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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

INFLUENCE OF HIGH TEMPERATURE ON ELECTROPHYSICAL PROPERTIES OF $La_{1-x}Ba_xMnO_3$ COMPOUNDS

Speciality: 2203.01 – Electronics

Field of science: Physics

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The work was performed at the Institute of Physics of Ministry of Science and Education of the Republic of Azerbaijan, laboratory "Physics and technology of high voltages".

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GENERAL DESCRIPTION OF WORK

Relevance and development of the work. The dissertation is devoted to studying the electronic properties of perovskite materials, which occupy a special place among complex oxides and have various physical properties. It is known that perovskite crystals have ferromagnetic, ferroelectric, semiconductor and other properties can be observed[1]. Although magnetic properties are mainly observed in perovskite-manganites at low temperatures, some compounds have magnetic properties at room temperature. Since $La_{1-x}Ba_xMnO_3$ compounds are crystals with magnetic properties at room temperature, they have wide application possibilities in modern electronics and spintronics. Therefore, the study of these compounds' structure, thermal, magnetic and electrical properties further expands the possibilities of their application.

$La_{1-x}Ba_xMnO_3$ compounds are compounds with interesting structural properties. Despite the change in the electron configuration during cation-cation substitution in these crystals, their crystal structure does not change. At x = 0.03-0.5 barium atom concentration, a cubic structure with an ideal perovskite structure is observed. On the other hand, since these compounds are complex oxides, oxidation does not occur on their surface and they can retain a stable chemical composition for a long time. Therefore, the results obtained in studying the electronic processes occurring in this system can be used as a model object to explain the processes occurring in other perovskites. It was found that with an increase in the concentration of lanthanum atoms in this system, the magnetic properties of the crystals also increased. Although several properties of the objects of study have been studied, the electronic processes and electrophysical properties occurring in them have been practically not studied. It is known that the devices and devices heat up during operation. The results obtained in the study of thermal and

[1] S.F. Yuk, K.C. Pitike, S.M. Nakhmanson, M. Eisenbach, Y.W. Li, V.R. Cooper, Towards an accurate description of perovskite ferroelectrics: exchange and correlation effects, Scientific Reports, 7, P.43482, 2017.

electrical properties at high temperatures are important for the acquisition of converters capable of operating in various environments. Therefore, in this work, $La_{1-x}Ba_xMnO_3$ (x = 0.03, 0.27 and 0.5) compounds were synthesised, and their structure, defect formation processes, and dielectric and electrical properties were studied. Dielectric and electrical properties were studied at a temperature of T = 25-225 °C and a frequency range of f = 20-106 Hz, the mechanism of electrical conductivity in these compounds was established depending on temperature and frequency. The results obtained have wide application possibilities. Thus, these materials, which have magnetic and electrical properties, are used in the production of memory devices, modern electronics, space devices, etc. can be used[2].

The dissertation was carried out according to the scientific research plan of the laboratory "Physics and Technology of high voltages" of the Institute of Physics of the Ministry of Science and Education of the Republic of Azerbaijan.

Object and Subject of the Research:

Synthesis of $La_{1-x}Ba_xMnO_3$ (x = 0.03, 0.27 and 0.5) polycrystals and investigation of their structure, defects, thermal, and electrophysical properties.

Objectives and tasks of the study:

The dissertation aims to study the crystal and electronic structures of the perovskites $La_{0.97}Ba_{0.03}MnO_3$, $La_{0.73}Ba_{0.27}MnO_3$ and $La_{0.5}Ba_{0.5}MnO_3$ synthesised via cation-cation substitution, to investigate the dielectric and electrical properties of these compounds at high temperatures and frequencies, and to determine the mechanisms of electronic processes occurring in them.

By the goal set in the dissertation, the following questions were resolved:

- Synthesis of $La_{1-x}Ba_xMnO_3$ polycrystals (x = 0.03, 0.27 and 0.5) with cation-cation substitutions La → Ba, determination of

[2] Q. Liu, S. Gao, L. Xu, W. Yue, C. Zhang, H. Kan, Y. Li, G. Shen, Nanostructured perovskites for nonvolatile memory devices, Chemical Society Revieüs, 51, P.3341-3379, 2022.

crystallographic parameters by studying the structural features of these compositions.

- Study of the electronic structure of perovskite compounds $La_{0.97}Ba_{0.03}MnO_3$, $La_{0.73}Ba_{0.27}MnO_3$ and $La_{0.5}Ba_{0.5}MnO_3$ based on fundamental principles, determination of the band gap for compounds obtained with different concentrations of Ba atoms.
- Study of the permittivity and dielectric losses of perovskites $La_{0.97}Ba_{0.03}MnO_3$, $La_{0.73}Ba_{0.27}MnO_3$ and $La_{0.5}Ba_{0.5}MnO_3$ under the influence of temperature and frequency.
- Determination of the electrical conductivity of $La_{1-x}Ba_xMnO_3$ compounds (x = 0.03, 0.27 and 0.5), study of the mechanism of activation of charge carriers in these compounds under the influence of high temperatures.
- Determination of the mechanism of change in the electrical conductivity of $La_{0.97}Ba_{0.03}MnO_3$, $La_{0.73}Ba_{0.27}MnO_3$ and $La_{0.5}Ba_{0.5}MnO_3$ compounds under the influence of frequency.
- Determination of changes in electron density, vacancies and defects depending on the concentration of barium atoms in $La_{1-x}Ba_xMnO_3$ compounds (x = 0.03, 0.27 and 0.5).

Research methods: The synthesis of the studied samples was carried out at high temperatures using a standard technique typical for complex oxides. The structural and phase analysis of the samples was carried out using X-ray diffraction. The obtained spectra were analyzed and the crystallographic parameters of the sample were determined: symmetry, space group, lattice parameters, atomic coordinates and interatomic distances. The X-ray diffraction method is one of the modern research methods for determining the structure of crystals in laboratory conditions and conducting phase analyses after the synthesis process.

