Structure of LaSrFeO$_4$: neutron diffraction, Mössbauer spectroscopy and modeling

L. Dabrowski[1], D. Neov[2]*, V. Antonov[2], M. Machkova[3], S. Neov[2], V. Kozhukharov[3]

[1] *Atomic Energy Institute, 05-400 Otwock, Swierk, Poland*
[2] *Institute for Nuclear Research and Nuclear Energy, Bulgarian Academy of Sciences, 1784 – Sofia, Bulgaria*
[3] *University of Chemical Technology and Metallurgy, 1756 – Sofia, Bulgaria*

Mössbauer spectroscopy and neutron diffraction experiments were carried out for study of LaSrFeO$_4$, synthesized by wet chemical method. The data obtained were interpreted on the basis of *ab initio* quantum-mechanical modeling. The experimental results from Mössbauer spectroscopy and model calculations show that occupational distribution of La and Sr atoms on (4e) Wyckoff positions of I4/mmm space group (confirmed by neutron diffraction) is not random as previously assumed, but predominantly in double layers of either La or Sr. The distribution of each double layer is however random. The quantum mechanical model calculations of La and Sr arrangement along the *c*-axis explain the presence of two Mössbauer sextets at low temperature despite the unique position of Fe in the unit cell.

Key words: Mössbauer spectroscopy, neutron diffraction, modeling

INTRODUCTION

The increased interest towards LaSrFeO$_4$ in recent years is invoked by the possibility of using this material as a cathode in solid oxide fuel cells (SOFC), operating at high temperature. The compound possesses high electron-ion conductivity, significant oxygen diffusion, thermo-mechanical stability and other properties suitable for SOFC cathode application. The compound crystallizes in K$_2$NiF$_4$ – type structure and constitutes a particular case of Ruddlesden-Popper phases A$_{n+1}$B$_n$O$_{3n+1}$ with n = 1. From the viewpoint of its structure the question if La^{3+} ion (ionic radius R = 1.03 Å) and Sr^{2+} (R = 1.18 Å) randomly occupy the same Wyckoff crystallographic position (4e) in tetragonal space group I4/mmm despite the difference in their effective ionic radii and valence, needs further experimental and model investigations. The diffraction experiments [1–3] provide rather averaged information about the local distribution of the atoms, whereas the Mössbauer spectroscopy is sensitive to the coordination polyhedron of atoms surrounding the Fe (forming the first coordination sphere). Mössbauer spectrum cumulates also the influence of more distant atoms around Fe atom that form the second coordination sphere. Hence,

the complementary data from both experimental methods and model calculations of fine parameters of the structure of LaSrFeO$_4$ could explain better the observed physical properties.

Practically all authors report random distribution of La and Sr ions in the „rock-salt" layers between "perovskite" layers formed by adjacent FeO$_6$ octahedra. Although seemingly natural, such distribution needs further unconventional assumptions in order to explain the experimentally obtained peculiarities of Mössbauer spectra and their temperature dependence. Additional argument for carrying out our investigation is the rather strong dependence of the Neel temperature (T$_N$) from the method of compound synthesis. In particular, depending on which one is used – solid-state reaction at various temperature regime or wet chemical method, T$_N$ deduced from the Mössbauer experiments varies from 300 to 380 K [3–6]. At the same time, electrical resistivity covers much wider range, 2.6.10^2 – 2.4.10^3 Ω.cm (almost tenfold variation) [5]. Because of the fact that crystal structure remains unchanged (in the experimental uncertainty range), such high variations indicate possible different oxygen content, different oxidation state of iron and different distribution of the cations in La-Sr-O rock-salt layers. All mentioned factors are strongly affected by the compound synthesizing conditions, namely by maximal temperature of synthesis and if oxidizing or reducing atmosphere was applied.

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* To whom all correspondence should be sent:
E-mail: dneov@abv.bg

The goal of the current study was applying neutron diffraction, Mössbauer spectroscopy together with first-principle quantum-mechanical modeling to reach more reliable interpretation of $LaSrFeO_4$ structural data.

