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Structure, Non-stoichiometry, Valence of Ions, Dielectric and Magnetic Properties of Single-Phase Bi$_{0.9}$La$_{0.1}$FeO$_{3-\delta}$ Multiferroics

A.V. Pashchenco$^{1,2,3,4,5}$, N.A. Liedienov$^{1,2,3,*}$, Quanjun Li$^1$, D.D. Tataruchuk$^6$, V.A. Turchenko$^7$, I.I. Makoe$^5$, V.Ya. Sycheva$^5$, A.V. Voznyak$^5$, V.P. Kladko$^{10}$, A.I. Gudimenko$^6$, A.T. Kozakov$^{11}$, G.G. Levchenko$^{1,2,3,*}$

$^1$ State Key Laboratory of Superhard Materials of Jilin University, 130012 Changchun, China
$^2$ International Center of Future Science of Jilin University, 130012 Changchun, China
$^3$ Donetsk Institute for Physics and Engineering named after O. O. Galkin, NASU, 03028 Kyiv, Ukraine
$^4$ Institute of Magnetism of NASU and MESU, 03142 Kyiv, Ukraine
$^5$ Donetsk National University of Economy and Trade named after Michael Tugan - Baranovsky, MESU, 50005 Kryvyi Rih, Ukraine
$^6$ National Technical University of Ukraine "Igor Sikorsky KPI", 03056 Kyiv, Ukraine
$^7$ Joint Institute for Nuclear Researches, 141980 Dubna, Russia
$^8$ A. S. Pushkin Brest State University, 224016 Brest, Belarus
$^9$ Donetsk Institute for Physics and Engineering named after O. O. Galkin, Donetsk, Ukraine
$^{10}$ V.E. Lashkaryov Institute of Semiconductor Physics, NASU, 03028 Kyiv, Ukraine
$^{11}$ Scientific-Research Institute of Physics at Southern Federal University, 344194 Rostov-na-Donu, Russia

* Corresponding author
E-mail address: nikita.ledenev.ssp@gmail.com (N.A. Liedienov)
g-levch@ukr.net (G.G. Levchenko)

Abstract
The structure, microstructure, valence states, non-stoichiometry, dielectric and magnetic properties of lanthanum-modified multiferroics have been studied by X-ray diffraction, thermogravimetric, iodometric titration, SEM, XPS, dielectric spectroscopy and magnetic methods. Multiferroics of bismuth ferrite have been obtained by a rapid liquid phase sintering method under different pressures, $P$, for compacting stoichiometric mixture of precursors. On the basis of the experimental data, the molar formulas of real BiFeO$_{3-\delta}$ and Bi$_{0.9}$La$_{0.1}$FeO$_{3-\delta}$ structures have been determined. The real structure contains Bi$^{3+}$, La$^{3+}$, Fe$^{3+}$, Fe$^{2+}$ and O$^-$ ions as well as cation V($a$) and anion V($o$) vacancies. The optimal temperature regimes of the rapid liquid phase sintering method for obtaining the single-phase Bi$_{0.9}$La$_{0.1}$FeO$_{3-\delta}$, whose composition corresponds to the concentration region of destruction of a spin cycloid, have been defined. It has been established that oxygen non-stoichiometry $\delta$ and concentration of Fe$^{2+}$ strongly depend on the pressure $P$. The initial dielectric permittivity of the Bi$_{0.9}$La$_{0.1}$FeO$_{3-\delta}$ multiferroics can be controlled and changed by the pressure $P$ more than 5000 times. The correlations between the composition, structure, non-stoichiometry, dielectric and magnetic properties in the BiFeO$_{3-\delta}$ and Bi$_{0.9}$La$_{0.1}$FeO$_{3-\delta}$ have been established. In the pure BiFeO$_{3-\delta}$ at room temperature, rhombohedral distortions of a hexagonal structure with indications of a ferromagnetic double exchange have been detected. The magnetic structure of the single-phase Bi$_{0.9}$La$_{0.1}$FeO$_{3-\delta}$ is homogeneous with a large value of coercitivity, $H_C \geq 10$ kOe, at room temperature. An analysis of the magnetic properties indicates the appearance of a weak ferromagnetism due to the destruction of the spin cycloid by lanthanum ions.

Keywords: multiferroics, non-stoichiometry, XPS, dielectric permittivity, coercitivity, ferromagnetic double exchange
1. Introduction

Bismuth ferrite, BiFeO$_3$, is a multiferroic and has a great prospect of its application in electronics and spintronics [1–3]. The uniqueness of the functional properties of the BiFeO$_3$ is associated to the possibility of the appearance of magnetoelectric [4], magnetocaloric [5], magnetodielectric [6], magnetostriction [7], piezoelectric [8], pyroelectric [9], and other galvanomagnetic effects in them, the coexistence of which is due to the structural, electrical and magnetic features of this metal oxide class.

The crystal lattice of the BiFeO$_3$ has a hexagonal $A{BO}_3$ perovskite structure with a rhombohedral $R3c$ type of elementary cell distortion [10], which is thermodynamically stable at room temperature. In the BiFeO$_3$, large bismuth cations occupy $A$-positions. Small iron cations occupy $B$-positions and form the FeO$_6$ octahedra with the coordination number (CN) = 6. The appearance of electric polarization in the BiFeO$_3$ is associated to a rhombohedral distortion of the ideal cubic perovskite lattice at which rotation of two adjacent FeO$_6$ octahedra around an [111] axis is occurred in an anti-phase regime [11]. The appearance of the electric polarization vector at such deformation of a crystal is associated to moving oxygen ions in a (111) plane towards the [111] axis in one part of the octahedron and from the [111] axis in the other part of the octahedron. As shown in [12], the angles of rotation of the two adjacent FeO$_6$ octahedra around the [111] axis are ±13.8°. At this rotation, the polarization vector along the [111] direction can be changed from 6.1 µC/cm$^2$ for a bulk single crystal to 100 µC/cm$^2$ for a thin BiFeO$_3$ film [13,14]. The above mechanism for appearance of electric polarization allows to assume that a deviation from stoichiometry $\delta$ in the BiFeO$_{3-\delta}$V$_\delta$ perovskite, associated with appearance of point defects of the vacancy type V, can cause not only local distortions of the FeO$_6$ octahedra, but also significant changes in electric polarization towards either its reduction or increase. Therefore, the study of influence of non-stoichiometry and defect chemistry of a vacancy type on the structure and properties of the bismuth ferrite is of particular interest both to determine the conditions of the stable state for a single-phase multiferroic and to improve its functional properties.

The coexistence of magnetic and electrical ordering in the BiFeO$_3$ is due to the fact that this composition at room temperature is simultaneously in both antiferromagnetic (AFM) and ferroelectric
states with Neel of $T_N \sim 650$ K and Curie of $T_C \sim 1100$ K temperatures [15], respectively. The coexistence and mutual influence of the magnetic and electronic subsystems in the BiFeO$_3$ explains the appearance of galvanomagnetic effects, one of which is a magnetoelectric (ME) effect [16]. The appearance of a magnetic order below $T_N$ is associated to AFM ordering of magnetic moments of iron. The appearance of uncompensated antiferromagnetism is a result of the appearance of a canted state in AFM lattice due to Dzyaloshinskii-Moriya interaction [17]. According to the high-resolution neutron powder diffraction data [18], the magnetic BiFeO$_3$ structure is spatially modulated since AFM ordered spins of Fe$^{3+}$ form a spin cycloid with a period which increases from 605 to 625 Å with increasing temperature from 4 to 300 K. Since the spin cycloid exists, the average value of a projection of AFM magnetization vector in towards of a magnetic field is zero and there is no linear ME effect. This strongly limits the ability to use the unique properties of the BiFeO$_3$ multiferroics for application purposes. The cycloid structure in the BiFeO$_3$ can be destroyed by a strong magnetic field $H \approx 200$ kOe [19], which is accompanied by a surge of electric polarization and the appearance of the linear ME effect [20]. The destruction of the spin cycloid and the appearance of the linear ME effect are also observed in the thin films [21], and bismuth nanopowders with a nanoparticle size not exceeding the spin cycloid period of $\sim 620$ Å [22].

The appearance of the linear ME effect in weak magnetic fields can be also induced by chemical substitution of the A-cation. According to the Mössbauer spectroscopy data [23], the substitution of Bi$^{3+}$ for La$^{3+}$ ions in the Bi$_{1-x}$La$_x$FeO$_3$ destroys a cycloidal antiferromagnetism at the concentrations of $x \geq 0.2$. Measurements of hysteresis loops $M(H)$ in a magnetic field up to 7 T were showed that the residual magnetization in the Bi$_{1-x}$La$_x$FeO$_3$ increases from $5 \cdot 10^{-4}$emu/g to 0.13 emu/g with an increase in the concentration of lanthanum $x$ from 0 to 0.05 [24]. Since the concentration $x = 0.1$ is in the boundary region of the appearance of the linear ME effect, an increased interest in a comprehensive study of the properties for the Bi$_{0.9}$La$_{0.1}$FeO$_3$ arises.

For obtaining large values of the ME effect in the multiferroics, it is necessary to have high polarization properties. The quantitative characteristic of polarization for the multiferroics is a dielectric
permittivity $\varepsilon'$, which depends on a frequency and can take values from $\varepsilon' \sim 10^4$ in low frequency (LF) $f = 1$ Hz – 1 MHz to $\varepsilon' \sim 12$ in ultra high frequency (UHF) $f = 8$ – 12GHz ranges for the BiFeO$_3$ [25,26].