The thermal properties of the crystals were comparatively studied using differential thermal analysis and thermogravimetric analysis. The obtained results were analyzed and the physicochemical processes occurring at high temperatures were studied. These methods allow us to determine a number of processes occurring in the samples at high temperatures, including phase transitions.

The device "Impedance Analyzer MNIPI E7-21" was used to study the dielectric and electrical properties. Experiments were carried out with the effects of frequency and temperature. Based on the obtained experimental data, frequency and temperature dependences of permittivity, dielectric losses and electrical conductivity were established for each crystal. Thanks to these studies, it is possible to study electronic processes occurring in semiconductor materials, to study the process of activation of charge carriers under the influence of frequency and temperature. Therefore, this method was used to study polycrystals of $La_{0.97}Ba_{0.03}MnO_3$, $La_{0.73}Ba_{0.27}MnO_3$ and $La_{0.5}Ba_{0.5}MnO_3$, and electronic processes were studied in a wide range of temperatures.

Using positron spectroscopy methods, electronic processes of $La_{1-x}Ba_xMnO_3$ compounds were studied and electron-phonon interaction in these manganites was investigated. The defect structure of the crystals was studied based on the electron pulse distribution spectra using Doppler spectroscopy. These methods have recently been widely used in studies that allow studying a number of electronic processes and defects in crystals based on electron-positron interaction in solids. The Quantumwise program was used to calculate the electronic structures of the studied crystals and determine the band gap values. X-ray structural spectra were obtained by the Rietveld method using the FullProf and Mag2Pol programs. The Diamond 3.2 program was used to obtain 3D crystal structures, and the Origin 9 program was used to analyze the DTA-TGA spectra.

Basic provisions of protection:

1. Obtaining polycrystals of $La_{1-x}Ba_xMnO_3$ (x = 0.03, 0.27 and 0.5), studying their crystal structure and determining crystallographic parameters.
2. Electronic structure of compounds of the $La_{1-x}Ba_xMnO_3$ system, change in the width of the forbidden band in these compounds depending on the concentration of barium atoms.
3. Temperature and frequency dependences of dielectric losses, permittivity and electrical conductivity of compounds $La_{1-x}Ba_xMnO_3$ (x = 0.03, 0.27 and 0.5).

4. Semiconductor-metal phase transition at temperature $T \sim 140$ °C in perovskite compounds $La_{0.97}Ba_{0.03}MnO_3$, $La_{0.73}Ba_{0.27}MnO_3$ and $La_{0.5}Ba_{0.5}MnO_3$ in the high-temperature range T = 25-225 °C.
5. In $La_{1-x}Ba_xMnO_3$ magnets, with increasing x value, the spherical radius of the gaps between the pores reaches R_{sf} = 0.400, 0.381, 0.330 nm, and the cylindrical radius reaches R_{sl} = 0.313, 0.295, 0.253 nm.
6. Observation of strong hybridization of Mn d – O p at low values of metallic barium concentration according to the analysis of the electron momentum distribution spectrum.

Scientific novelty of the study:

1. Polycrystals of $La_{1-x}Ba_xMnO_3$ (x = 0.03, 0.27 and 0.5) were synthesized by partial replacement of La atoms with Ba atoms in the $LaMnO_3$ manganite. It was found that these compounds were obtained in a single-phase state and have a cubic symmetry of the structure of the ideal perovskite Pm-3m. As the concentration of Ba atoms increased, an increase in the lattice parameters was observed, which was explained by the difference in the ionic radii of the elements lanthanum and barium.
2. The electronic structure of the $La_{1-x}Ba_xMnO_3$ system was studied and it was found that the band gap width increases with an increase in the concentration of metallic barium in the samples. For the compound $La_{0.97}Ba_{0.03}MnO_3$, the band gap widths were determined to be Eg = 0.28 eV, Eg = 0.32 eV for the compound $La_{0.73}Ba_{0.27}MnO_3$, and Eg = 0.41 eV for the compound $La_{0.5}Ba_{0.5}MnO_3$.
3. When studying the temperature (T = 25-225 oC) and frequency (f = 20-10^6 Hz) dependences of dielectric losses, permittivity, and electrical conductivity of the compounds $La_{1-x}Ba_xMnO_3$ (x = 0.03, 0.27, and 0.5), it was found that with an increase in temperature and frequency, the electrical conductivity increases because charge carriers at deeper levels become free due to the influence of thermal energy or an external electric field in these compounds.
4. In the high-temperature range T = 25-225 °C, a semiconductor-metal phase transition was detected at $T \sim 140$ °C, corresponding to

free charge carriers at deep levels in the perovskite compounds $La_{0.97}Ba_{0.03}MnO_3$, $La_{0.73}Ba_{0.27}MnO_3$ and $La_{0.5}Ba_{0.5}MnO_3$.

5. During the studies of positron annihilation in $La_{1-x}Ba_xMnO_3$ magnets, a strong electron-phonon interaction was discovered due to the influence of the element lanthanum. In these compounds, 0D defects associated with vacancies and cation gaps, and 3D defects associated mainly with lattice distortions were observed. It was found that with an increase in the x value, the spherical radius of the gaps between the pores decreases to R_{sf} = 0.400, 0.381, 0.330 nm, and the cylindrical radius decreases to R_{sl} = 0.313, 0.295, 0.253 nm.

