CRYSTAL AND MAGNETIC STRUCTURE OF OXYGEN-DEFICIENT $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ FERRITE AT ROOM AND LOW TEMPERATURE

K.A. Gavrilicheva[1], A.V. Rutkauskas[2], S.S. Nikitin[1] and O.I. Barkalov[1]

[1] *Osipyan Institute of Solid State Physics RAS, Chernogolovka, Russia*
[2] *Joint Institute for Nuclear Research, Dubna, Russia*

E-mail: xenia.gavrilicheva@issp.ac.ru

Perovskite-type ferrites ($R_{1-x}A_xFeO_{3-\delta}$, where R is a rare-earth element and A is Ca, Sr, or Ba) exhibit unique electrical, magnetic, and catalytic properties. These make them suitable for various applications, such as cathode materials for solid oxide fuel cells [1–3] and catalysts [4,5]. In substituted $La_{1-x}Sr_xFeO_{3-\delta}$ ferrite, an increase in the number of oxygen vacancies can be achieved by high-temperature vacuum annealing. Our previous work showed that this process was accompanied by a change in the oxidation state of iron ions from a mixed Fe^{3+}/Fe^{4+} state to a purely Fe^{3+} [6–9]. The resulting compositions can be described by the formula $La_{1-x}Sr_xFeO_{3-x/2}$. The equiatomic $La_{0.5}Sr_{0.5}FeO_{2.75}$ composition corresponds to the maximum oxygen vacancy concentration in the series and exhibits a cubic structure (Pm$\bar{3}$m space group) for the metal sublattice[8]. Notably, these compounds have antiferromagnetic ordering, for instance, the $LaFeO_3$ and $SrFeO_{2.5}$ ferrites are antiferromagnets at room temperature (T_N ~750 K [10,11] and ~690 K [12], respectively).

Although the $La_{0.5}Sr_{0.5}FeO_{2.75}$ ferrite is considered a key composition for practical applications, it remains unexplored within the La-Sr ferrite system. Low-temperature behavior has been observed for La-Sr ferrites [13, 14]. We decided to study this ferrite using neutron diffraction as a direct method to investigate its crystal and magnetic structures.

A polycrystalline $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ sample was synthesized by a glycine-nitrate combustion method and subsequently annealed at 1100°C for 10 h in air. Details of the preparation procedure are described in [6]. After synthesis, the as-prepared $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ ferrite was annealed in vacuum (10^{-6} Torr) at 650°C for 10 h to reduce oxygen concentration.

Neutron diffraction data were acquired on the DN-12 diffractometer at the IBR-2 reactor with the detector rings positioned at 55° scattering angles. The powder bulk sample of $La_{0.5}Sr_{0.5}FeO_{2.75}$ in an aluminum container was cooled in a closed-cycle cryostat to about 14 K and diffraction patterns were collected at eight temperature points up to RT (292 K).

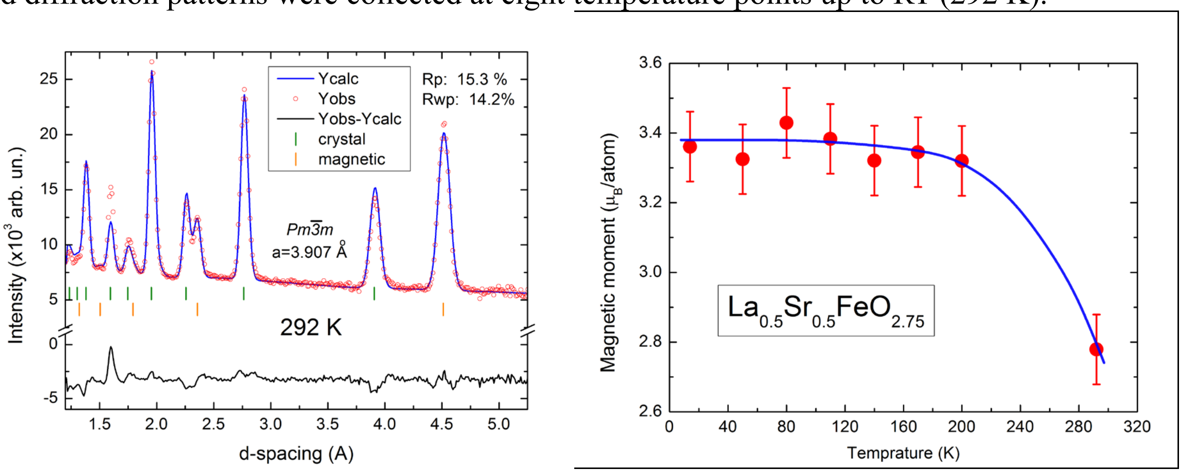

Fig. 1 Left: Neutron diffraction pattern of $La_{0.5}Sr_{0.5}FeO_{2.75}$ at 292 K. The bottom curve (Yobs-Ycal) represents the difference between the experimental data and calculated data. The vertical bars indicate the position of magnetic (bottom) and nuclear Bragg (top) peaks. Right: Temperature dependence of the magnetic moment values of Fe ions obtained by Rietveld refinement. The blue curve is a guide to the eye