The complexity of the obtaining single-phase BiFeO$_3$ multiferroics is associated to the features of the Bi$_2$O$_3$-Fe$_2$O$_3$ state diagram [27]. Obtaining the BiFeO$_3$ by the solid state reaction method is a complex task which can be solved only within a narrow range of temperatures, compositions, and oxygen pressure [28]. In a state of stable equilibrium, three intermediate phases coexist: (i) the BiFeO$_3$ multiferroic with a perovskite structure; (ii) a Bi$_{25}$FeO$_{40}$ phase with a sillenite structure; and (iii) a Bi$_2$Fe$_4$O$_9$ bismuth ferrite with a mullite structure. The availability of the impurity Bi$_{25}$FeO$_{40}$ and Bi$_2$Fe$_4$O$_9$ phases leads to the appearance of a leakage current and degrades the functional properties of the BiFeO$_3$ [29]. Obtaining the single-phase BiFeO$_3$ is complicated by a volatility of bismuth above the melting point of 817 °C for a Bi$_2$O$_3$ oxide and thermodynamic instability of the BiFeO$_3$ in the air [30]. Using high temperature X-ray diffraction and isothermal heat treatment methods [31], the temperature effect on the thermodynamic stability of the BiFeO$_3$ was investigated and it was found out that the appearance and increase in the concentration of the second Bi$_{25}$FeO$_{40}$ and Bi$_2$Fe$_4$O$_9$ phases were observed within the temperature range of 600 – 817 °C. In the temperature range from 817 to 926 °C, the BiFeO$_3$ perovskite is a thermodynamically stable. Therefore, for obtaining the single-phase BiFeO$_3$ it is necessary to rapidly heat the stoichiometric Bi$_2$O$_3$-Fe$_2$O$_3$ mixture up to the synthesis temperature to prevent the formation of the Bi$_{25}$FeO$_{40}$ and Bi$_2$Fe$_4$O$_9$ phases, and at the final stage of the synthesis, the obtained BiFeO$_3$ perovskite needs to be rapidly cooled to prevent its decomposition into the Bi$_{25}$FeO$_{40}$, Bi$_2$Fe$_4$O$_9$ and Bi$_2$O$_3$. A rapid liquid phase sintering (RLS) method satisfies these conditions [32,33]. In the RLS method, the synthesis of the BiFeO$_3$ occurs at temperatures slightly above the melting point $t = 817$ °C of the low-melting component of Bi$_2$O$_3$. The process of mutual diffusion is much more intensively due to the higher transfer rate of the substance in a liquid phase. Such sintering is several minutes unlike solid state reaction synthesis with tens of hours. Using the RLS method allows to obtain the single-phase compositions of bismuth ferrite multiferroics in a record short time.
In an ideal BiFeO$_3$ perovskite structure, ions of bismuth, iron, and oxygen are in the valence states of Bi$^{3+}$, Fe$^{3+}$ and O$^{2-}$. A real perovskite structure is defective and contains vacancies which strongly affect the physical properties of this metal oxide class [34]. As shown in [35], the perovskite structure can contain point defects of a vacancy type not only in an anion, but in a cation sublattice as well. At studying the effect of vacancies on the electrical properties of the BiFeO$_3$ multiferroics [36], a domain wall appears in the agglomeration region of cation V$^{(c)}$ vacancies in the A-positions of bismuth, when a domain structure of the ferroelectric state is formed.

Bismuth in the BiFeO$_3$ multiferroic can have Bi$^{3+}$ and Bi$^{5+}$ valence with a valence electron configuration 5d$^{10}$6s$^2$ and 5d$^{10}$, respectively. Bismuth ions do not contribute to the magnetization of the BiFeO$_3$ since their electron shells are completely filled and the total spin of the ion is zero. According to the X-ray photoelectron spectroscopy (XPS) data [37], the valence of bismuth is Bi$^{3+}$ in the single-phase BiFeO$_3$ perovskite, and Bi$^{5+}$ appears in impurity phase of Bi$_{24}$[Bi$^{5+}$Fe$^{3+}$]O$_{40}$ sillenite.

The deviation from stoichiometry in an oxygen sublattice of the BiFeO$_3$ leads to a decrease in its negative charge by anion V$^{(a)}$ vacancies, which is compensated by the appearance of Fe$^{2+}$. According to the results of XPS analysis [38], iron ions can be in Fe$^{2+}$ state up to 28% in BiFeO$_3$. With the appearance of Fe$^{2+}$, an increase in conductivity and dielectric loss as well as a decrease in electrical polarization and dielectric constant are observed [38]. Taking into account the local reduction of the CN from 6 to 4 in the B-position by the V$^{(a)}$, it allows to assume that not only FeO$_6$ octahedra, but also FeO$_4$ tetrahedra exist. In this case, Fe$^{3+}$ ions can be found both in the FeO$_6$ octahedra and FeO$_4$ tetrahedra, and Fe$^{2+}$ are only in the FeO$_6$ octahedra [39]. Such effect of the non-stoichiometry on the change in the valence state and coordination environment of iron should cause a change in the formation of magnetic and conductive properties of the BiFeO$_3$.

Taking into account the non-stoichiometry and the possible valence state of the ions in the replaced Bi$_{1-x}$La$_x$FeO$_3$, the molar formula of its real structure

\[\text{is } \{\text{Bi}^{3+}_{1-x'}\text{Bi}^{5+}_{x'}\text{V}^{(c)}_{x}\}_A[\text{Fe}^{3+}_{y'}\text{Fe}^{3+}_{1-y'}\text{V}^{(c)}_{y}]_B\text{O}_{3-\delta}\text{V}^{(a)}_{\delta},\]

where $x$ and $y$ are the concentration of the cation V$^{(c)}$ vacancies in the A- and B-sublattices, $x'$ and $y'$ are the concentration of Bi$^{5+}$ and Fe$^{2+}$, $\delta$ is the number of
the anion $V^{(a)}$ vacancies per molar formula, the concentration of which equals to $\delta/3$. The problem determining the type and concentration of point defects is an important task in chemistry, physics and engineering of functional materials.

Taking into account the above mentioned, the main tasks of this work can be formulated:

(i) obtaining the bismuth ferrite $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ multiferroic, whose composition with lanthanum concentration of $x = 0 – 0.1$ is located in the region of destruction of the spin cycloid;

(ii) determining the optimal conditions for the preparation of the single-phase $\text{Bi}_{0.9}\text{La}_{0.1}\text{FeO}_3$ multiferroics by the RLS method;

(iii) defining the molar formulas of the real $\{\text{Bi}_{1-x-y}\text{Bi}^{3+}_{y} \text{V}^{(c)}_{x}\}_{A}[\text{Fe}^{3+}_{x-1}\text{Fe}^{3+}_{y-y} \text{V}^{(c)}_{y}\}_{B}\text{O}_{3-\delta} \text{V}^{(a)}_{\delta}$ structure containing different valence bismuth and iron ions as well as anion $V^{(a)}$ and cation $V^{(c)}$ vacancies;

(iv) studying the structure, dielectric and magnetic properties of the $\text{Bi}_{0.9}\text{La}_{0.1}\text{FeO}_{3-\delta}$ with establishing regularities of the influence of composition, non-stoichiometry and structure on these properties.

2. Experimental section

The ceramic $\text{BiFeO}_3$ and $\text{Bi}_{0.9}\text{La}_{0.1}\text{FeO}_3$ samples were prepared by the RLS method. A mixture of high purity $\text{La}_2\text{O}_3$ ($\geq 99.5\%$), $\text{Bi}_2\text{O}_3$ ($\geq 99.5\%$) and $\text{Fe}_2\text{O}_3$ ($\geq 99.5\%$) powders in a stoichiometric ratio was calcined at $180^\circ\text{C}$ (4 h) for dehydration and pressed into tablets ($\phi = 8 \text{ mm}, h = 3 \text{ mm}$) under pressure $P = 200 \text{ MPa}$ and ($\phi = 6 \text{ mm}, h = 3 \text{ mm}$) under $P = 400 \text{ MPa}$. The obtained samples were sintered in the air at a temperature of $t_{\text{ann}} = 850 \text{ }^\circ\text{C}$ for 480 sec in the mode of rapid heating at a speed of $100 \text{ C}/\text{sec}$ in a temperature range from a room temperature to $770 \text{ }^\circ\text{C}$ and at a speed of $10 \text{ C}/\text{min}$ in the range from 770 to $850 \text{ }^\circ\text{C}$. After sintering, the samples were rapidly cooled from 850 to a room temperature at a rate of $100 \text{ C}/\text{sec}$. Two batches of the samples were obtained, which were different by $P = 200$ and $400 \text{ MPa}$ of the initial mixture of powders.

The symmetry, lattice parameters and phase composition were measured by using PANalitical X-Pert PRO MRD high resolution diffractometer in $\text{CuK}_{\alpha1}$-radiation. Qualitative phase analysis was performed using database ICDD, PDF-2 Release 2012 and Crystallographica Search-Match Version 3, 1,
The concentration of available phases was evaluated by the corundum numbers method [40]. Additional studies of temperature dependences of lattice parameters for the Bi$_{0.9}$La$_{0.1}$FeO$_3$ were performed by Empyrean X-ray diffractometer (PANalytical) in Cu-radiation. Low-temperature studies of the crystal structure were carried out in the temperature range from 18 to 290 K with using a closed cycle refrigerator and a low temperature Phenix X-ray prefix from Oxford Cryosystems. The analysis of experimental data was carried out using the HighScorePlus and FullProf software.