Theoretical and practical significance of the research: Perovskite-manganites are materials that are widely used in electronics and spintronics due to their semiconductor and ferromagnetic properties. Scientific innovations obtained during the dissertation work open up new possibilities for the application of these materials. The results obtained in the study of electrical properties and explanation of electronic processes are very important for the purchase of new converters based on these materials and the manufacture of memory elements. The semiconductor-metal phase transition obtained at high temperatures is of particular importance for the preparation of converters based on $La_{0.97}Ba_{0.03}MnO_3$, $La_{0.73}Ba_{0.27}MnO_3$ and $La_{0.5}Ba_{0.5}MnO_3$ compounds.

The dissertation work is also of great scientific importance. It is known that the objects of the study are compounds of ideal perovskite structure. In perovskites, the perovskite structure is often distorted and the cubic structure is disrupted when cation-cation substitutions occur. Such compounds are called perovskite-like compounds. However, the ideal perovskite structure is preserved in the perovskite compounds $La_{0.97}Ba_{0.03}MnO_3$, $La_{0.73}Ba_{0.27}MnO_3$ and $La_{0.5}Ba_{0.5}MnO_3$. Therefore, these compounds can be used as model objects in the study of similar perovskite compounds. For this reason, the results obtained in the course of the study are of great importance.

Approbation and application:

The scientific results obtained in the dissertation work were presented at national and international events:

1. Azərbaycan xalqının ümummilli lideri Heydər Əliyevin anadan olmasının 99-cu ildönümünə həsr olunmuş tələbə və gənc tədqiqatçıların "Gənclər və elmi innovasiyalar" mövzusunda respublika elmi-texniki konfransı, 4-5 may 2022-ci il, Bakı, Azərbaycan.
2. International Conference "Condensed Matter Research at the IBR-2", Dubna, Russia, April 25-29, 2022, p.188.
3. Международная конференция «Фазовые переходы, критические и нелинейные явления в конденсированных средах», 10-15 сентября 2023 г., с.222-223, Махачкала, Россия.
4. II-международная конференция «Фундаментальные и прикладные проблемы физики полупроводников, микро- и наноэлектроники», 27-28 октября 2023 г., с.36-38, Ташкент, Узбекистан.
5. Energetika ixtisasları üzrə kadr hazırlığının aktual məsələləri III Respublika Elmi Konfransı, 17-18 noyabr 2023-cü il, s.118-119, Sumqayıt, Azərbaycan.
6. III международная научная конференция «Современные тенденции развития физики полупроводников: достижения, проблемы и перспективы», 26-27 сентября 2024 г., Ташкент, Узбекистан.

Publications. The dissertation's main materials were published in 12 scientific papers. Six are articles (each indexed in the Web of Science and Scopus databases), and six are conference abstracts. The results were published in the annual scientific research reports of the Institute of Physics of the Ministry of Science and Education of the Republic of Azerbaijan.

Name of the organisation where the dissertation work was completed:

The dissertation work was completed at the "Physics and Technology of High Voltages" laboratory of the Institute of Physics under the Ministry of Science and Education of the Republic of Azerbaijan.

Volume, structure and main content of the dissertation:

The dissertation consists of an introduction, 4 chapters, a conclusion and a bibliography consisting of 140 articles. The work consists of 140 pages, 1 table, 56 figures and 175831 characters.

CONTENTS OF THE WORK

The **introduction** substantiates the relevance and level of development of the dissertation topic, the main objective of the dissertation, scientific innovations, scientific and practical significance, the stated goal and the provisions to be defended.

Chapter I of the dissertation work is devoted to the analysis of the results obtained during the studies conducted to study the structure of compounds with perovskite structure and the electronic processes occurring in them. Structural properties of $A'_{1-x}A''_xBO_3$ perovskite compounds obtained by cation-cation substitutions were analyzed, and structural changes observed in these compositions during substitutions were shown. The magnetic and electrical properties of perovskite manganites were detailed, and the magnetic and electrical properties of $LaMnO_3$ and $BaMnO_3$ compounds were analyzed. It has been shown that although manganites mainly show magnetic properties at low temperatures, there are also manganites with magnetic properties at room temperature. These manganites have more applications in modern electronics. Memory elements based on them allow long-term storage of large volumes of materials. Electronic processes in $A'_{1-x}A''_xBO_3$ perovskite compounds synthesized by substitutions with metal atoms with different ionic radii, as well as the results obtained during the study of the electronic structures of these compounds, are presented. It has been shown that during partial substitutions fundamental changes occur in the electronic configuration of the crystals and therefore the electronic properties of the material change. The mechanism of electrical conductivity of $A'_{1-x}A''_xBO_3$ perovskite compounds is shown, and the processes specific to semiconductors are explained. After the results obtained during the previous studies, the topic of the dissertation was justified and the importance of studying electronic processes occurring in $La_{0.97}Ba_{0.03}MnO_3$, $La_{0.73}Ba_{0.27}MnO_3$ and $La_{0.5}Ba_{0.5}MnO_3$ perovskite compounds was shown. As a result of literature research, it has been shown that perovskite manganites and their solid solutions are functional materials with wide application possibilities. Studying their electrical conductivity, and studying the effect of

external electric field frequency and high temperatures on electrical conductivity is of great scientific importance for solid-state electronics. The study of these properties also determines the possibilities of practical application for these materials. Therefore, the topic of the dissertation is relevant and fully corresponds to the modern research conducted in the field of electronics.

Chapter II is devoted to the experimental methods used in conducting experimental studies, various methods of analyzing the results obtained, and devices and installations on which the experiments are conducted. It is shown that the experiments were carried out on modern equipment of the latest generation.

Polycrystals of the objects of study were synthesized by the standard method, and their phase analysis and crystal structure were studied by X-ray diffraction on a Bruker D8 Advance X-ray diffractometer with the parameters of 40 kV, 40 mA, CuKα radiation (λ = 1.5406 Å). The studies were carried out at room temperature and under normal conditions.