EXPERIMENT

Synthesis of $LaSrFeO_4$ was carried out by a nitrate-citrate method. Highly pure La_2O_3, $Sr(NO_3)_2$ and $Fe(NO_3)_3.9H_2O$ were used as starting materials. The oxides and nitrates in respective stoichiometric ratio were dissolved in aqueous solution of nitric acid at heating and stirring. After complete dissolution citric acid in molar ratio 3.3:1 in relation to metal ions was added. The obtained clear solution was concentrated and dried at 200 °C. After drying, the self-combustion of the dry residue gave powdered precursors. A thermal treatment at temperatures from 700 to 1100 °C for 2 hours and simultaneous thermogravimetry/ differential thermal analysis (TG/DTA) was performed to observe the thermal decomposition of precursors. The TG/DTA measurements were made using Q-1500-D derivatograph at heating rate of 10 °C/min in the temperature range from 15 °C to 1000 °C in air atmosphere. The ceramic powder was pressed to bars and sintered at 1250 °C for 5 h and at 1400 °C for 1 h. Phase composition of obtained ceramic powders was characterized by X-ray diffraction. The microstructure of sintered samples was observed by scanning electron microscopy (SEM) using JEOL-JSM-35CF microscope.

Neutron diffraction (*ND*) experiment was carried out on E9 – Fine Resolution Powder Diffractometer at the BER II reactor of Helmholtz Centre Berlin for Materials and Energy. The powder sample 5g in weight was measured at room temperature. The wavelength of neutron beam was $\lambda = 0.1797$ nm. The structure was refined using FullProf program [7], by minimization of the weighted sum: $\chi^2 = \Sigma_i w_i [y_{iobs}(2\theta) - y_{ical}(2\theta)]^2$.

Mössbauer spectroscopy measurements were implemented using a standard transmission technique with a source of ^{57}Co in Pd. The sample was mounted in close-cycle helium cryostat and the resonance γ-ray absorption spectra were measured in the temperature range from 9.3 K to 295 K. Calibration of the velocity scale was made by ARMCO iron as standard absorber.

MODELLING

The model calculations were performed via the ultrasoft pseudopotentials and a plane wave basis set as implemented in the Quantum Espresso (QE) integrated suite of computer codes [8]. The generalized gradient approximation (GGA) of Perdew, Burke and M. Ernzerhof (PBE) [9] was used. The applied pseudopotentials with QE were ultrasoft, generated by the Vanderbilt scheme [10] and taken from the QE distribution [8]. The wave functions at each k-point are represented by the numerical coefficients of a finite set of plane waves, determined by a kinetic energy cut-off. The k-point sets were generated automatically, following the Monkhorst – Pack (MP) scheme [11]. To decrease the number of k-points needed to sample the Brillouin zone, the crystallographic symmetry of the sample was considered. The computation of interatomic forces was performed by the Hellmann-Feynman theorem [12]. Hubbard corrections (GGA+U) as implemented in QE approach were performed in order to take into account the strong on-site Coulomb interaction (U) presented in the localized 3d electrons of Fe, and in turn to describe well the band gap. In the present work, the GGA+U corrections of Dudarev et al. [13] are used, which depends on the effective Coulomb interaction $U_{eff}=U-J$, with J being the screened exchange energy. The used in calculations value for U_{eff} was taken to be 4.5 eV [13]. A Gaussian electron energy level smearing with width of 0.08 eV was introduced.

The initial calculations started with convergence studies to determine the kinetic energy cut-off and the size of the MP grid. Iterations using self-consistent field (SCF) cycles were performed until the difference of the total energy was checked less than 10^{-5} eV. The forces in the unit cell and the lattice vectors were relaxed using ground state structural optimization via the Broyden algorithm as implemented in the QE. Calculations were performed until the interatomic force became less than 7×10^{-3} eV/Å and the cell pressure (for the lattice constant calculations) was less than 0.05 kbar.

EXPERIMENTAL RESULTS
AND DISCUSSION

Rietveld analysis of neutron diffraction data of $LaSrFeO_4$ collected at room temperature [3], Fig. 1, was performed using scattering lengths 8.24, 7.02, 9.450 and 5.803 fm [10^{-15}m], for La, Sr, Fe and O nuclei, respectively. The background of multidetector data was approximated by six parameters polynomial curve.

The fit with tetragonal I4/mmm space group, i.e. K_2NiF_4-type structure [14], Fig. 2, was successful. The Bragg R-factor was 4.52 and $\chi^2 = 3.05$. The calculated unit cell parameters are a = b = 3.8694 Å and c = 12.7322 Å, respectively. These values are in agreement with the previously reported data, which depending on the synthesis conditions lie in the

range: a = 3.86–3.88 Å, and c = 12.687–12.760 Å, [1,2]. The atomic positions, isotropic temperature factors (B) and the occupancy of equivalent positions are given in Table 1.