The method of iodometric titration was used to determine the average valence of iron ions in the air at room temperature for a model where the cation sublattice of bismuth ferrite doped by lanthanum can contain Bi$^{3+}$, La$^{3+}$, Fe$^{2+}$, Fe$^{3+}$, Fe$^{4+}$ ions. In this case, the principle of electrical neutrality can be achieved as a result of both changes in a valence of iron and an oxygen index with the appearance of anion vacancies. The method of iodometric titration allows to determine the oxygen index in $ABO_{3-\delta}$ perovskites, which contain variable valence 3$d$-ions in $B$-positions, with an accuracy of $\delta = \pm0.02$ per formula unit [41]. Such a systematic error in the determination of the oxygen content and the corresponding $0.02/3$ relative error allow to calculate the filling factors for the $A$- and $B$-positions in a real $ABO_{3-\delta}$ perovskite structure with an accuracy up to 1%.

The non-stoichiometry, defect chemistry of a vacancy type and oxygen content were determined on the basis of comparative analysis of the X-ray diffraction, thermogravimetric and iodometric titration experimental data as well as previously established defect formation mechanism for $ABO_3$ perovskites [42–44]. Refinement of the oxygen index and verification of the correctness of the molar formulas obtained for the real BiFeO$_{3-\delta}$ and Bi$_{0.9}$La$_{0.1}$FeO$_{3-\delta}$ structures were controlled by the established early correlation between the relative change of the lattice parameter $\Delta a/a$ and the relative change of the average ionic radius $\Delta \bar{R} / \bar{R}$ in a perovskite structure [42].

The microstructure and size of crystallites in the ceramic samples were determined by the scanning electron microscopy (SEM) method using JEOL JSM-6490LV and FEI Magellan 400 scanning microscopes. The elemental analysis was carried out by the energy dispersive X-ray spectroscopy method. The survey was carried out in the mode of secondary and back scattered electrons with an
accelerating voltage of 20 kV with a magnification of 30–20000 times and focusing the electron beam on the sample surface up to 10 nm.

X-ray photoelectron spectra of the ceramics and initial Fe$_2$O$_3$, Bi$_2$O$_3$, La$_2$O$_3$ oxide powders were obtained at room temperature with the X-ray photoelectron microprobe ESCALAB 250. The spectra were excited with a monochromatized radiation of AlK$_{\alpha}$. Clean surfaces of the samples were obtained by a diamond scribing file in a vacuum chamber under pressure of about $10^{-6}$ Pa. The state of the surfaces was monitored with C1s line with a very small intensity. However, the line was still detectable on the background which allowed using it for the calibration of the energy scales for all spectra. C1s line binding energy was taken to be 285 eV. The flow of slow electrons was used to counteract the charging of samples. The absolute energy resolution was 0.6 eV that was determined from the Ag3d$_{5/2}$ line profile. The Fe$_2$O$_3$, Bi$_2$O$_3$ and La$_2$O$_3$ powders were deposited by fine layer on a double-sided conductive adhesive tape. The flow of slow electrons was used to counteract the charging of powders as well. The background of X-ray photoelectron lines was cut off by Shirley [45].

The dielectric properties were studied on the basis of the analysis of the frequency dependences of the relative dielectric constant, $\varepsilon'(f)$, and the dielectric loss tangent, tan\(\Delta(f)\), measured by the dielectric spectroscopy in the LF ($f = 1$ Hz – 1 MHz) and UHF ($f = 8.24$–12.05 GHz) ranges at room temperature [46,47].

Magnetic measurements were carried out by using Quatum Design SQUID MPMS 3. Magnetic properties were determined on the basis of the analysis of the temperature $M(T)$ and magnetic field $M(H)$ dependences of magnetization. The $M(T)$ dependences were measured in two $M_{ZFC}(T)$ and $M_{FC}(T)$ modes, when the sample was heated after its cooling in a zero magnetic field (ZFC–mode) and when the sample was cooled in a magnetic field (FC–mode). The $M_{ZFC}(T)$ and $M_{FC}(T)$ dependences were measured in two magnetic fields of $H = 50$ Oe and 7 T. The hysteresis $M(H)$ curves were measured in a magnetic field up to 7 T at $T = 4$ and 300 K.
3. Structure and microstructure

An analysis of the X-ray patterns for the ceramic BiFeO$_3$ and Bi$_{0.9}$La$_{0.1}$FeO$_3$ samples obtained under different pressures $P = 200$ and 400 MPa (see Fig. 1) allows to conclude that the matrix structure of all samples studied is a rhombohedral distorted hexagonal perovskite structure. In the BiFeO$_3$ sample ($P = 200$ MPa), a rhombohedral $R3m$ type of distortion with the lattice parameters of $a = 5.5737$ Å and $c = 6.9339$ Å and the unit cell of $Z = 3$ formula units is observed. In this sample, the available of additional phases of the Bi$_2$Fe$_4$O$_9$ with a mullite structure (orthorhombic $Pbam$ structure; $a = 7.965$ Å, $b = 8.44$ Å, $c = 5.994$ Å; $Z = 2$; ICCD No. 55) and Bi$_{25}$FeO$_{40}$ with a sillenite structure (cubic $I23$ structure; $a = 10.1812$ Å; $Z = 1$; ICCD No. 197) was observed as well. The content of each phase does not exceed 2 vol. %. The diffraction maxima for the Bi$_2$Fe$_4$O$_9$ and Bi$_{25}$FeO$_{40}$ are indicated by the * symbol in the region of angles $2\theta = 27.5–29.0^\circ$ (see Fig. 1 (a)). With increase in the pressure up to $P = 400$ MPa, the lattice parameters decrease and the structure is a rhombohedrally $R\bar{3}m$ distorted with $a = 5.5694$ Å and $c = 6.8927$ Å parameters. In this sample, the content of the perovskite phase decreases to 79.5 % and instead of the Bi$_2$Fe$_4$O$_9$ and Bi$_{25}$FeO$_{40}$ the phases of Bi$_2$O$_3$ oxide (cubic $I23$ structure, $a = 10.08$ Å, $Z = 12$, ICCD No. 197) and metallic Bi$_4$ bismuth (monoclinic $C2/m$ structure, $a = 6.67256$ Å, $b = 6.1108$ Å, $c = 3.30013$ Å, $Z = 1$, ICCD No. 10) are appeared with concentrations of 12.6 and 7.9 %, respectively (see Table 1). The diffraction maxima of the Bi$_2$O$_3$ and Bi$_4$ phases in Fig. 1 (b) are within the region of $2\theta = 28.0 – 29.3^\circ$ angles.

![Fig. 1. X-ray patterns for the Bi$_{1-x}$La$_x$FeO$_3$ ceramics with $x = 0$ and 0.1 obtained by the RLS method under different pressures of $P = 200$ (a) and 400 MPa (b). The symbol * denotes the region of the diffraction maxima from the second additional phases.](image-url)
While replacing bismuth with lanthanum, all $\text{Bi}_{0.9}\text{La}_{0.1}\text{FeO}_3$ samples, regardless of pressure $P$, are single-phase and have a rhombohedral $R3c$ type of distortion (see Fig. 1). The lattice parameters vary from $a = 5.5730$ Å and $c = 13.8480$ Å for a sample with $P = 200$ MPa to $a = 5.5734$ Å and $c = 13.8025$ Å for a sample with $P = 400$ MPa (see Table 1). An absence of diffraction maxima in the region of $2\theta = 27.5–29.3^\circ$ angles indicates the complete polymorphic transformation of the initial oxides to the $\text{Bi}_{0.9}\text{La}_{0.1}\text{FeO}_3$ perovskite without the formation of the additional $\text{Bi}_2\text{Fe}_4\text{O}_9$, $\text{Bi}_{25}\text{FeO}_{40}$, $\text{Bi}_2\text{O}_3$ and $\text{Bi}_4$ phases.

At analyzing the X-ray data, two facts should be noted. Firstly, in the $\text{BiFeO}_3$ sample, the $R3m$ ($P = 200$ MPa) and $R\bar{3}m$ ($P = 400$ MPa) types of rhombohedral distortion are found (see Table 1), but the $R3c$ type of distortion was observed for the hexagonal $\text{BiFeO}_3$ multiferroic [10]. The appearance of the $R3m$ phase is possible at high temperatures when the cubic $Pm\bar{3}m$ structure of the perovskite is transformed to the $R3c$ structure through two intermediate $R\bar{3}c$ and $R3m$ phases [48,49]. The nonpolar $R\bar{3}c$ phase appears when the structure is distorted by only the rotation of the FeO$_6$ octahedra around the [111] axis without displacing the ions along the [111] direction [50]. The ferroelectric $R3m$ phase appears with polar distortions, which is caused by the displacement of ions along [111] direction without rotation of the FeO$_6$ octahedra [48]. Interpreting the result, it can be said that the rapid cooling of the samples using the RLS method freezes the structure in an intermediate state at which the displacement of ions along [111] axis has already begun, but the rotation of the FeO$_6$ octahedra has not occurred. It should be noted that the $R3m$ distortion of the structure prevents the appearance of the linear ME effect [51].