Extensive information on the methods for studying the thermal properties of $La_{1-x}Ba_xMnO_3$ polycrystals is also given. It is shown that differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used in the dissertation work. The studies were carried out on a DSC3 STARe device manufactured by Mettler Toledo in the temperature range of 25 °C < T < 950 °C. During the experiments, the temperature was regulated using Multistar sensors. The measurements were carried out in an argon (Ar) atmosphere at a heating rate of 20 ml/min, 5 deg/min. It is shown that the cooling process was carried out using the analyzer cooling system Nitrogen Un 1977 Sofrigered Liquid.

The electrical and dielectric properties of the objects of study were measured by a standard method. The geometric parameters of the samples used in the experiments were 5×3×3 mm^3. The study of dielectric properties was carried out on the impedance analyzer MNIPI E7-25. When studying the dielectric properties of these materials, silver electrodes were used as electrical contacts. In the course of the studies, the value of electrical capacity was determined and based on this value, the permittivity, dielectric losses and

electrical conductivity were calculated. The experiments were carried out at high temperatures T = 25-225 °C and a frequency range f = 20-10^6 Hz.

The electronic properties and defect states of $La_{0.97}Ba_{0.03}O_3$, $La_{0.73}Ba_{0.27}O_3$ and $La_{0.5}Ba_{0.5}O_3$ compounds were studied using positron and Doppler spectroscopy, respectively. These methods make it possible to determine the electronic properties, vacancies and cation gaps, defects and lattice distortions of materials as a result of electron-positron interaction, including the spherical or cylindrical shape of defects.

Chapter III presents the results obtained in studying the structure and thermal properties of $La_{1-x}Ba_xMnO_3$ perovskites. When studying the structure of complex oxides $La_{0.97}Ba_{0.03}O_3$, $La_{0.73}Ba_{0.27}O_3$ and $La_{0.5}Ba_{0.5}O_3$ by X-ray diffraction, it was found that these compounds have a perovskite structure at room temperature. With partial substitution La → Ba, the ideal perovskite structure is not violated and the cubic crystal structure with the Pm-3m space group is preserved. For each compound, the crystallographic parameters, symmetry, space group, lattice parameters and interatomic distances were determined. The Fullprof and Mag2Pol programs were used to analyze the spectra.

Thermal properties of $La_{0.5}Ba_{0.5}MnO_3$, $La_{0.73}Ba_{0.27}MnO_3$ and $La_{0.97}Ba_{0.03}MnO_3$ compounds were studied in the temperature range 25 °C ≤ T ≤ 950 °C. The studies were carried out using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). It was found that although several thermal effects were observed in the objects of study, these transitions occurred practically by the same mechanism. The effect occurring at temperatures T ~ 100 °C in the DSC spectrum is explained by the splitting of hydroxide groups formed by water crystals suspended in the samples and leaving the samples. Thermal effects occurring at higher temperatures were explained by the oxidation of free metal atoms on the surface of the samples. Thermal effects observed in the DSC spectrum were confirmed in the TGA spectrum obtained from the change in mass under the influence of temperature. At the end of the chapter, the results obtained in the study of the structure and thermal properties of

the compounds $La_{0.5}Ba_{0.5}MnO_3$, $La_{0.73}Ba_{0.27}MnO_3$ and $La_{0.97}Ba_{0.03}MnO_3$ are summarized and presented.

Chapter IV studies the electronic structure, dielectric and electrical properties of $La_{1-x}Ba_xMnO_3$ (x = 0.03, 0.27, 05) compounds. The study of the electronic structure of $La_{0.5}Ba_{0.5}MnO_3$, $La_{0.73}Ba_{0.27}MnO_3$ and $La_{0.97}Ba_{0.03}MnO_3$ compounds revealed that these materials possess semiconductor properties. The band gap increases with increasing concentration of metallic barium in the samples. The band gaps E_g = 0.28 eV were determined for $La_{0.97}Ba_{0.03}MnO_3$, E_g = 0.32 eV for $La_{0.73}Ba_{0.27}MnO_3$ and E_g = 0.41 eV for La0.5Ba0.5MnO3. This difference is explained by the difference in the electronic configuration of the elements lanthanum and barium.

The dielectric and electrical properties of the semiconductors $La_{0.5}Ba_{0.5}MnO_3$, $La_{0.73}Ba_{0.27}MnO_3$ and $La_{0.97}Ba_{0.03}MnO_3$ were also investigated in a wide range of temperatures and frequencies. The tests were carried out at a temperature of T = 25-225 °C and a frequency range of f = 20-10^6 Hz. An analysis of the results obtained in the study of the dielectric properties showed that these compounds exhibit interesting physical properties under the action of an external electric field and high temperature. The effects that arise were explained by the formation of additional charge carriers in the samples under the action of frequency and temperature. It is known that the most suitable method for studying the formation of charge carriers in semiconductor materials and their participation in conductivity is the study of electrical conductivity in these compounds. For this purpose, the electrical conductivity in perovskite compounds $La_{1-x}Ba_xMnO_3$ (x = 0.03, 0.27, 05) was also investigated (Figs. 1-3). Frequency and temperature dependencies of the electrical conductivity of these compounds were obtained. From the dependences, it was established that unique effects are observed in each sample.

