressure» that increases as the ionic radius decreases strengthens the structural instability and creates conditions for the phase transition to begin at lower external pressures<sup>24</sup>.

5. High-pressure Raman spectroscopy revealed sharp changes

occurring in the phonon modes with increasing pressure (shifting of the modes, change of their width, emergence of new modes), which confirms at the dynamic level the phase transitions determined by X-ray and neutron diffraction. Grüneisen parameters were calculated and evaluated for the selected Raman modes<sup>18</sup>.

6. For the first time, a complementary combination of X-ray diffraction, neutron diffraction and Raman spectroscopy was applied

in order to study the behavior of  $\text{Ln}_2\text{Ti}_2\text{O}_7$  ( $\text{Ln} = \text{La}, \text{Nd}, \text{Pr}$ ) layered perovskites at high pressure. This integrated approach created the possibility of a comprehensive and reliable analysis of the structural, static and dynamic changes<sup>17, 18, 19, 24, 25</sup>.

### **LIST OF SCIENTIFIC WORKS PUBLISHED ON THE TOPIC OF THE DISSERTATION:**

1. Asadov, A.G. A structural phase transition in  $\text{La}_2\text{Ti}_2\text{O}_7$  at high pressure / D.P. Kozlenko, A. Mammadov, R. Mehdiyeva, et al. // *Physica B: Condensed Matter*, - 2023. vol.655 - p.414753. <https://doi.org/10.1016/j.physb.2023.414753>
2. Asadov, A.G. The effects of high pressure on the crystal structure and vibration spectra of layered perovskite-like  $\text{Nd}_2\text{Ti}_2\text{O}_7$  / A.I. Mammadov, D.P. Kozlenko, R.Z. Mehdiyeva, et al. // *Solid State Ionics*, - 2024. vol.406. <https://doi.org/10.1016/j.ssi.2023.116447>
3. A.G. Asadov, A.I. Mammadov, D.P. Kozlenko, R.Z. Mehdiyeva, VIBRATIONAL AND X-RAY MEASUREMENTS OF  $\text{La}_2\text{Ti}_2\text{O}_7$  UNDER HIGH PRESSURE CONDITION” *Advanced Physical Research* vol.6, No.2, -2024, pp.113-122 <https://doi.org/10.62476/apr62113>
4. Asadov, A.G. A search for pressure-induced phase transition in the layered perovskite-like  $\text{Pr}_2\text{Ti}_2\text{O}_7$  / A.I. Mammadov, D.P. Kozlenko, R.Z. Mehdiyeva, et al. // *Journal of Alloys and Compounds*, - 2024. vol.1003 - p.175461. <https://doi.org/10.1016/j.jallcom.2024.175461>
5. Asadov, A.G. The structural mechanisms of pressure-induced phase transitions in the Carpy-Galy phase layered perovskites / D.P. Kozlenko, A.I. Mammadov, R.Z. Mehdiyeva, et al. // *Solid State Sciences*, - 2024. vol.156 - p.107676. <https://doi.org/10.1016/j.solidstatesciences.2024.107676>

The list of conference materials submitted on the topic of the dissertation, published at the end of the dissertation:

1. The XXVI International Scientific Conference of Young Scientists and Specialists (AYSS-2022) - <https://indico.jinr.ru/event/3154/contributions/17643>
2. 57th meeting of the PAC for Condensed Matter Physics – (Dubna 2023) [https:// indico.jinr.ru/event/3755/](https://indico.jinr.ru/event/3755/)
3. Conference on the use of neutron scattering in condensed matter research (RNIKS-2023) <https://rniks2023.imp.uran.ru/?q=ru/partisipants>
4. Neutron Studies of Condensed Matter (2023) - [https://oiks.pnpi.spb.ru/events/ nicons-2022/participants](https://oiks.pnpi.spb.ru/events/nicons-2022/participants)
5. 135th session of the Scientific Council-2024 - <https://indico.jinr.ru/event/4232/>
6. Youth School on Condensed Matter Physics (School FKS-2024) - [https:// oiks.pnpi.spb.ru/events/fks-2024/participants](https://oiks.pnpi.spb.ru/events/fks-2024/participants)
7. 11th International Conference on Superconductivity and Magnetism - ICSM2026 & 4th International Conference on Quantum Materials and Technologies - ICQMT2026 - Muğla, Türkiye. <https://icsmforever.org/scientific-program/abstractbook/>

A handwritten signature in blue ink, featuring a stylized 'A' inside a circle followed by a series of loops and a long horizontal stroke.

The defense will be held on 28 octyabr 2026 at 14:00 at the meeting of the Dissertation council FD1.14 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at the “Institute of Physics” PLE of the Ministry of Science and Education of the Republic of Azerbaijan.

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