Secondly, the results of the phase analysis indicate the appearance of the $\text{Bi}_2\text{O}_3$ bismuth oxide and metallic $\text{Bi}_4$ bismuth in the $\text{BiFeO}_3$ ($P = 400$ MPa) sample instead of the phases of the $\text{Bi}_2\text{Fe}_4\text{O}_9$ mullite and $\text{Bi}_{25}\text{FeO}_{40}$ sillenite. It should be noted that with the appearance of the $\text{Bi}_4$ a sharp decrease in the lattice parameter $a$ from 5.5737 to 5.5694 Å is observed with an increase in the pressure $P$ from 200 to 400 MPa (see Table 1). Such a decrease in $a$ parameter is possible as a result of the chemical pressure
because of the influence of metallic bismuth being in the intercrystalline zones of the BiFeO₃ microstructure.

**Table 1**

Phase composition, type of structure and lattice parameters for the BiFeO₃ and Bi₀.₉La₀.₁FeO₃ obtained by the RLS method under different pressures of \( P = 200 \) and 400 MPa

<table>
<thead>
<tr>
<th>( x )</th>
<th>( P ) (MPa)</th>
<th>Space group</th>
<th>ICDD No.</th>
<th>Lattice parameters</th>
<th>Second phase, vol.%</th>
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<td>primitive</td>
<td>( a ) (Å)</td>
<td>( c ) (Å)</td>
</tr>
<tr>
<td>0</td>
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<td>( R3m )</td>
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<td>5.5737</td>
<td>6.9339</td>
</tr>
<tr>
<td>0.1</td>
<td>200</td>
<td>( R3c )</td>
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<td>5.5730</td>
<td>13.8480</td>
</tr>
<tr>
<td>0</td>
<td>400</td>
<td>( R̅3m )</td>
<td>166</td>
<td>5.5694</td>
<td>6.8927</td>
</tr>
<tr>
<td>0.1</td>
<td>400</td>
<td>( R3c )</td>
<td>161</td>
<td>5.5734</td>
<td>13.8025</td>
</tr>
</tbody>
</table>

The results of the SEM investigations for the microstructure of the BiFeO₃ and Bi₀.₉La₀.₁FeO₃ samples are shown in Fig. 2. The SEM spectroscopy data confirmed the chemical and phase composition for all samples. The Bi₂FeO₄ impurity is located in an intergranular space of the BiFeO₃ (\( P = 200 \) MPa) and denotes as white spots in Fig. 2 (a). Assumption about the localization of the metallic Bi₁₄ bismuth in the crystallite boundaries of the BiFeO₃ (\( P = 400 \) MPa) is confirmed by Fig. 2 (f).
Fig. 2. Microstructure of the BiFeO$_3$ (a) and Bi$_{0.9}$La$_{0.1}$FeO$_3$ (b) under $P = 200$ MPa, the BiFeO$_3$ (c) and Bi$_{0.9}$La$_{0.1}$FeO$_3$ (d) under $P = 400$ MPa as well as EDS pattern of the BiFeO$_3$ (e) under $P = 400$ MPa and increased concentration of bismuth in the vicinity of crystallite boundaries for the BiFeO$_3$ (f) under $P = 400$ MPa obtained by the SEM method.

According to the SEM investigations, the crystallite size decreases from ~ 10 to ~ 1 μm (see Fig. 2 (a) and (b)) for the samples obtained at $P = 200$ MPa when bismuth is replaced by lanthanum. It leads to the formation of finely porous cellular microstructure in the Bi$_{0.9}$La$_{0.1}$FeO$_3$. Such type of the
microstructure should accumulate a large charge in the LF range. With increasing the pressure $P$ from 200 to 400 MPa, the microstructure of the samples shows a well-formed surface consisting of small crystallites, the average size of which slightly varies from $\sim$ 500 nm in the BiFeO$_3$ ($P = 400$ MPa) to $\sim$ 450 nm in the Bi$_{0.9}$La$_{0.1}$FeO$_3$ ($P = 400$ MPa) with increasing La content.

4. Non-stoichiometry and molar formulas of a real structure

In bismuth ferrite, an isovalent substitution of Bi$^{3+}$ for La$^{3+}$ ions with the same ionic radii should not result in the significant changes in its structural properties, since with such a substitution neither changes in the valence of other ions, nor changes in interionic distances should occur [52]. To explain such changes, it is necessary to introduce an additional parameter into consideration. This parameter is a non-stoichiometry. The non-stoichiometry depends on the concentration of the cation $V^{(c)}$ and anion $V^{(a)}$ vacancies and affects the valence and charge state of cations, the length of metal-oxygen bonds, the coordination number and heterogeneity of the coordination environment, which leads to the changes in the stability of structure and its properties.

The appearance of the $V^{(c)}$ and $V^{(a)}$ vacancies in the perovskite structure is observed at high temperatures of synthesis and annealing. The $V^{(a)}$ vacancies are formed as a result of the thermal dissociation in the positions formally occupied by oxygen vented to the atmosphere. Reduction of an iron to Fe$^{2+}$ preserves the electroneutrality of a unit cell. The appearance of $V^{(c)}$ occurs during the oxidative process while the sample is cooled after the appearance of new metal-oxygen bonds at the “solid solution-atmosphere” interface. As a result of the greater mobility of a cation sublattice [43], the $V^{(c)}$ vacancies are formed at the site of the cations moved to the interface.

On the basis of the defect formation mechanism taking into account the phase composition [53], X-ray diffraction and thermogravimetric data as well as the results of iodometric titration for determining the average iron valence [42], the molar formulas of the real BiFeO$_3$-$\delta$ and Bi$_{0.9}$La$_{0.1}$FeO$_3$-$\delta$ structure were determined (see Table 2). The molar formulas were determined taking into account the fact that the Bi$^{3+}$, Bi$^{5+}$, Fe$^{3+}$, Fe$^{2+}$, O$^{2-}$ ions as well as the $V^{(c)}$ and $V^{(a)}$ vacancies can be in the perovskite structure.
The molar formulas of the real perovskite structure and concentration of the anion \( V^{(a)} \) vacancies for the BiFeO\(_3\)-\( \delta \) and Bi\(_{0.9}\)La\(_{0.1}\)FeO\(_3\)-\( \delta \) ceramics obtained under different pressure \( P \)

<table>
<thead>
<tr>
<th>( P ) (MPa)</th>
<th>Molar formulas of defect perovskite structure</th>
<th>( V^{(a)} ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( [\text{Bi}^{3+}<em>{0.99}\text{V}^{(c)}</em>{0.01}]<em>A[\text{Fe}^{3+}</em>{0.03}\text{Fe}^{3+}<em>{0.51}\text{V}^{(c)}</em>{0.01}]<em>C\text{O}^{2-}</em>{2.78}\text{V}^{(a)}_{0.22} )</td>
<td>7.3</td>
</tr>
<tr>
<td>0.1</td>
<td>( [\text{Bi}^{3+}<em>{0.88}\text{La}^{3+}</em>{0.12}\text{V}^{(c)}<em>{0.02}]<em>A[\text{Fe}^{2+}</em>{0.27}\text{Fe}^{3+}</em>{0.72}\text{V}^{(c)}<em>{0.01}]<em>C\text{O}^{2-}</em>{2.82}\text{V}^{(a)}</em>{0.18} )</td>
<td>6.0</td>
</tr>
<tr>
<td>0</td>
<td>( [\text{Bi}^{3+}<em>{0.99}\text{V}^{(c)}</em>{0.01}]<em>A[\text{Fe}^{3+}</em>{0.10}\text{Fe}^{3+}<em>{0.89}\text{V}^{(c)}</em>{0.01}]<em>C\text{O}^{2-}</em>{2.92}\text{V}^{(a)}_{0.08} )</td>
<td>2.7</td>
</tr>
<tr>
<td>0.1</td>
<td>( [\text{Bi}^{3+}<em>{0.88}\text{La}^{3+}</em>{0.12}\text{V}^{(c)}<em>{0.02}]<em>A[\text{Fe}^{2+}</em>{0.05}\text{Fe}^{3+}</em>{0.94}\text{V}^{(c)}<em>{0.01}]<em>C\text{O}^{2-}</em>{2.93}\text{V}^{(a)}</em>{0.07} )</td>
<td>2.3</td>
</tr>
</tbody>
</table>

The real structure of the BiFeO\(_3\)-\( \delta \) and Bi\(_{0.9}\)La\(_{0.1}\)FeO\(_3\)-\( \delta \) is non-stoichiometric and in addition to the \( A \)-cations of Bi\(^{3+}\), the \( B \)-cations of Fe\(^{3+}\) and Fe\(^{2+}\), and the anions of O\(^2-\) oxygen it also contains the \( V^{(a)} \) and \( V^{(c)} \) vacancies (see Table 2). The quantity of the \( V^{(c)} \) vacancies in the \( A \)- and \( B \)-positions is an insignificant to 1-2 \% and it can be considered that the both cation sublattices are completely filled. The criterion for the correctness of definition of the molar formulas is the established correlation between the experimental values of the relative changes in the \( \Delta a_P/\alpha_P \) lattice parameter (\( a_P \) is a parameter of the primitive cell) and the calculated values of the relative changes in the \( \Delta \bar{R} / \bar{R} \) average ionic radius [43,54]. To determine the relative changes \( \Delta a_P/\alpha_P \), the parameters of \( a \) and \( c \) of the hexagonal structure were recalculated for the \( a_R \) and \( \alpha_R \) parameters of the rhombohedral structure [55]. Since the angle of the rhombohedral distortion \( \alpha_R = 89.4 - 89.6^\circ \) is slightly different from 90°, the parameter \( a_R \) can be considered as the parameter \( a_P \) of the primitive elementary cell for the studied samples (see Table 1 and Fig. 3).