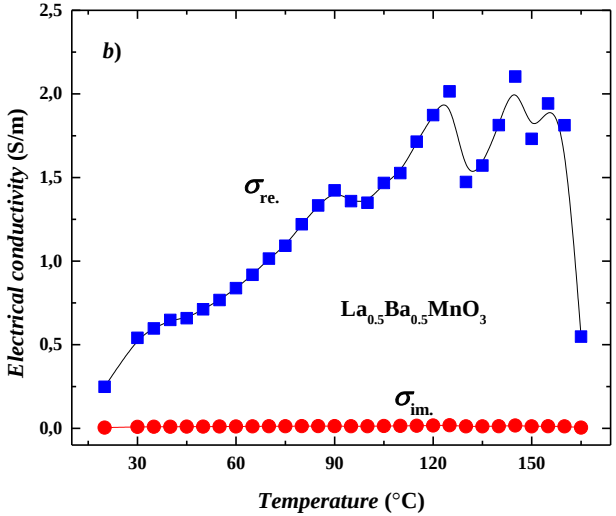

Fig. 1. Temperature dependence of electrical conductivity of the compound $La_{0.5}Ba_{0.5}MnO_3$.

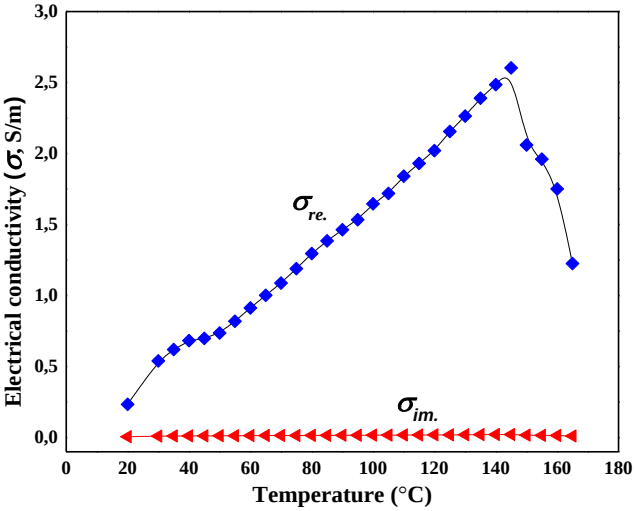

Fig. 2. Temperature dependence of electrical conductivity of the compound $La_{0.73}Ba_{0.27}MnO_3$.

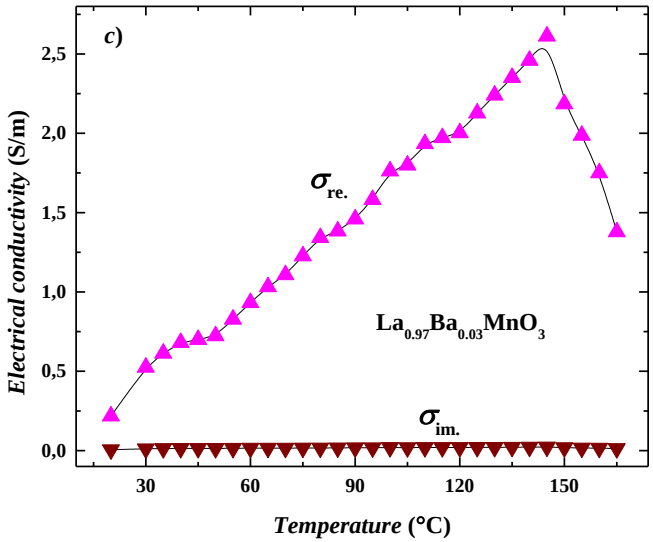

Fig. 3. Temperature dependence of electrical conductivity of the compound $La_{0.97}Ba_{0.03}MnO_3$.

In the frequency dependence of the real part of the electrical conductivity of the $La_{0.5}Ba_{0.5}MnO_3$ compound, a relatively chaotic behaviour was observed in the low-frequency region. The observed chaos can be explained similarly to the explanation of the effects obtained in the study of dielectric properties. However, a slightly different situation was observed in the frequency dependence of the imaginary part of the electrical conductivity. Thus, in this dependence, the electrical conductivity remained virtually constant in the frequency range $f < 5\times10^5$ Hz. However, starting with the frequency $f > 5\times10^5$ Hz, the electrical conductivity increased proportionally to the frequency. This effect can be explained by the mechanism of formation of additional charge carriers, which begin to actively participate in conductivity at relatively high frequencies. Due to the effect of the external electric field, charge carriers at deeper levels began to participate in the conductivity process, as a result of which an increase in the numerical value of the electrical conductivity was observed. On the other hand, as can be seen from the temperature dependence of the electrical conductivity, these

compounds exhibited similarities with the cases observed in the mechanism of change in permittivity. Therefore, the temperature dependence of electrical conductivity can be explained using similar approaches to the laws given in explaining the dielectric properties.

When studying the electrical properties of the $La_{0.73}Ba_{0.27}MnO_3$ compound, some differences were observed from the results obtained for the $La_{0.5}Ba_{0.5}MnO_3$ compound. No chaos was observed in the temperature dependence of electrical conductivity in the high-temperature region. In a general approach, it can be said that the semiconductor-metal phase transition was observed in the region of temperature T = 140 ºC, which corresponds to the results obtained in studying the dielectric properties. From the dependencies, it is evident that in the temperature range T < 140 ºC the sample behaves as a semiconductor. As a result of the activation of charge carriers located at deeper levels in the sample due to thermal energy, an increase in the electrical conductivity value was observed with increasing temperature. As can be seen from the temperature dependence of electrical conductivity, the $La_{0.73}Ba_{0.27}MnO_3$ compound behaves as a metal at temperatures T > 140 ºC. According to the physical properties of metals, the electrical conductivity of the sample decreases with increasing temperature in the range T > 140 ºC.