The calculated axial and equatorial bond lengths Fe-O2$_{axial}$ = 2.172Å and Fe-O1$_{eq}$ = 1.935Å in FeO$_6$ octahedron differ by nearly 10%, but the axial symmetry along the c-axis is preserved and the angle O2-Fe-O2 is exactly 180°. Surprisingly high is the difference between the isotropic temperature factors of oxygen O1 (B = 0.699 Å²) and O2 (B = 1.724 Å²) as is shown in Table 1. This difference seems to be characteristic for all A-substituted R-P phases [4–6]. Most probably, it is a direct result of the quasi-random distribution (as calculated by *ab initio* modeling) of La^{3+} and Sr^{2+}-ions in the rock-salt layer (bilayer) around the apical oxygen (O2) of FeO$_6$ octahedron. The different arrangement, effective ionic radii and electrical charge of La^{3+} (R=1.032Å) and Sr^{2+} (R = 1.18 Å) disturb the equilibrium position of O2, what is registered by neutron scattering as a higher value of the Debye-Waller factor. The significant influence of La and Sr distribution on the resonance γ-spectra was observed by low temperature Mössbauer experiment, as well.

Neutron diffraction data of LaSrFeO$_4$ point to tetragonal structure in which lanthanum and strontium atoms are distributed randomly among the (4e) Wyckoff positions. Moreover, from diffraction data it follows that the Fe atoms are crystallographically equivalent and hence experimentally undistinguishable. Fig. 3 shows the Mössbauer resonance absorption spectrum of LaSrFeO$_4$ measured at 9.3 K. A model of two sextets with equal effective magnetic field (H$_{eff}$), isotrope shift (IS) and different quadroupole splitting (Q) plus a small contamination singlet was accepted. Fig. 3 and Table 2 illustrate a good coincidence with the experimental data. A posible interpretation of this result can be done by the admission (in contradiction with diffraction data) of two non equivalent Fe ions in the unit cell. In reality, the variable distribution of La^{3+} and Sr^{2+} ions in the second coordination sphere of Fe ions influences (as follows from the model calculations) the spatial electrons distribution, as well as,
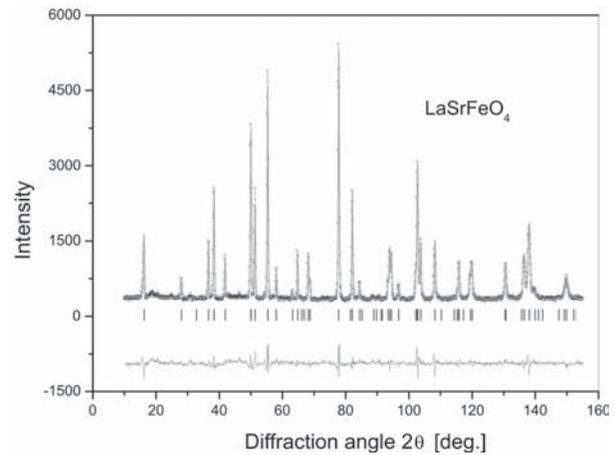
Fig. 1. Neutron diffraction spectrum of LaSrFeO$_4$. Peak positions and difference curve are shown below the experimental points and fitting curve
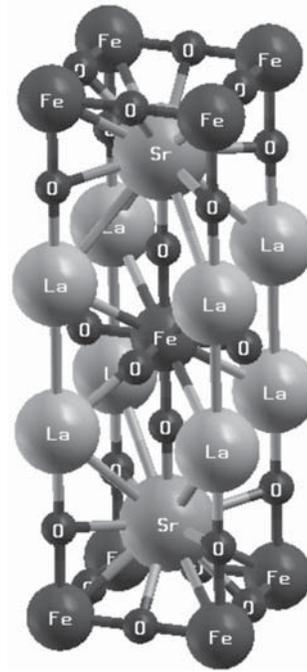
Fig. 2. Crystal structure of LaSrFeO$_4$

Table 1. Crystal structure parameters of LaSrFeO$_4$, obtained by Rietveld analysis of neutron diffraction data, T = 298 K; La and Sr ions occupy the Wyckoff position (4e)