The average ionic \( \bar{R} \) radius was calculated from the equations [42], in which the fill factors of all crystallographic positions (see Table 2) and the radii of ions in according to their valence state and coordination number were used [52]. It should be noted that in an ideal cubic perovskite structure, a bismuth is in the \( A \)-position with CN = 12. In the rhombohedral \( R3c \) structure, the \( A \)-position is strongly
distorted and only 6 out of 12 oxygen anions are the nearest environment of bismuth [50], and thus, La and Bi in the A-positions are in the octahedra of LaO$_6$ and BiO$_6$ with CN = 6.

The correlation established between the relative changes of the $\Delta a_p/a_p$ parameter of the primitive cell and the average $\Delta \bar{R}/\bar{R}$ ionic radius of the perovskite structure for the BiFeO$_{3-\delta}$ and Bi$_{0.9}$La$_{0.1}$FeO$_{3-\delta}$ samples (see Fig. 3) confirms the correctness of the molar formulas of the real structure determined (see Table 2).

![Fig. 3](image.png)

**Fig. 3.** Concentration changes in the parameter $a_p$ of the primitive cell and the average $\bar{R}$ ionic radius for the perovskite Bi$_{1-x}$La$_x$FeO$_{3-\delta}$ structure under different pressures $P = 200$ (a) and 400 MPa (b). The inset shows the correlation between the relative changes in the $\Delta a_p/a_p$ parameter and the average $\Delta \bar{R}/\bar{R}$ ionic radius.

As can be seen from Table 2, all samples are non-stoichiometric in oxygen. With an increase in the La content, the concentration of the V$^{(a)}$ vacancies slightly decreases from 7.3 % in the BiFeO$_{3-\delta}$ to 6.0 % in the Bi$_{0.9}$La$_{0.1}$FeO$_{3-\delta}$ for $P = 200$ MPa and from 2.7 % in the BiFeO$_{3-\delta}$ to 2.3 % in the Bi$_{0.9}$La$_{0.1}$FeO$_{3-\delta}$ for $P = 400$ MPa. Increasing the pressure $P$ from 200 to 400 MPa reduces the concentration of the V$^{(a)}$ vacancies in all compositions by almost 2.5 times. The deviation from stoichiometry ~ 1 % of the V$^{(c)}$ vacancies in the cation A- and B-sublattices is insignificant and does not depend either on the lanthanum content or the pressure $P$. The large concentration of Fe$^{2+}$ in the B-positions is of particular interest. The amount of Fe$^{2+}$ depends on the concentration of the V$^{(a)}$ vacancies, since a decrease in the oxygen sublattice of charge by anion vacancies at high synthesis temperatures is compensated by the appearance of Fe$^{2+}$ in the cation sublattice. The high concentration of the V$^{(a)}$ and Fe$^{2+}_B$ is the result of a rapid cooling
of the samples (100 °C/sec). At this cooling rate, the partially deoxidized Fe\(^{2+}\) cations have no time to reach the sample surface in order to oxidize to Fe\(^{3+}\). This is the reason for the small deviation from stoichiometry in the cation sublattice and the high concentration of the V\(^{(a)}\) and Fe\(^{2+}\)\(_{\mu}\) in the BiFeO\(_3\)\(_{\delta}\) and Bi\(_{0.9}\)La\(_{0.1}\)FeO\(_3\)\(_{\delta}\) samples under \(P = 200\) MPa. As can be seen from Table 2, an increase in the pressure \(P\) from 200 to 400 MPa greatly reduces the concentration of Fe\(^{2+}\)\(_{\mu}\) from 38 to 10 % in the BiFeO\(_3\)\(_{\delta}\) and from 27 to 5 % in the Bi\(_{0.9}\)La\(_{0.1}\)FeO\(_3\)\(_{\delta}\). Such a significant effect of non-stoichiometry on the change in the valence state of iron ions in the bismuth ferrite should strongly influence its structure, magnetic and dielectric properties.

5. Structure, dielectric and magnetic properties of the non-stoichiometric single-phase

Bi\(_{0.9}\)La\(_{0.1}\)FeO\(_3\)\(_{\delta}\) composition

5.1. Structural properties of the non-stoichiometric Bi\(_{0.9}\)La\(_{0.1}\)FeO\(_3\)\(_{\delta}\) perovskite

Since the greatest deviation from stoichiometry among single-phase samples is observed in the Bi\(_{0.9}\)La\(_{0.1}\)FeO\(_3\)\(_{\delta}\) sample under \(P = 200\) MPa with a concentration of V\(^{(a)}\) = 7.3 % vacancies (see Table 2), the studying its structural properties in a wide temperature range is an increased interest.

According to X-ray diffraction data, the Bi\(_{0.9}\)La\(_{0.1}\)FeO\(_3\)\(_{\delta}\) sample is a single-phase and has a rhombohedral \(R3\bar{c}\) (ICDD: 98-001-5299) structure which is not changed within a temperature range from 18 to 290 K as shown in Fig. 4 and 5. An analysis of its crystal structure is performed in according to the model proposed [56]. The hexagonal unit cell of the Bi\(_{0.9}\)La\(_{0.1}\)FeO\(_3\) composition contains six formula units (\(Z = 6\)) (Fig. 6). The lattice parameters of the solid Bi\(_{0.9}\)La\(_{0.1}\)FeO\(_3\)\(_{\delta}\) solution monotonically decrease with a decrease of temperature (Fig. 7 and Table 3).

**Fig. 4.** X-ray patterns of the Bi$_{0.9}$La$_{0.1}$FeO$_{3-\delta}$ sample at different temperatures $T$. The label * denotes the reflex of the sample holder.

**Fig. 5.** X-ray pattern of the Bi$_{0.9}$La$_{0.1}$FeO$_{3-\delta}$ at room temperature treated by the Rietveld method. The experimental points, calculated function and difference curve normalized to the statistical error are shown. Vertical strokes designate the positions of the peaks for the Bi$_{0.9}$La$_{0.1}$FeO$_{3}$ crystal structure.
**Fig. 6.** The elementary cell for the Bi$_{0.9}$La$_{0.1}$FeO$_{3-\delta}$ in a hexagonal installation plotted by using data of Table 3. Ion indication: O is a blue color, Bi / La is a green color, Fe is a red color.

**Table 3**

The parameters of the Bi$_{0.9}$La$_{0.1}$FeO$_{3-\delta}$ crystal structure, standard calculation and experimental factors, coordinates of the atoms determined by the Rietveld method within the framework of the space group $R3c$ (No 161) at different temperatures. The ions are in the positions of Bi/La (6a) (0, 0, 0); Fe (6a) (0, 0, z); O (18b) (x, y, z)

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>Structure parameters and criteria of fit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$a$ (Å)</td>
</tr>
<tr>
<td></td>
<td>$z$</td>
</tr>
<tr>
<td>18</td>
<td>5.5695(2)</td>
</tr>
<tr>
<td>30</td>
<td>5.5691(1)</td>
</tr>
<tr>
<td>60</td>
<td>5.5696(1)</td>
</tr>
<tr>
<td>90</td>
<td>5.5703(1)</td>
</tr>
<tr>
<td>120</td>
<td>5.5708(2)</td>
</tr>
<tr>
<td>190</td>
<td>5.5730(2)</td>
</tr>
<tr>
<td>230</td>
<td>5.5744(2)</td>
</tr>
<tr>
<td>290</td>
<td>5.5778(1)</td>
</tr>
</tbody>
</table>
Fig. 7. Temperature dependences of the lattice parameters, $a$ and $c$, and the volume cell, $V$, for the Bi$_{0.9}$La$_{0.1}$FeO$_{3-\delta}$.

On the basis of the analysis of X-ray diffraction data, the microstructural parameters of the Bi$_{0.9}$La$_{0.1}$FeO$_3$ ceramics were additionally determined. The microstrain $\varepsilon$ and an average size of the coherent scattering region $<D_{CSR}>$ were equal to 0.16 % and 820 nm, respectively. This size is close to the average crystallite size $\sim 1 \mu$m from SEM measurements (see Fig. 3(b)). The contributions of the real physical broadening were determined from the difference between a broadening of the diffraction peaks of the Bi$_{0.9}$La$_{0.1}$FeO$_3$ and calibration LaB$_6$ samples. The separation of the $\varepsilon$ and $<D_{CSR}>$ contributions into the broadening of the observed diffraction peaks was performed by the Williamson-Hall method [57]. Using the HighScorePlus software, the Debye-Scherrer method additionally allowed to determine $\varepsilon = 0.179 \%$ and $<D_{CSR}> = 137.3$ nm. The discrepancies obtained by two methods in the sizes of the coherent scattering region are observed. In the Debye-Scherrer method, a single diffraction line located in a region of small angles $\theta$ is used. In the Williamson-Hall method, an analysis is conducted for all lines with extrapolation to the region of small angles excluding the contribution from microstrains.