Frequency and temperature studies of the electrical conductivity of the $La_{0.97}Ba_{0.03}MnO_3$ compound were carried out similarly. From the frequency and temperature dependences of the electrical conductivity, it was found that the mechanism of change in electrical conductivity under external influences occurs almost the same as in the $La_{0.73}Ba_{0.27}MnO_3$ compound. The conductivity value at room temperature was σ = 0.217 S/m. As the temperature increased, the conductivity value also increased, which at a temperature of T = 140 ºC had a value of σ = 2.612 S/m. As can be seen from the obtained values, a multiple increase in the conductivity value was observed in this temperature range. This is because under the influence of temperature, a sufficient number of additional charge carriers participating in the conductivity were formed in the system. Such an increase in the electrical conductivity value is the first sign

of the appearance of metallic properties. At subsequent temperature values, a significant decrease in the conductivity value began to be observed. As can be seen from the obtained dependence, up to the temperature T = 165 ºC, the value of electrical conductivity in the $La_{0.97}Ba_{0.03}MnO_3$ compound decreased to σ = 1.378 S/m. It is known that metals do not have a forbidden zone and therefore the charge carriers present in the system can easily participate in conductivity. With an increase in the temperature value as a result of an increase in the amplitude of thermal oscillations, an increase in the resistance value is observed, and, consequently, a decrease in the electrical conductivity value occurs. In semiconductors, the reverse process occurs. Since the system has a forbidden zone, charge carriers in the valence zone cannot participate in conductivity. As the temperature value increases, due to thermal energy, some charge carriers can become free and participate in conductivity. Therefore, with an increase in temperature in semiconductor materials, electrical conductivity increases accordingly. The temperature dependence of electrical conductivity in the compound $La_{0.97}Ba_{0.03}MnO_3$ clearly shows the processes occurring according to these mechanisms, with the semiconductor-metal phase transition occurring at a temperature of T = 140 ºC.

When studying the electrical properties of the compounds $La_{1-x}Ba_xMnO_3$ (x = 0.03, 0.27, 0.5), it was found that these compounds are materials with semiconductor properties under normal conditions and at room temperature. No significant changes in electrical conductivity were observed with cation-cation substitutions in these compounds. However, the mixtures contained in the samples had a serious effect on the conductivity value. The dependencies shown in Figure 1 reveal that in the $La_{0.5}Ba_{0.5}MnO_3$ compound, chaotic behaviour in electrical conductivity values occurs when adsorbed water molecules leave the sample at temperatures above 100°C. It is known that the water molecules included in the composition combine with cations in the crystal, forming hydroxide groups. The most important thing is that such hydroxide groups occupy a certain volume inside the sample. As the temperature increases, they disintegrate under the influence of thermal energy and the water

molecules leave the sample. During this process, small defects can form in the structure, leading to partial capture of charge carriers. It is at this temperature that a sharp decrease in the electrical conductivity can be observed. With a subsequent increase in temperature, either the conductivity is corrected due to additional charge carriers, or the defects recombine and the conductivity mechanism specific to the sample is restored. In this case, certain fluctuations in the electrical conductivity of the samples can be observed.

It is known that water molecules inside the sample leave the sample under the influence of temperature, on the other hand, defects that can appear in the sample during these processes can recombine at high temperatures. Therefore, in studies carried out under the influence of temperature, the resulting chaos is either very small or almost not observed. However, a different picture of the effect of temperature is obtained in studies carried out at different frequencies of the external electric field. Radicals and water molecules in the sample cannot leave the sample. Therefore, the resulting chaos in the frequency dependence of electrical conductivity can be continuously observed in a wide range.

Perovskite manganites $La_{0.97}Ba_{0.03}MnO_3$, $La_{0.73}Ba_{0.27}MnO_3$ and $La_{0.5}Ba_{0.5}MnO_3$ were studied by spectroscopy and Doppler spectroscopy. In these crystals, vacancies and cation gaps, defects and distortions of the lattice were studied. Positron spectra were recorded and normalized for each of the compounds under normal conditions and separately. It was found from the spectra that, despite the detection of vacancy-type defects in one of these compounds, the changes were less noticeable. To visualize these differences, and to show the changes occurring depending on the concentration during the partial substitution of lanthanum atoms by barium atoms, the dependences of the positron lifetime components obtained during positron-spectroscopic studies on the concentration of barium atoms were established. The obtained dependencies are shown in Figure 4 and Figure 5.

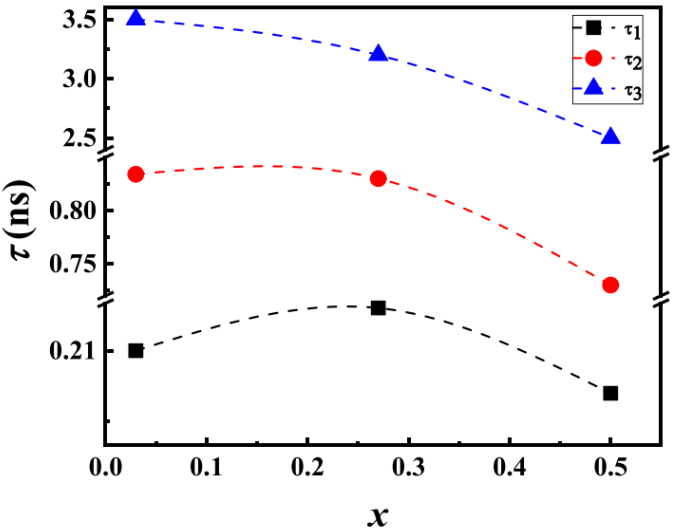

Fig. 4. Components of the positron lifetime for different concentrations of the Ba element in $La_{1-x}Ba_xMnO_3$ samples (x = 0.03, 0.27, 0.5).