Atom	Atomic positions			B	Occupancy	
	x	y	z			
La, Sr	0.	0.	0.3580(5)	0.643	4	(4e)
Fe	0.	0.	0.	0.565	2	(2a)
O1	0.	0.5	0.	0.699	4	(4c)
O2	0.	0.	0.1703(7)	1.724	4	(4e)
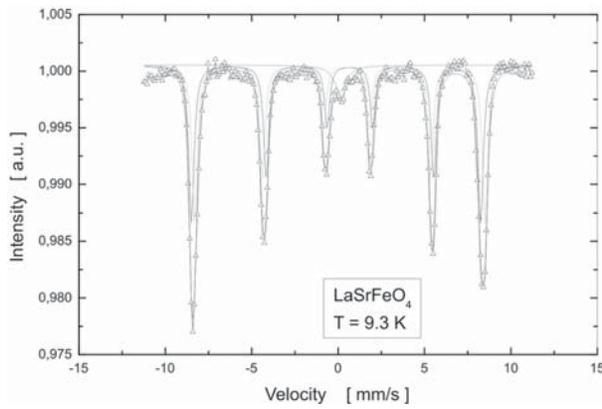
Fig. 3. Mössbauer spectrum of LaSrFeO₄ at 9.3 K. The singlet is due to <5% contamination phase
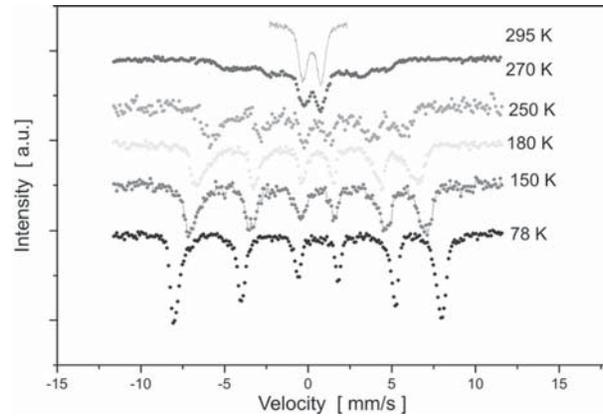
Fig. 4. Mössbauer spectra of LaSrFeO₄ measured in the interval 78–295 K

the position of the apical oxygen O2, thus changing the symmetry and intensity of the electrical field in FeO_6 octahedron. The Q value of the sextets is relatively stable as a function of T below the liquid nitrogen temperature and converges to nearly equal value above 150 K. The obtained values of isomer shift are characteristics for high spin state of Fe^{3+} (S=5/2).

Mössbauer spectra collected in the temperature interval from 78 K to 295 K are presented in Fig. 4. The Mössbauer spectroscopy measurements at room temperature reveal a small quantity of Fe^{4+} in the studied sample in good accordance with [2], where by direct chemical method (titration) Fe^{4+} content of about 10% was detected in LaSrFeO₄. The best fit of resonance curve at T = 295 K was done by two-component quadroupole doublet. Taking into account the unique position of Fe ions in the structure, a model with equal Q and different IS of constituent doublets was applied. The values of Q and IS

of components are given in Table 2. The presence of two doublets: IS = 0.42 mm/s and 0.27 mm/s is a contribution from the different oxidation states of iron atoms. According to [2], these two components can be attributed to Fe^{3+} and mixed $Fe^{3+} – Fe^{4+}$ state of iron, respectively. The deduced parameters of hyperfine interactions parameters H_{eff}, Q and IS are summarized in Table 2.

MODEL OF THE LOCAL MICROSTRUCTURE

The crystal structure of LaSrFeO₄, [1–3], is tetragonal, space group No 139 – I4/mmm. Every Fe atom is followed by oxygen and then either La or Sr atoms along the Z axis. All possible local configurations are numbered by 1 to 4 as follows: (1) La-O-Fe-O-La, (2) La-O-Fe-O-Sr, (3) Sr-O-Fe-O-La and (4) Sr-O-Fe-O-Sr, respectively. Such configurations

Table 2. Mössbauer hyperfine interactions parameters calculated from the data presented in Fig. 2 and Fig. 3.

