Effects of vacancy co-doping on the structure, magnetic and dielectric properties of LaFeO₃ perovskite nanoparticles

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Abstract

Perovskite nanoparticles La₁₋ₓ□ₓFe₁₋ₓ□ₓO₃, (y = x = 0.0, 0.01 and 0.02) were prepared using the citrate combustion method. The samples were crystallized in a single phase orthorhombic structure. The energy dispersive spectroscopy (EDS) confirms that the chemical composition is very close to the nominal one. The particle size values indicated that the samples were prepared in nano scale. The selected area electron diffraction (SAED) pattern shows the good crystallinity of the samples. The magnetic hysteresis loops indicate the antiferromagnetic properties of the samples. The molar magnetic susceptibility (χₘ) of LaFeO₃ sample was enhanced by vacancy doping. The value of Mₛ of the sample La₀.₉₈□₀.₀₂Fe₀.₉₈□₀.₀₂O₃ increased by a factor 1.9 than that of sample LaFeO₃. The investigated samples have semiconductor-like behavior as clear from the increase in the conductivity with raising the temperature and the values of activation energies. The main conduction mechanisms in the investigated samples are the small polaron tunneling (SP) and the correlated barrier hopping (CBH).

Keywords Perovskites · LaFeO₃ · Nanoparticles · Vacancy substitution

1 Introduction

The perovskite materials have a general formula of ABO₃, where A is a rare earth element and is coordinated by 12 oxygen anions. While B cation is a 3d transition metal and coordinated to six oxygen anions. Metals with different oxidation states can be replaced by the metal ions at the A and B sites due to the great stability of the ABO₃ materials [1]. Thus, novel materials can be designed with various properties for different applications.

Lanthanum orthoferrite (LaFeO₃) has a perovskite structure with space group Pbnm and has attracted great interest due to its unique physical and chemical properties. LaFeO₃ has G-type antiferromagnetic (AFM) behavior with a Neél temperature (Tₑ) ~ 730 K [2]. The ordering of ferroelectric or antiferroelectric dipole moments determines the electrical properties of LaFeO₃. The < FeO₆ > octahedron in LaFeO₃ drives the coexisting magnetic and electrical configurations. The perovskite LaFeO₃ was synthesized using different methods such as electrochemical [3], solid-state [4], and sol–gel combustion [5, 6] techniques. LaFeO₃ was prepared in nano scale easily using the citrate nitrate combustion method [7].

The perovskite structure ABO₃ contains an equal amount of A and B site cations (i.e., the A/B cation ratio = 1). When the A/B cation ratio is deviated significantly from unit, the perovskite lattice structure can still be stable. Introduction of the vacancy on both A and B cation sites tilts the < BO₆ > octahedron. The octahedral tilting lowers the coordination number of the A cation from 12 to 8 [8], reducing the tension in A–O bonds and increasing lattice energy. The presence of an octahedral tilting distortion affects not only the crystal structure, but also has a profound influence on the physical properties such as electrical conductivity, magnetic superexchange interactions and other electrical properties [9]. The nonstoichiometric A-site cation perovskite ABO₃ were developed as cathodes for solid-oxide fuel cells (SOFCs) and improve the oxygen reduction reaction (ORR) activity at high temperatures [10, 11].

Spinicci et al. [12] were prepared La₁₋ₓFeO₃ (3–1.5ε) with ε = 0.0, 0.1, 0.2, 0.3 using thermal low-temperature decomposition, a method which ensures a high surface area. La₁₋ₓFeO₃ (3–1.5ε) have been used in catalytic methane combustion in the range 300–450 °C. Scafetta et al. [13] have studied the effect of La and Fe deficiency on the ε-axis...
lattice parameter and optical absorption in La$_{1-x}$Fe$_{1.3}$O$_{3.6}$ films. Fe vacancies expanded out-of-plane lattice parameters while La deficiency leads to an increase in absorption throughout the spectral range probed. Zhu et al. [14] prepared the A-site cation deficient perovskites (La$_{0.9}$Fe$_{1.8}$O$_3$) by a simple and cost-effective process. La$_{0.9}$Fe$_{1.8}$O$_3$ samples have highly-efficient bifunctional electrocatalysts for ORR and oxygen evolution reaction (OER) in alkaline solutions.