As can be seen from Figure 4, three lifetime components (τ_1, τ_2, τ_3) were observed as a result of the PALS studies. The obtained results showed that in the $La_{1-x}Ba_xMnO_3$ (x = 0.03, 0.27, 0.5) samples, all three lifetime components decreased accordingly with an increase in the barium cation concentration and a decrease in the lanthanum cation concentration. Thus, with an increase in the barium concentration in these compounds, the value of the τ_1 parameter decreased from 0.210 nsec to 0.201 nsec, the value of the τ_2 parameter decreased from 0.834 nsec to 0.730 nsec, and the value of the τ_3 parameter decreased from 3.5 nsec to 2.5 nsec. Although each of the parameters τ_1, τ_2 and τ_3 characterizes the positron lifetime in the sample, each of them has certain physical properties and is of great scientific importance. The short-lived component τ_1 with a relative intensity of 72-90% and values of 201-219 psec is due to the annihilation of positrons in free volumes. The lifetime component τ_2 is a component due to the partial capture of positrons in cavity-type defects or in some regions of reduced electron density in the sample.

This process of decreasing τ_2 can be explained either by a decrease in the defect sizes or by a process occurring due to the electron entering the surface of a smaller atom. The change in the value of the long-lived component τ_3 within 2.5-3.5 nsec is due to the formation of positrons in defects or free volume.

During the analysis of the spectra, it was found that the intensity values corresponding to the parameters τ_2 and τ_3 decreased. This decrease can be due to the accumulation of Ba^{2+} ions at the boundaries of the crystallites forming the samples and in large cluster cavities. As a result of positron annihilation from Ba^{2+}, point defects and vacancies become desirable positron capture sites. With increasing Ba^{2+} ion concentration, the values of the three components of the positron annihilation lifetime (τ_1, τ_2, τ_3) decrease, indicating defects in the material structure and a change in its electronic properties. A change in the τ_3 lifetime component in the range of 3.5-2.5 nsec and the I_3 intensity in the range of 2.9-2.6% is an indicator of positron annihilation mainly on the sample surface and is the result of the formation of ortho-positrons (o-Ps) in the intercrystalline regions of the samples. Due to an increase in the concentration and size of crystallites, Ba^{2+} ions occupy La^{3+} vacancies, and subsequently, the number of positron captures at the crystallite boundaries begins to increase.

Based on the parameters τ_1, τ_2 and τ_3 obtained in the course of studies conducted by the positron spectroscopy method, the average positron lifetime (τaverage) in the samples was calculated. In the $La_{1-x}Ba_xMnO_3$ samples (x = 0.03, 0.27, 0.5), the values of the average positron lifetime component were determined as τ_{mean} = 0.363, 0.354, 0.312 ns, respectively.

During the analysis of the spectra it was found that with the increase of the concentration of barium atoms in the compounds included in the $La_{1-x}Ba_xMnO_3$ system (x = 0.03, 0.27, 0.5), there is a significant decrease in the parameter τ_{av}, which characterizes the average lifetime of positrons. This effect is an indicator of the fact that with a decrease in the concentration of La atoms in crystals and an increase in Ba atoms, the electron density inside the compounds changes. From the results obtained in the course of structural studies

carried out by the X-ray diffraction method, it is known that with an increase in the concentration of barium atoms, the values of the lattice parameters also increase. This effect is explained by the fact that the ionic radius of barium atoms is larger than the ionic radius of lanthanum atoms. From the results of positron spectroscopic studies, it is clear that the difference in ion radii affects not only the lattice parameters, which play a key role in the formation of the structure but also the electronic properties of the samples. The same mechanism can explain the increase in the positron lifetime in the samples. With increasing concentration of barium atoms in the samples, the decrease in the positron lifetime can be explained by the increase in electron density in the samples. Thus, with increasing concentration of barium atoms, the electron density in the crystals also increases, and as a consequence, the positron lifetime decreases. More precisely, the decrease in the average positron lifetime is associated with an increase in the electron density at the sites of positron annihilation. In the $La_{1-x}Ba_xMnO_3$ system, the maximum decrease in the concentration of Ba atoms was observed for the sample with $x = 0.5$. Therefore, this concentration value can be considered the optimal concentration, at which the electron density is highest in the $La_{1-x}Ba_xMnO_3$ system.

The concentration and sizes of defects present in the samples can also be determined using positron spectroscopy. It is known that defects of various shapes can exist in crystals. Volume defects exist in both spherical and cylindrical shapes. The radii of both spherical and cylindrical defects based on the Tao-Eldrup interpore space model in $La_{1-x}Ba_xMnO_3$ compounds ($x = 0.03, 0.27, 0.5$) were calculated using the Psc_v12 program. The dependences of the defect radii on the concentration of barium atoms in the samples are shown in Figure 5.

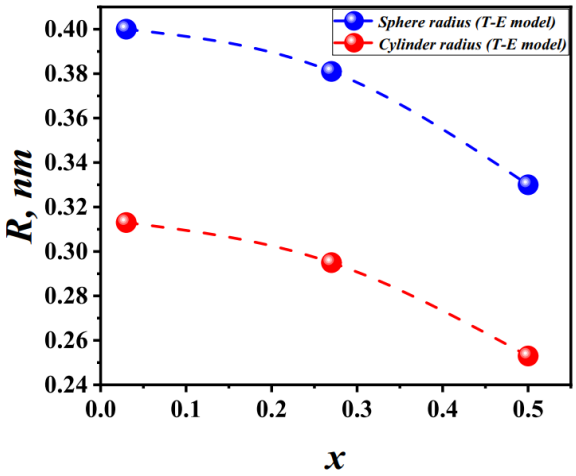

Fig. 5. Measurements of defect radii for different concentrations of Ba atoms in $La_{1-x}Ba_xMnO_3$ compounds (x = 0.03, 0.27, 0.5).