5.2. Valence states in the single-phase non-stoichiometric Bi$_{0.9}$La$_{0.1}$FeO$_{3-\delta}$ perovskite

Fig. 8 shows a comparative analysis of the X-ray photoelectron spectra of the initial Fe$_2$O$_3$ powder and the Bi$_{0.9}$La$_{0.1}$FeO$_{3-\delta}$ ($P = 200$ MPa) sample. As shown in Fig. 8 and Table 4, Fe2p spectrum of the Fe$_2$O$_3$ powder consists of two maxima A and C at a distance of 13.6 eV related to Fe2p$_{3/2}$ and Fe2p$_{1/2}$.
levels, respectively. In addition to these main features of the spectra, at a distance of 7.8 eV from the maximum of A there is a singularity B (719 eV) and after the peak C there is a diffuse shelf D (733 eV). The features of C and D refer to satellites of charge transfer. Moreover, the availability of singularity C and the value of binding energy equal to 711.2 eV indicate that the iron ions in the investigated powder are in the trivalent state [58,59].

Fig. 8. X-ray photoelectron spectra of Fe2p for the Fe2O3 powder (a) and the Bi0.9La0.1FeO3-δ (P = 200 MPa) sample (b) and its decomposition into components related to the Fe2p spectrum from Fe2+ ions (green curve) and Fe3+ (blue curve).

Fig. 8 (b) shows the appearance of an additional bend A’ in the spectrum for the Bi0.9La0.1FeO3-δ sample. This bend A’ has energy lower than the maximum of A at a distance of about 1.8 eV. In addition, there is no feature B in the spectrum. These differences from Fe2p spectrum in Fig. 8 (a) allow to conclude that the spectrum for the Fe3O4 sample [59], which has Fe2+ and Fe3+ ions, is the similar to Fig. 8 (b).
Table 4

The binding energies of Fe2p, Bi4f, La3d, and O1s levels in the Bi_{0.9}La_{0.1}FeO_{3-δ} ceramics and the Fe_{2}O_{3}, Bi_{2}O_{3}, La_{2}O_{3} powders

<table>
<thead>
<tr>
<th>Sample</th>
<th>Binding energies of levels</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe2p</td>
<td>Bi4f</td>
<td>La3d</td>
<td>O1s</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2p3/2</td>
<td>2p1/2</td>
<td>4f7/2</td>
<td>4f5/2</td>
<td>3d5/2</td>
<td>3d1/2</td>
</tr>
<tr>
<td>Fe_{2}O_{3}</td>
<td>711.2</td>
<td>724.8</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Bi_{2}O_{3}</td>
<td>–</td>
<td>–</td>
<td>158.7</td>
<td>164.0</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>La_{2}O_{3}</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>834.5</td>
<td>851.1</td>
</tr>
<tr>
<td>Bi_{0.9}La_{0.1}FeO_{3-δ}</td>
<td>711.3</td>
<td>724.8</td>
<td>158.7</td>
<td>164.0</td>
<td>834.4</td>
<td>850.8</td>
</tr>
</tbody>
</table>

To clarify the available of different valance iron ions in the ceramic Bi_{0.9}La_{0.1}FeO_{3-δ} sample the experimental spectrum was decomposed (see Fig. 8 (b)) using the approach described for the components related to bivalent and trivalent iron ions [58]. Fe2p spectra of divalent and trivalent iron used as components of decomposition were taken by analogy with work [58]. Fe2p spectrum of the ceramic sample is described quite well by the sum of the components related to Fe^{2+} and Fe^{3+} with proportions of 26 % and 74 %, respectively (see Fig. 8). At estimating the contributions, it was taken into account that the ionization probability of the 2p shell in Fe^{2+} ion is twice higher than in Fe^{3+} ion [58]. These values correspond to the values of 27.3 % (Fe^{2+}) and 72.7 % (Fe^{3+}) obtained from the molar formulas of the real structure with very good accuracy (see Table 2). Therefore, the availability of different valence iron Fe^{2+} and Fe^{3+} ions in the Bi_{0.9}La_{0.1}FeO_{3-δ} sample at the isovalent substitution of Bi^{3+} by La^{3+} ions has been confirmed by XPS method as well.

The analysis of X-ray photoelectron spectra of Bi4f (see Fig. 9 (a)) shows that they practically coincide and have the same energies (Table 4). The spectra have two components, Bi4f_{7/2} and Bi4f_{5/2},
separated by a spin-orbital interaction. The energy position of Bi$4f_{7/2}$ component equals to 158.7 eV in both samples that suggests the trivalent state of bismuth in the Bi$_{0.9}$La$_{0.1}$FeO$_{3-\delta}$ [58].

**Fig. 9.** X-ray photoelectron spectra of Bi$4f$ for the Bi$_2$O$_3$ powder and the Bi$_{0.9}$La$_{0.1}$FeO$_{3-\delta}$ ceramics (a) and of La$3d$ for the La$_2$O$_3$ powder and the Bi$_{0.9}$La$_{0.1}$FeO$_{3-\delta}$ ceramics (b).

Fig. 9 (b) shows X-ray photoelectron spectra of La$3d$. The nominal content of lanthanum in the Bi$_{0.9}$La$_{0.1}$FeO$_{3-\delta}$ sample is 1 mol. %. Despite the low content of lanthanum, we were able to obtain La$3d_{5/2}$ and La$3d_{3/2}$ spectra, although with much worse statistics. Nevertheless, the main contours of La$3d_{5/2}$ and La$3d_{3/2}$ are reproduced. In addition, it was possible to determine the energy of maximum component of La$3d_{5/2}$ and La$3d_{3/2}$ peaks (Table 4). As shown in Fig. 9 (b), the spectra are almost identical and have the same energy (Table 4). The La$3d$ spectra were calculated [60]. In the one-electron approximation, the spectra have two components of La$3d_{5/2}$ and La$3d_{3/2}$ which are separated by the spin-orbital interaction. In addition to these main features of the spectra, they have an extra fine structure due to the availability of charge transfer satellites, plasmon satellites and contribution of the Auger-line MNN components [61]. A detailed analysis of La$3d$ spectrum for the La$_2$O$_3$ was conducted [60–62]. According to these papers, sufficient broad features, located at 13.5 eV on the high-energy side of each main doublet line, is due to from Auger MNN electron lines and plasmon excitations. Expressed features on the main components, located approximately 4 eV from the main maximum of each line, are the charge transfer satellites.
reflecting the formation of the screening states 3d^1 4f^1 L^{-1} (L = ligand), during "shaking off" the valence electrons on free 4f-orbitals [62]. The equal energy position of La3d_{5/2} and La3d_{3/2} components for the La_2O_3 powder and the Bi_{0.9}La_{0.1}FeO_3-\delta ceramics allows to conclude that the lanthanum ions in the Bi_{0.9}La_{0.1}FeO_3-\delta sample are in the trivalent state.

5.3. Dielectric properties of the single-phase Bi_{0.9}La_{0.1}FeO_3-\delta multiferroics with varying non-stoichiometry \( \delta \)

The investigation of dielectric properties for the Bi_{0.9}La_{0.1}FeO_3-\delta multiferroics has showed that the complex relative dielectric permittivity \( \varepsilon^* = \varepsilon' + i\varepsilon'' \) and dielectric loss tangent \( \tan \Delta = \varepsilon'' / \varepsilon' \) have a relaxation type of dispersion (Fig. 10). At room temperature, the Bi_{0.9}La_{0.1}FeO_3-\delta \((P = 200 \text{ MPa})\) with oxygen non-stoichiometry \( \delta = 0.18 \) (see Table 2) has anomalously high values of the \( \varepsilon' = 5 \cdot 10^5 \) at 1 Hz, the values of which exponentially decrease to \( \varepsilon' \sim 209 \) with increase in a frequency to \( f = 1 \text{ MHz} \). In the Bi_{0.9}La_{0.1}FeO_3-\delta \((P = 400 \text{ MPa})\) with \( \delta = 0.07 \), the dielectric permittivity decreases sharply to \( \varepsilon' = 82 \) at 1 Hz and then slightly decreases to \( \varepsilon' = 50 \) with increasing frequency to \( f = 1 \text{ MHz} \) (see Fig. 10). The colossal values of the \( \varepsilon' \) in the LF range for the Bi_{0.9}La_{0.1}FeO_3-\delta \((P = 200 \text{ MPa})\) sample, as we expect, are associated to the charge accumulation at the boundaries of the finely crystalline structure (see Fig. 2 (b)).