Arman et al. [15] were investigated the effect of cation deficiency on NdFeO$_3$. The self-doped vacancies on A and B sites of NdFeO$_3$ increased the saturation magnetization ($M_s$) of the sample Nd$_{0.97}$Fe$_{1.03}$O$_3$ by 1.5 times more than the parent sample NdFeO$_3$. The antiferromagnetic properties of NdFeO$_3$ perovskites were originated from magnetic interactions such as Nd–Nd, Nd–Fe, and Fe–Fe. While LaFeO$_3$ has Fe–Fe magnetic interaction only. The difference in ionic radii of La$^{3+}$ ion (1.216 Å) and that of Nd$^{3+}$ ion (1.163 Å) affects the tolerance factor and tilting of $<BO_6>$ octahedron.

In this present work, we studied the effect of vacancy co-doping on the physical properties such as the magnetic and dielectric properties of LaFeO$_3$ nanoparticles. The substitution of the vacancy on both A and B cation sites simultaneously is influenced by the structure, morphology and all physicochemical properties of the samples. The introduction of vacancy on A and B-cation vacancies in LaFeO$_3$ enhanced Fe–Fe magnetic interaction and improved the hybridization between the La 3d and O 2p states. Furthermore, the presence of La and Fe defects increases the specific surface area. The vacancy doped samples are more applicable in many applications, such as the heavy metal removal from wastewater, cathode catalysts for lithium-oxygen (Li–O$_2$) batteries [16–18].

2 Experimental techniques

The perovskite samples La$_{1-x}$Fe$_{1.3}$O$_{3}$, (0.0 ≤ y ≤ 0.02, step 0.01) were prepared by citrate nitrate combustion method [14, 16]. The precursor metal nitrates (purity 99.9%, Sigma–Aldrich) were mixed in stoichiometric ratios with an equivalent molar ratio of citric acid in aqueous medium to enhance the homogeneous mixing. To produce La and Fe vacancies, the La(NO$_3$)$_3$·6H$_2$O and Fe(NO$_3$)$_3$·9H$_2$O are stoichiometrically decreased by 1% and 2% to generate non-stoichiometric La and Fe defects [12, 16]. To ensure complete complexation, the pH value was adjusted to 7 using the ammonia solution as a fuel. The (citric acid/nitrate) ratio is kept constant for all samples and is equal to 1. The samples were heated on a hot plate to obtain the final product that gives a fluffy powder with a single-phase orthorhombic structure. Thermal dehydration resulted in a highly viscous liquid. The citrate nitrate combustion method is simple, low cost, and quick.

X-ray powder diffraction (XRD) was carried out to study the crystal structure of the samples using a Proker D8 advanced X-ray diffractometer with Cu-K$_\alpha$ radiation ($\lambda$ = 1.5418 Å). The crystalline phases of the samples were identified using the International Centre for Diffraction Data (ICDD) card number 74–2203.

The samples were characterized by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) to study the morphology of the samples using OXFORD INCA PentaFETX3–England. The shape and size of the particles were studied using a high-resolution transmission electron microscope (HRTEM) model (JEOL-2100). The magnetic properties of the samples were studied by two techniques: the first is the H–M hysteresis loop using a vibrating sample magnetometer (VSM; 9600–1 LDJ, USA) with a maximum applied field of 20 kOe at room temperature. While the second technique is measurements of dc magnetic susceptibility ($\chi_M$) using Faraday’s method [19] at different magnetic field intensities as a function of absolute temperature.

The powdered samples were pressed to obtain pellets using a press of value $8 \times 10^5$ N/m$^2$ [7]. The two surfaces of each pellet were checked for good conduction by coating the surfaces with silver paste. The electrical properties were measured on pellets of samples using the LCR meter (Hioki model 3532 Japan). The dielectric constant ($\varepsilon'$) and ac conductivity of the samples were measured as a function of temperature in the frequency range 100 Hz to 5 MHz. The data was triplet and taken the average value.