T [K]		H [T]	Q [mm/s]	IS (δ) [mm/s]	
9.3	Sextet 1	52.00	−0.40	0.377	
	Sextet 2	52.21	−0.195	0.391	
	Singlet	–		0.226	
78	Sextet 1	49.30	−0.39	0.376	
	Sextet 2	49.47	−0.20	0.446	
150	Sextet 1	42.06	−0.28	0.378	
	Sextet 2	44.55	−0.29	0.391	
180	Sextet 1	38.44	−0.284	0.344	
	Sextet 2	41.68	−0.29	0.367	
295	Doublet 1	–	−1.09	0.27	56%
	Doublet 2	–	−1.00	0.42	44%

Table 3. Positioning of atoms in the perovskite unit cell. X,Y,Z are the coordinates in case of local configurations (2) La-Sr and (3) Sr-La (I4/mmm symmetry) and XYZ' are the coordinates in case local configurations (1) La-La and (4) Sr-Sr (P4/mmm symmetry)

Atom	X	Y	Z	Z'
O	0.0	0.0	0.1706	0.1729
	0.0	0.0	0.8294	0.82710
O	0.5	0.5	0.3294	0.3539
	0.5	0.5	0.6706	0.6461
O	0.0	0.5	0.0	0.0
	0.5	0.0	0.0	0.0
O	0.5	0.0	0.5	0.5
	0.0	0.5	0.5	0.5
Fe	0.0	0.0	0.0	0.0
	0.5	0.5	0.5	0.5
Sr	0.0	0.0	0.3581	0.3690
	0.0	0.0	0.6419	0.6310
La	0.5	0.5	0.1419	0.1630
	0.5	0.5	0.8581	0.8370

should lead to different environment for the Fe atoms and hence Mössbauer effect should distinguish three different sextets since configurations (2) and (3) are equivalent in the terms of local environment and lead to the same sextet. In case of random distribution of La and Sr atoms in the crystal unit cell all configurations (1)–(4) should take place with equal frequency and all three sextets should be present. If configurations (1) and (4) are more likely we should observe two sextets and if only (2) and (3) are eligible we should observe only one sextet contrary to the experiment. It should be noticed in addition, that configurations (2) and (3) disrupt the local symmetry along *c*-axis – the inversion substitutes La atom with Sr and the opposite. Furthermore, La³⁺ and Sr²⁺ have different ionic radii and it is rather doubtful that their unique positions in the unit cell are preserved after substitution. Atomic positions in the unit cell are arranged in Table 3 in the case of local configurations (1) La-La and (4) Sr-Sr.

The computer simulation of the local configurations (1) and (4) mentioned before, revealed that strontium and lanthanum positions, as well some of oxygen positions listed in Table 3 are not stable. Minimum of the internal energy is reached if they are slightly displaced along the c-axis; these new values are designated in Table 3 by Z'. Such change of the atomic positions causes the change of the space group from I4/mmm to P4/mmm, as well.

To find the most suitable positions of La atoms substituted by Sr ones, different structures representing the geometrically equivalent positions were tested. In order to obtain results for the stability of the different structures, calculations were

performed for a fixed volume with relaxation of the atomic positions. The most stable configuration was found to be the structure where the Sr and La atoms are grouped in double layers, randomly distributed between perovskite layers formed by FeO_6 octahedra.

When the concentration of Sr and La equals to ½ (the case of $LaSrFeO_4$), the ratio of probability of configurations (1) or (4) – P_{1+4} and probability of configurations (2) or (3) – P_{2+3} can be represented by the Boltzman factor $P_{1+4}/P_{2+3} = \exp(-V/2kT)$. The configuration potential $V \approx -0{,}22$ eV was calculated under the assumption of finding the atoms in their X,Y and Z' equilibrium positions, given in Table 3. At room temperature the Boltzman factor is $\exp(V/2kT) \approx 70.5$ hence the low-symmetry configurations (2) and (3) should not take place. It should be noted that this conclusion refers to the equilibrium state of $LaSrFeO_4$ which is not necessary the case. Taking into account the moderate maximal temperature at which the sample was synthesized and assuming equilibrium temperature of the compound of about 600K, we obtain factor $\exp(V/2kT) \approx 8{,}4$. Therefore, from this result it follows that low symmetry configurations should be observed with very low intensity or not observed at all.