Figure 1 (Left) presents the results of the Rietveld refinement of the room-temperature diffraction pattern performed using the FullProf program suite. The fit converged with R_p = 15.3% and R_{wp} = 14.2%. The lattice parameter a=3.907 Å are agrees with the cubic $Pm\bar{3}m$ structure reported recently [8] for the metal sublattice of the ferrite. The crystal phase Bragg R-factor is 11.5%. An excess intensity is observed in the difference curve for the (211) reflection. This reflection is purely crystallographic, with no magnetic contribution. This effect is likely due to higher oxygen content in these planes, since oxygen ions contribute significantly to the overall scattering. Consequently, the symmetry of the structural refinement should be lowered to resolve this discrepancy.

A magnetic reflection at 4.5 Å corresponding to the antiferromagnetic phase was observed. The magnetic contribution was fitted using a model with G-type antiferromagnetic ordering and a doubled lattice parameter. A magnetic R-factor of 3.61% was obtained.

The temperature dependence of the magnetic moment of the iron ions is shown in Fig. 1, Right. The variations of the magnetic moment below ~200 K are rather sluggish, while a small drop (~18%) is observed above ~200 K. Additional experiments planned in the near future will help to determine the exact temperature interval of this change and provide insights into its origin.

[1] A. Shaula, et al. (2006). Ionic conductivity of brownmillerite-type calcium ferrite under oxidizing conditions. *Solid State Ionics*. **177**, 2923.

[2] M. V. Patrakeev, et al. (2003). Electron/hole and ion transport in $La_{1-x}Sr_xFeO_{3-\delta}$. *Journal of Solid State Chemistry*. **172**, 219.

[3] Y. Shin, et al. (2020). Effect of oxygen vacancies on electrical conductivity of $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ from first-principles calculations. *J. Mater. Chem. A*. **8**, 4784.

[4] Z.-X. Wei, Y.-Q. Xu, H.-Y. Liu, and C.-W. Hu (2009). Preparation and catalytic activities of $LaFeO_3$ and Fe_2O_3 for HMX thermal decomposition. *Journal of Hazardous Materials*. **165**, 1056.

[5] S. N. Tijare, et al. (2012). Photocatalytic hydrogen generation through water splitting on nano-crystalline $LaFeO_3$ perovskite. *International Journal of Hydrogen Energy*. **37**, 10451.

[6] V. D. Sedykh, et al. (2019). Effect of the Oxygen Content on the Local Environment of Fe Atoms in Anion-Deficient $SrFeO_3$. *Phys. Solid State*. **61**, 1099.

[7] V. Sedykh, et al. (2022). Role of Fe atom valence states and oxygen vacancies in substituted lanthanum ferrite $La_{0.67}Sr_{0.33}FeO_{3-\gamma}$. *Journal of Physics and Chemistry of Solids*. **171**, 111001.

[8] V. Sedykh, et al. (2023). Fe ion valence states and oxygen vacancies in the $La_{0.5}Sr_{0.5}FeO_{3-\gamma}$ ferrite under vacuum annealing. *Ceramics International*. **49**, 25640.

[9] O. I. Barkalov, et al. (2022). Strontium ferrite $SrFeO_{3-\delta}$ ($2.50 \leq 3-\delta \leq 2.87$) studied by Raman and Mössbauer spectroscopy. *Solid State Communications*. **354**, 114912.

[10] J. B. Goodenough (1963). *Magnetism and the Chemical Bond*, Vol. 1.

[11] C. Boekema, et al. (1978). Super transfer in doped $LaFeO_3$. *Hyperfine Interactions*. **45**.

[12] M. Schmidt and S. J. Campbell (2001). Crystal and Magnetic Structures of $Sr_2Fe_2O_5$ at Elevated Temperature. *Journal of Solid State Chemistry*. **156**, 292.

[13] N. Sivakumar, et al. (2023). Crystal structure, dielectric and magnetic studies of pure and Sr substituted $LaFeO_3$ single crystal grown by optical floating zone technique. *Journal of Alloys and Compounds*. **943**, 169161.

[14] A. I. Dmitriev, et al. (2024). Effect of oxygen content variations on structural and magnetic features in $La_{0.5}Sr_{0.5}FeO_{3-\delta}$. *Physics of the Solid State*. **66**, 386–391.