3 Results and discussion

Figure 1 illustrates the XRD patterns of the samples that have the formula of La$_{1-x}$Fe$_{1.3}$O$_{3}$, (0.0 ≤ y ≤ 0.02, step 0.01). The prepared samples were crystallized in a single phase orthorhombic structure with space group Pbnm. The data was indexed with ICDD card number 74–2203. The main peak (100%) of LaFeO$_3$ is observed for (200) plane at $2\theta$ = 34.5°. The lattice parameters (a, b and c) were calculated based on orthorhombic unit cell from Eq. (1) and listed in Table 1. The crystallite size ($L$) was determined using Scherrer’s equation which is given by Eq. (2). [20]

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

(1)

$$L = \frac{0.9\lambda}{\beta \cos \theta}.$$

(2)
where \( L \) is the average crystallite size, \( \theta \) is the Bragg angle, \( \lambda \) is the wave length of the X-ray radiation (\( \lambda = 1.5406 \) Å), and \( \beta \) is the full width at half maximum intensity of the powder pattern peak. The values of \( L \) were listed in Table 1 and indicated that the samples are prepared in nano scale.

The crystallite size (\( L_{WH} \)) of the samples and the average lattice strain (\( \varepsilon \)) were calculated using the well-known Williamson–Hall equations [21]:

\[
\beta \cos \theta = 4 \varepsilon \sin \theta + \frac{K \lambda}{L_{WH}},
\]

where \( K \) is the dimensionless shape factor (\( K = 0.9 \)) and \( \theta \) is the Bragg angle. Figure 2 illustrates the relation between \( \beta \cos \theta \) and \( 4 \sin \theta \). The value of \( \varepsilon \) was determined from the slope of the plot in Fig. 2 and reported in Table 1. The crystallite size (\( L_{WH} \)) was calculated from the intercept of the fitting line with y-axis and its values confirm that the samples were crystallized in nano scale. The W–H plot shows the negative value of the strain and indicates the compressive nature of it which leads to lattice shrinkage [18].

The unit cell volume and the theoretical density were calculated using the following equations, respectively.

\[
V = abc \tag{4}
\]

\[
D_x = \frac{ZM}{N_A V}, \tag{5}
\]

where \( Z (Z=4) \) is the number of molecules per unit cell, \( N_A \) is the Avogadro’s number, \( M \) is the molecular weight, and \( V \) is the unit cell volume. The values of \( D_x \) of the vacancy-doped samples are less than that of \( \text{LaFeO}_3 \) owing to the decrease of \( \text{La}^{3+} \) and \( \text{Fe}^{3+} \) content with investigated samples. The values of experimental density were calculated using the relation \( D_{exp} = \frac{m}{V} \) and reported in Table 1. The values of \( D_{exp} \) are smaller than the theoretical density owing to oxygen deficiency.

The tolerance factor was calculated using the following equation [22]:

\[
t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}, \tag{6}
\]

### Table 1

| Samples | \( a \) (Å) (0.0001) | \( b \) (Å) (0.0001) | \( c \) (Å) (0.0001) | \( V \) (Å³) (0.1) | \( D_x \) (g/cm³) (0.0002) | \( D_{exp} \) (g/cm³) (0.0002) | \( L \) (XRD) (nm) (0.5) | \( L_{WH} \) (nm) | \( L \) (HREM) (nm) (0.5) | \( \varepsilon \) \( 10^{-4} \) | \( t \) (0.0002) |
|---------|----------------|----------------|----------------|--------------|-----------------|----------------|----------------|-----------|----------------|----------------|---------|
| \( x=y=0.00 \) | 5.5372 | 5.6066 | 7.8471 | 243.615 | 6.6182 | 2.8660 | 34 | 25 | 29 | 5.645 | 0.9550 |
| \( x=y=0.01 \) | 5.5525 | 5.5575 | 7.8116 | 240.804 | 6.0334 | 5.3969 | 26 | 22 | 38 | 6.265 | 0.9531 |
| \( x=y=0.02 \) | 5.5615 | 5.5457 | 7.8505 | 242.132 | 5.9578 | 2.4812 | 28 | 24 | 62 | 5.884 | 0.9514 |

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Fig. 1 XRD of the samples \( \text{La}_{1-x} \square \text{Fe}_x \square \text{O}_3 \) as compared with ICDD card number 74–2203. The main peak (100%) is observed for (200) plane at \( 2\theta = 34.5° \).