In the UHF range \( f = 8 \text{ – } 12 \text{ GHz} \), the relative permittivity \( \varepsilon_\infty \) and dielectric loss \( \tan \Delta \) become frequency-independent for all samples. With decreasing non-stoichiometry \( \delta \) from 0.18 to 0.07, a decrease in \( \varepsilon_\infty \) from 10.5 \((P = 200 \text{ MPa})\) to 7.7 \((P = 400 \text{ MPa})\) and an increase in \( \tan \Delta \) from 1.7 \cdot 10^{-3} \((P = 200 \text{ MPa})\) to 1.3 \cdot 10^{-2} \((P = 400 \text{ MPa})\) are observed. It should be noted that for the pure BiFeO_3-\delta bismuth ferrite, the values of the \( \varepsilon_\infty \) and \( \tan \Delta \) are equal to 34.5 and 2.9 \cdot 10^{-3} \( \) for \( \delta = 0.22 \) and equal to 13.6 and 3.9 \cdot 10^{-3} \( \) for \( \delta = 0.08 \), respectively. Such high values of \( \varepsilon_\infty \) for the BiFeO_3-\delta are possibly associated to the influence of the Bi_2Fe_4O_9 and Bi_25FeO_40 impurity phase (see Table 1).
The model spectra of the $\varepsilon^*$ components, which are in good agreement with the experimental data, can be described by the relations [63–65]:

$$
\varepsilon' = \varepsilon_\infty + \frac{(\varepsilon_s - \varepsilon_\infty)[1 + (\omega \tau)^{i\alpha} \sin(\pi \alpha/2)]}{1 + 2(\omega \tau)^{i\alpha} \sin(\pi \alpha/2) + (\omega \tau)^{2i\alpha}} + \frac{(\varepsilon_s - \varepsilon_\infty)[1 + (\omega \tau_2)^{i\gamma} \sin(\pi \gamma/2)]}{1 + 2(\omega \tau_2)^{i\gamma} \sin(\pi \gamma/2) + (\omega \tau_2)^{2i\gamma}},
$$

where $\varepsilon_s$ is a static dielectric permittivity, $\varepsilon_\infty$ is a high-frequency dielectric permittivity. The parameters $\alpha$, $\gamma$, $\beta$ characterize the distributions of the relaxation times $\tau$ determined in the first approximation from the condition $\omega_{\text{max}} \cdot \tau = 1$, where $\omega_{\text{max}}$ is a frequency corresponding to the maximum of tan$\Delta$. The second and third terms in Eq. (1) are mathematical expressions describing the Debye model in different frequency intervals with the Cole-Cole and Cole-Davidson distributions of relaxation times [63,64], respectively.

The second term in Eq. (1) can be related to the electron hopping mechanism between Fe$^{2+} \leftrightarrow$ Fe$^{3+}$ ions, which is in the frequency range from $10^3$ to $10^6$ Hz [66,67]. In this frequency range, the decrease observed in the tan$\Delta$ while decreasing non-stoichiometry $\delta$ well correlates with the decrease in the amount of Fe$^{2+}$ ions (see Table 2 for $x = 0.1$). An insufficient frequency dependence of the real component of the dielectric constant for the sample synthesized under $P = 400$ MPa is due to the low
polarization of the highly localized states of Fe$^{3+}$ ions. In the sample obtained under $P = 200$ MPa, the fraction of Fe$^{2+}$ ions is significantly higher, that promotes an increase in dielectric losses in this frequency range.

The third term in Eq. (1) describes the high-frequency relaxation mechanism of the dielectric polarization, the nature of which has not been finally clarified. A possible mechanism of the dielectric polarization in the frequency range from $10^7$ to $10^9$ Hz is the motion of the walls of ferroelectric domains [67].

In the LF limit which is described by the last term in Eq. (1) and (2), the large values of the tan$\Delta$ are due to the contributions of quasi-free carriers of the electric current to the dielectric polarization, i.e. dielectric losses are related to the conductivity and accumulation of electric charge on the intercrystalline boundaries, inhomogeneities and structure defects within a framework of the Maxwell-Wagner and Kups models [25,68]. The using of Eq. (1) and (2) allows to obtain model spectra (see Fig. 10). The deviation between the theoretical calculations and the experimental data does not exceed an error of the experiment within the frequency interval. The parameters of the model spectra are given in Table 5.

Table 5

<table>
<thead>
<tr>
<th>$P$ (MPa)</th>
<th>$\tau$ ($10^{-5}$ s)</th>
<th>$\alpha$</th>
<th>$\varepsilon_s$</th>
<th>$\varepsilon_\infty$</th>
<th>$\sigma_1$ ($10^7$ $\Omega^{-1}$ m$^{-1}$)</th>
<th>$\beta_1$</th>
<th>$\sigma_2$ ($10^7$ $\Omega^{-1}$ m$^{-1}$)</th>
<th>$\beta_2$</th>
<th>$\tau_2$ (s)</th>
<th>$\gamma$</th>
<th>$\varepsilon_{s1}$</th>
<th>$\varepsilon_{\infty1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>3.92</td>
<td>0.05</td>
<td>2100</td>
<td>10.65</td>
<td>29.99</td>
<td>0.898</td>
<td>32.99</td>
<td>0.770</td>
<td>1.26 $10^{-3}$</td>
<td>0.987</td>
<td>3700</td>
<td>2100</td>
</tr>
<tr>
<td>400</td>
<td>0.08</td>
<td>0.01</td>
<td>73</td>
<td>7.4</td>
<td>0.0001</td>
<td>0.500</td>
<td>0.0001</td>
<td>0.500</td>
<td>0.08</td>
<td>0.220</td>
<td>80</td>
<td>73</td>
</tr>
</tbody>
</table>

The increase in the value of real component of dielectric constant in the Bi$_{0.9}$La$_{0.1}$FeO$_{3-\delta}$ samples ($P = 200$ MPa) compared with the results obtained on the samples ($P = 400$ MPa) within the frequency range of $10^5$ – $10^8$ Hz is associated to a large concentration of structure defects. The effect of structure
defects in Fig. 10 is shown in the region of notable relaxation behavior of dielectric functions. An increased content of anion vacancies (a large δ value) and a high content of Fe$^{2+}$ (see Table 2) lead to a significant increase of the dielectric constant in the static limit. At a frequency $f \to 0$, the formation of dielectric properties is influenced by the high conductivity of the samples due to the contribution to polarization. This contribution is caused by the availability of quasi-free charge carriers which move within the crystallites under the action of an external alternating electric field. Charge accumulation at the crystallite boundaries provides the formation of a polarized state. This interpretation of the experimental data is supported by a large scatter of the relaxation times described by α and γ parameters as well as high conductivities $\sigma_1$ and $\sigma_2$ in the Bi$_{0.9}$La$_{0.1}$FeO$_{3-\delta}$ samples with $P = 200$ MPa (see Table 5). The availability of a minimum in the tanΔ($f$) dependence within the range $10^3 – 10^4$ Hz is due to the coexistence of different dielectric polarization mechanisms. With decreasing frequency, the processes associated with electron hopping between different valence cations of iron reach saturation, which leads to the establishment of a constant value of tanΔ. However, at a frequency corresponding to the minimum value of tanΔ, not all possible defects contribute to the polarization of the material. As the frequency decreases, the number of quasi-free charge carriers reacting to a change in the sign of the external electric field increases, which leads to an increase in the dielectric loss tangent. In the Bi$_{0.9}$La$_{0.1}$FeO$_{3-\delta}$ samples ($P = 400$ MPa), this mechanism does not affect the dielectric constant due to the small amount of Fe$^{2+}$ ions that is evidenced by decreasing the α parameter in five times. A small value of the relaxation time τ corresponds to relatively high frequency, below which saturation occurs due to the contribution caused by electron hopping between different valence cations of iron. The availability of the last ones, though in a small amount (see Table 2), was found in the Bi$_{0.9}$La$_{0.1}$FeO$_{3-\delta}$ ($P = 400$ MPa). On the basis of the relaxation time $\tau = 0.08$ obtained in course of the simulation (at the first approximation from the relation $2\pi f_{\text{max}}\tau \approx 1$), the frequency $f_{\text{max}} \approx 2$ Hz can be estimated, where the maximum of loss tangent should be observed.
5.4. Magnetic properties of the single-phase BiFeO$_{3-\delta}$ and Bi$_{1-x}$La$_x$FeO$_{3-\delta}$ perovskites

In order to study the effect of lanthanum on the magnetic properties of the Bi$_{1-x}$La$_x$FeO$_{3-\delta}$ multiferroics, the samples with non-stoichiometry $\delta$ weakly depending on the concentration $x$ were selected. The samples with $P = 400$ MPa, in which $\delta$ decreases slightly from 0.08 for the BiFeO$_{3-\delta}$ to 0.07 for the Bi$_{0.9}$La$_{0.1}$FeO$_{3-\delta}$ (see Table 2), satisfy this condition. The behavior of the hysteresis $M(H)$ curves at the magnetization of the samples in a magnetic field up to $H = 7$ T testifies the availability of the ferromagnetic (FM) interactions in both samples (see Fig. 11). With increase in the La concentration from $x = 0$ to 0.1, the magnetization in the highest field 7 T decreases from $M(7 \text{ T}) = 0.9373$ to 0.6669 emu/g at $T = 4$ K and increases from $M(7 \text{ T}) = 0.5842$ to 0.6568 emu/g at $T = 300$ K (see Table 6). The coercive field of $H_C$ increases both at a temperature $T = 4$ K from $H_C = 1832$ to 14664 Oe and at $T = 300$ K from $H_C = 5392$ to 11624 Oe. The residual magnetization of $M_r$ increases from $M_r = 0.04105$ to 0.13221 emu/g at $T = 4$ K and from $M_r = 0.04603$ to 0.11866 emu/g at $T = 300$ K as well.