According to the Tao-Eldrup model, the spherical and cylindrical radii of o-Ps are determined by the size and distribution of the voids of free volume in the material. These voids act as traps for o-P. As can be seen from Figure 5, both the spherical and cylindrical radii of the void volume decreased with increasing x. Thus, the spherical radius decreases from 0.400 nm to 0.381 nm and 0.330 nm, and the cylindrical radius decreases from 0.313 nm to 0.295 nm and 0.253 nm. From this, it can be concluded that with an increase in the concentration of barium atoms in the samples, the sizes of defects significantly decrease. It is also possible to determine the concentration of defects by positron spectroscopy. The concentration dependences of intensities obtained in the course of the studies make it possible to determine the concentration of defects as the concentration of barium atoms in the samples increases. With an increase in the concentration of Ba atoms in $La_{1-x}Ba_xMnO_3$ crystals, the number of void-type defects increased. This can be evidenced by an increase in the relative intensity of I_1. The presence of more voids improved the trapping of o-P and shortened the lifetime. Thus, the spherical radius of o-Ps decreased. This is because o-P has a higher chance of colliding with these additional voids and getting trapped.

Thus, the spherical and cylindrical radii of o-Ps decreased with increasing concentration x in the compounds of the $La_{1-x}Ba_xMnO_3$ system. For example, at $x = 0.03$, there were more voids in the crystal lattice, which resulted in relatively larger spherical and cylindrical radii of o-Ps. It is important to note that this explanation is based on the assumptions of the Tao-Eldrup model, and only the effect of defects and vacancies on the behaviour of o-Ps was taken into account in the analysis of the study results. In the $La_{1-x}Ba_xMnO_3$ system, other factors, such as partial distortion of the lattice structure and changes in the electronic structure, may also influence the observed decrease in the spherical radius of o-Ps with increasing *x*. When studying the compounds $La_{0.5}Ba_{0.5}MnO_3$, $La_{0.73}Ba_{0.27}MnO_3$ and $La_{0.97}Ba_{0.03}MnO_3$ by the positron lifetime spectroscopy method, it was found that cation-cation substitutions have a rather serious effect on the electronic processes in these compounds. Thus, first of all, the electron density changes in these compounds. It is known that significant changes in the band gap also occur with cation-cation substitutions in these compounds. The band gap in the compound $La_{0.97}Ba_{0.03}MnO_3$ is $E_g = 0.28$ eV, in the compound $La_{0.73}Ba_{0.27}MnO_3$ $E_g = 0.32$ eV and in the compound $La_{0.5}Ba_{0.5}MnO_3$ $E_g = 0.41$ eV. As can be seen, with the increase in the band gap, the electron density was created both in the conduction band and in the valence band, which was confirmed by the results obtained by the positron lifetime method. When comparing the results obtained with the results obtained by other methods, it is evident that the partial replacement of lanthanum atoms by barium atoms leads to significant changes in the electronic properties. With an increase in the concentration of barium atoms, both the electron density and the band gap change significantly.

CONCLUSION

1. When studying the crystal structure of $La_{1-x}Ba_xMnO_3$ ($x = 0.03$, 0.27 and 0.5) compounds, synthesized by partial substitution of La atoms with Ba atoms in the perovskite manganite $LaMnO_3$, it was found that these compounds were obtained in a single-phase state

and their crystal structure corresponds to the ideal structure of perovskite with Pm-3m symmetry. As the concentration of Ba atoms increased, an increase in the lattice parameters was observed, which was explained by the difference in the ionic radii of the elements lanthanum and barium.

2. The electronic structure of compounds of the $La_{1-x}Ba_xMnO_3$ (x = 0.03, 0.27 and 0.5) system was studied and it was found that the band gap width increases with increasing concentration of barium atoms in crystals. For the $La_{0.97}Ba_{0.03}MnO_3$ compound, the band gap widths were determined to be E_g = 0.28 eV, E_g = 0.32 eV for the $La_{0.73}Ba_{0.27}MnO_3$ compound and E_g = 0.41 eV for the $La_{0.5}Ba_{0.5}MnO_3$ compound.

3. When studying the temperature (T = 25-225°C) and frequency (f = 20-10^6 Hs) dependences of dielectric losses, permittivity and electrical conductivity in $La_{0.97}Ba_{0.03}MnO_3$, $La_{0.73}Ba_{0.27}MnO_3$ and $La_{0.5}Ba_{0.5}MnO_3$ perovskite compounds, it was found that with an increase in the temperature and frequency, the electrical conductivity in these compounds increases. This effect was explained by the release of charge carriers at deeper levels under the influence of thermal energy or an external electric field in the crystals.

4. Based on the temperature dependence of electrical conductivity in perovskite compounds $La_{0.97}Ba_{0.03}MnO_3$, $La_{0.73}Ba_{0.27}MnO_3$ and $La_{0.5}Ba_{0.5}MnO_3$ in the high-temperature range T = 25-225 °C, a semiconductor-metal phase transition was discovered at $T \sim 140$ °C. It was found that, due to thermal energy, charge carriers at deep levels participate in conductivity, which leads to the appearance of metallic properties in these crystals.

5. When studying $La_{1-x}Ba_xMnO_3$ magnets (x = 0.03, 0.27 and 0.5) by the positron annihilation spectroscopy method, it was found that with an increase in the concentration of barium atoms in these crystals, fundamental changes in the values of the observed radii of the gaps between the pores occur. When studying 0D (vacancies and cation vacancies) and 3D (lattice distortions and pores) defects, it was found that in the concentration range x = 0.03, 0.27, 0.5, the spherical radius of the voids is R = 0.4 nm, 0.381 nm and 0.33 nm, and the

radius of the cylinder decreases by the values R = 0.313 nm, 0.295 nm and 0.253 nm.

6. In the course of studies conducted by the method of positron lifetime spectroscopy in compounds of the $La_{1-x}Ba_xMnO_3$ system (x = 0.03, 0.27 and 0.5), it was established that the positron lifetime increases with increasing concentration of barium atoms in crystals. It was established that this effect corresponds to an increase in the electron density in the samples as the concentration of barium atoms increases.

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