LOCAL CHARGE DENSITY DISTRIBUTION

For both practical and theoretical point of view it is important to determine how the electron density around Fe ions changes at the substitution of La by Sr. Lanthanum has one 5d electron and two 6s electrons or 3 valence electrons. The rest of the electrons (54 = 57–3) belong to the "core" and do not participate in chemical bonds. Using *"ab initio"* methods for
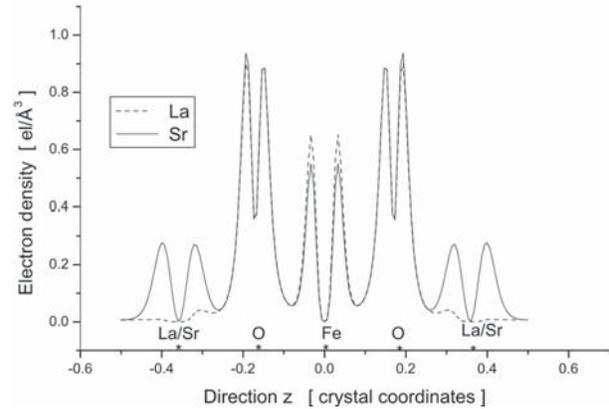
Fig. 5. Local distribution of the electron density along (001) direction for La-O-Fe-O-La and Sr-O-Fe-O-Sr configurations

calculation of electronic structure of Sr-containing compounds it is common to take into consideration not only two 5s electrons of strontium but also six 4p electrons or eight electrons altogether. Charge distribution corresponding to local configuration (1) and (4) is depicted in Fig. 5.

Comparing the charge distribution in both cases we observe significant influence of La and Sr on the electron density around Fe atoms, Fig. 5. Evidently, the wide accepted opinion that the oxygen is shielding Fe ion from the influence of La and Sr is not justified in the case of $LaSrFeO_4$. The electron density around Fe is higher in presence of La atom. The model calculations of electron density distribution clearly demonstrate the influence of atoms from the second coordination sphere of Fe-ion on the electric field in FeO_6 octahedron thus providing a plausible explanation of the observed two Mössbauer sextets at low temperature.

CONCLUSIONS

Results of neutron diffraction and Mössbauer spectroscopy study of $LaSrFeO_4$, synthesized by nitrate citrate method, were compared with quantum mechanical model calculations. The random substitution of lanthanum by strontium, although widely accepted, was found to be energetically non favorable. It was found that the internal energy is minimal in the case when La^{3+} and Sr^{2+} ions form La-La and Sr-Sr bilayers in the rock-salt layers which are randomly distributed in the structure. The data from low temperature Mössbauer spectroscopy were interpreted on the basis of established K_2NiF_4 – type crystal structure. A model of two sextets verified by model calculations of electron density distribution was used for deconvolution of the resonance absorption spectra.

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СТРУКТУРА НА LaSrFeO$_4$: НЕУТРОННА ДИФФРАКЦИЯ, МЬОСБАУРЕВА СПЕКТРОСКОПИЯ И МОДЕЛИРАНЕ

L. Dabrowski[1], Д. Неов[2]*, В. Антонов[2], М. Мачкова[3], С. Неов[2], В. Кожухаров[3]

[1] *Atomic Energy Institute, 05-400 Otwock, Swierk, Poland*
[2] *Институт за ядрени изследвания и ядрена енергетика, Българска академия на анауките, 1784 София, България*
[3] *Химикотехнологичен и металургичен университет, 1756 – София, България*

(Резюме)

Повишеният интерес към сложните окиси на преходните метали с перовскитна и перовскитоподобна структура през последните години е предизвикан от откриването на високо-температурната свръхпроводимост, а също така от възможността за приложението на тези окиси в високотемпературните горивни клетки (SOFC). В настоящето изследване бяха извършени опити по Мьосбаурова спектроскопия и неуронна дифракция върху съединението LaSrFeO$_4$, представляващо частен случай на Рудлесден-Попер фаза A$_{n+1}$B$_n$O$_{3n+1}$ с n=1. Синтезът на LaSrFeO$_4$ беше проведен по сравнително рядко използван метод от разтвори на изходните вещества. Получните данни бяха обяснени на базата на квантово-механично моделиране по метода *ab initio*. Експериментът по Мьосбаурова спектроскопия и моделните пресмятания показват че La и Sr атоми не се разпределят случайно в Уайкоф позициите (4e) на I4/mmm пространствена група както се предполагаше предварително, а преимуществено в двойни слоеве съставени от La или Sr. Тези двойни слоеве обаче не следват определена последователност в кристала. Моделните пресмятания на разположението на лантан и стронциевите атоми по оста *c* обяснява съществуването на два Мьосбаурови секстета при ниски температури въпреки единствената кристалографска позиция на желязото в елементарната клетка.