**Fig. 11.** Hysteresis curves of the $M(H)$ for the BiFeO$_{3-\delta}$ (a) and Bi$_{0.9}$La$_{0.1}$FeO$_{3-\delta}$ (b) in a magnetic field up to $H = 7$ T at temperatures of $T = 4$ and 300 K.
Table 6

Magnetic properties of the Bi$_{1-x}$La$_x$FeO$_3$ (P = 400 MPa) ceramics

<table>
<thead>
<tr>
<th>x</th>
<th>$H_C$ (Oe)</th>
<th>$M_r$ (emu/g)</th>
<th>$M$(7 T) (emu/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4 K</td>
<td>300 K</td>
<td>4 K</td>
</tr>
<tr>
<td>0</td>
<td>1832</td>
<td>5392</td>
<td>0.04105</td>
</tr>
<tr>
<td>0.1</td>
<td>14664</td>
<td>11624</td>
<td>0.13221</td>
</tr>
</tbody>
</table>

An increase in the coercivity of the $H_C$ and the change of magnetizations of the $M$(7 T) and $M_r$ at the replacement of bismuth by lanthanum in the Bi$_{1-x}$La$_x$FeO$_3$ are a logical result which is caused by the destruction of the spin cycloid by lanthanum [23]. However, the appearance of ferromagnetism in the BiFeO$_{3-\delta}$ is an unexpected result and requires more detailed discussion. The residual magnetization $M_r$ = 0.04105 emu/g in our sample BiFeO$_{3-\delta}$ at $T$ = 4 K (see Table 6) is significantly ~ 70 times greater than $M_r$ = 0.0006 emu/g for the same composition BiFeO$_3$, in which a cycloidal antiferromagnetism is observed [24]. The appearance of FM interactions in the pure BiFeO$_3$ can be caused by the appearance of the ferromagnetic $\text{Fe}^{2+}_B - \text{O}^{2-} - \text{Fe}^{3+}_B$ double exchange through oxygen between the $\text{Fe}^{2+}(3d^{6}, S=2)$ and $\text{Fe}^{3+}(3d^5, S=5/2)$ provided that $\text{Fe}^{2+}$ ions are available in the $B$-positions of the perovskite [69]. The appearance of such FM clusters was observed in the BiFeO$_3$ films, in which FM ordering can be realized through a double-exchange of the Zener mechanism and is not associated to the Dzyaloshinskii-Moriya interaction [70]. A confirmation of this mechanism is the fact that the concentration of Fe$^{2+}$ reaches 10 % (see Table 2) in the studied BiFeO$_{3-\delta}$ ($P = 400$ MPa) sample.

An absence of any anomalies in the $M_{ZFC}(T)$ and $M_{FC}(T)$ dependences (see Fig. 12) indicates a magnetic homogeneity and the absence of magnetic phase transitions in the temperature $T = 2 – 400$ K range. There is no discrepancy between the temperature dependences of the $M_{ZFC}(T)$ and $M_{FC}(T)$ magnetization (see Fig. 12). It means an absence of spin-glass behavior [71], and a phase separation of the magnetic subsystem in our samples regardless of the La content [72]. The magnetization $M$ of all samples weakly varies over the whole temperature $T = 2 – 400$ K range and increases from $M = 0.0020 –$
0.0022 emu/g in a magnetic field $H = 50$ Oe to $M = 0.58 – 0.68$ emu/g in the $H = 7$ T. The sharp increase in the $M_{ZFC}$ and $M_{FC}$ magnetizations for the BiFeO$_{3-\delta}$ sample in the low-temperature region from 50 to 2 K (see Fig. 12 (a)) is due to the magnetic and spin heterogeneity [25, 73]. An absence of such a sharp increase in the $M_{ZFC}$ and $M_{FC}$ when $T \rightarrow 0$ in the Bi$_{0.9}$La$_{0.1}$FeO$_{3-\delta}$ sample (see Fig. 12 (b)) indicates its high magnetic purity, which once again confirms the magnetic homogeneity and correctness of the determined molar formulas of the real structure (see Table 2) with a low content of Fe$^{2+}$ (5 %) in this sample.

![Fig. 12. The dependences of the $M_{ZFC}(T)$ and $M_{FC}(T)$ magnetization for the BiFeO$_{3-\delta}$ (a) and Bi$_{0.9}$La$_{0.1}$FeO$_{3-\delta}$ (b) in the magnetic fields of $H = 50$ Oe and 7 T.](image)

**Conclusions**

X-ray diffraction, thermogravimetric, iodometric titration, SEM, XPS, dielectric spectroscopy and magnetic methods have been used for investigating the structure, microstructure, valence states, non-stoichiometry, dielectric and magnetic properties of the lanthanum-modified multiferroics obtained by the rapid liquid phase sintering method under different pressures $P$.

Taking into account the defect formation mechanism, the molar formulas of the real perovskite structure for the BiFeO$_{3-\delta}$ pure and lanthanum-doped Bi$_{0.5}$La$_{0.1}$FeO$_{3-\delta}$ bismuth ferrite have been determined. It has been found out that the real structure contains Bi$^{3+}$, Fe$^{2+}$, Fe$^{3+}$, O$^{2-}$ ions as well as anion
V\(^{(a)}\) and cation V\(^{(c)}\) vacancies. Due to the low concentration of the V\(^{(c)}\) vacancies, the deviation from stoichiometry in the cation sublattice can be neglected. The non-stoichiometry of the oxygen sublattice \(\delta\) depends on the composition and the pressure \(P\) and can be varied in the range of \(\delta = 0.07 – 0.22\), which corresponds to a change in the concentration of the V\(^{(a)}\) vacancies from 2.3 to 7.3 %. The SEM results confirm the chemical composition. The XPS data evidence valence state of ions in the single-phase Bi\(_{0.9}\)La\(_{0.1}\)FeO\(_{3-\delta}\) multiferroics.

In the rapid liquid phase sintering method, the temperature regimes of rapid heating have been determined at a rate of 100 °C/sec (from room temperature to 770 °C) and 10 °C/min (from 770 to 850 °C) up to 850 °C with a subsequent rapid cooling at a rate of 100 °C/sec down to room temperature for obtaining the single-phase Bi\(_{0.9}\)La\(_{0.1}\)FeO\(_{3-\delta}\) multiferroics, whose composition corresponds to the concentration region of a destruction of the spin cycloid. It has been established that the concentration of Fe\(^{2+}\) from 27 to 5 % in the single-phase Bi\(_{0.9}\)La\(_{0.1}\)FeO\(_{3-\delta}\) multiferroics by can be controlled by the changing pressure \(P\) from 200 to 400 MPa.

According to X-ray diffraction data, the crystal structure of the single-phase Bi\(_{0.9}\)La\(_{0.1}\)FeO\(_{3-\delta}\) is a rhombohedrally \(R3c\) distorted hexagonal perovskite structure, the lattice parameters of which do not depend on the pressure \(P\). Monotonic reductions in the lattice and volume of the unit cell while decreasing temperature from 290 to 18 K are observed without structure transformation.

According to the SEM data and dielectric spectroscopy, the crystal structure of the Bi\(_{0.9}\)La\(_{0.1}\)FeO\(_{3-\delta}\) sample obtained under \(P = 200\) MPa is small-porous with crystallite size \(~ 1\mu m\), which induces the accumulation of a charge at the crystallite boundaries and the appearance of colossal dielectric constant \(\varepsilon'\) \(~ 5 \cdot 10^5\) in the low-frequency range. In this sample, relatively large losses \(\tan\Delta \sim 1.5\) are associated to increasing conductivity with the appearance of a ferromagnetic Fe\(^{2+}\)\(_B\) – O\(^{2-}\) – Fe\(^{3+}\)\(_B\) double exchange.

Increasing the pressure \(P\) up to 400 MPa reduces the crystallite size to \(~ 450\) nm and homogenizes the microstructure. Reducing non-stoichiometry \(\delta\) from 0.18 to 0.07 decreases the concentration of Fe\(^{2+}\) from 27 to 5 % and lowers the initial dielectric constant. The initial dielectric constant of the Bi\(_{0.9}\)La\(_{0.1}\)FeO\(_{3-\delta}\)
multiferroics can be controlled and changed in ~ 5000 times from $\varepsilon' = 5 \cdot 10^5$ to 100 by variation of the pressure of the initial mixture of precursors from 200 to 400 MPa.

According to magnetic measurements, the magnetic structure of the Bi$_{0.9}$La$_{0.1}$FeO$_{3-\delta}$ single-phase multiferroics obtained by the RLS method is homogeneous with a large value of the coercitivity of $H_C \geq 10$ kOe at room temperature. The magnitude of the magnetization and an absence of anomalies in its temperature dependence indicate the appearance of a weak ferromagnetism and the destruction of the spin cycloid in this sample by the lanthanum impurity.

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References

22. F. Huang, Z. Wang, X. Lu, J. Zhang, K. Min, W. Lin, R. Ti, Peculiar magnetism of BiFeO3 nanoparticles with size approaching the period of the spiral spin structure, Scientific Reports. 3 (2013) 2907.
26. Y. Li, X. Fang, M. Cao, Thermal frequency shift and tunable microwave absorption in BiFeO3 family, Scientific Reports. 6 (2016) 24837.
Szymczak, Structure, phase transitions, 55Mn NMR, magnetic and magnetotransport properties of the magnetoresistance La0.9–xAgxMn1.1O3–δ ceramics, J. Alloys Comp. 709 (2017) 779–788.


Graphical abstract
Highlights

1. Real molar formulas for BiFeO$_{3-\delta}$ and Bi$_{0.9}$La$_{0.1}$FeO$_{3-\delta}$ multiferroics were determined
2. Real structure contains Bi$^{3+}$, La$^{3+}$, Fe$^{2+}$, Fe$^{3+}$, O$^{2-}$ ions and V$^{(a)}$, V$^{(c)}$ vacancies
3. Dielectric constant $\epsilon^\prime$ reduces in 5000 times at 1 Hz with rising $P$ from 200 to 400MPa
4. Bi$_{0.9}$La$_{0.1}$FeO$_{3-\delta}$ multiferroics show a large value of $H_C \geq 10$ kOe at room temperature
5. “Composition, Structure, Non-stoichiometry, Properties” correlation was established