Fig. 2 The Williamson–Hall plot for \( \text{LaFeO}_3 \) sample. The crystallite size (\( L_{WH} \)) was calculated from the intercept of the fitting line with y-axis.
where \( r_A \), \( r_B \) and \( r_O \) are the ionic radii of the A, B and oxygen ions respectively. The values of tolerance factors were listed in Table 1. The tolerance factor \((t)\) is less than 1 which indicates that tilting of the \(<BO_6>\) octahedra occurs for all the samples. The tolerance factor indicates the orthorhombic structure of the samples \(La_{1-x}Fe_yO_3\) and these results agree with the data obtained from XRD analysis. The values of the tolerance factor decrease with increasing the vacancy content \((x \text{ and } y)\) at the expense of \(La^{3+}\) and \(Fe^{3+}\) ions, which means that the distortion of the perovskite unit cell increases. This means that the \(Fe-O-Fe\) angle decreases with increasing the vacancy content \((x \text{ and } y)\). On the other hand, the tilting angle decreases. Besides, the values of \(t\) \((0.9550 < t < 0.9514)\), indicated that the structure distorts.

To confirm the chemical composition of the samples, the energy dispersive spectroscopy EDS analysis was performed. Table 2 illustrates the EDS data of the investigated samples. The figure shows that the prepared samples are nearly equal to the starting chemical composition without any noticeable impurities. The weight percentage (wt%) of elements \((La, Fe, \text{ and } O)\) are calculated theoretically from the chemical formula \(La_{1-x}Fe_yO_3\), \((0.0 \leq y, x \leq 0.02, \text{ step } 0.01)\) and that obtained from EDS elemental analysis are shown in Table 2. The results confirm that the chemical composition is very close to the nominal one. The small variation between the values of weight percentage \((\text{wt%})\) \((La, Fe, \text{ and } O)\) due to oxygen deficiency and converting some \(Fe^{3+}\) to \(Fe^{2+}\).

| Elements | (a) \(LaFeO_3\) | (b) \(La_{0.99}Fe_{0.01}O_3\) | (c) \(La_{0.98}Fe_{0.02}O_3\) |
|----------|----------------|----------------|----------------|
|          | Weight percentage (wt%) | Weight percentage (wt%) | Weight percentage (wt%) |
| From EDX | Theoretically | From EDX | Theoretically | From EDX | Theoretically |
| O K      | 23.39          | 19.77       | 21.82         | 19.93       | 19.28         | 20.10         |
| Fe K     | 20.95          | 23.01       | 23.23         | 22.96       | 23.36         | 22.91         |
| La L     | 55.66          | 57.22       | 54.94         | 57.11       | 57.36         | 56.99         |

Figure 3 shows HRTEM images of the samples \(La_{1-x}Fe_{1-y}O_3\). The images illustrate the orthorhombic structure of nanocrystalline samples. The values of particle size were listed in Table 1 and indicated that the samples were prepared in nano scale. The values of particle size agree with those obtained from XRD. The particles are agglomerated as shown in Fig. 3 owing to the magnetic properties of the samples. Different brightness from one crystal lattice to another appears as a result of different orientations of the crystal structure. The insets in Fig. 3 show the d-spacing of the investigated samples with values 0.26, 2.5 and 0.49 nm of the samples \(La_{1-x}Fe_{1-y}O_3\), \((0.0 \leq x \text{ and } y \leq 0.02, \text{ step } 0.01)\), respectively. The selected area electron diffraction (SAED) pattern of the investigated samples is illustrated in the insets in Fig. 3. The patterns show the good crystallinity of the samples.

Figure 4 shows the relation between the molar magnetic susceptibility \((\chi_M)\) and the absolute temperature for \(LaFeO_3\) nanoparticles. The sample has antiferromagnetic behavior where the values of \(\chi_M\) decreased rapidly with temperature until the Néel temperature then decreased slowly with temperature. The magnetic interactions originated from the superexchange interaction between the \(Fe^{3+}\) ions, while there is no magnetic interaction between \(La^{3+}\) ion and \(Fe^{3+}\) ion because \(La^{3+}\) ion is not magnetic. By increasing the vacancies in the sample, the tilting of \(<FeO_6>\) octahedron increases, leading to a weak ferromagnetic ordering along with other crystal directions [23].

The comparative study between the vacancy doped samples in the molar magnetic susceptibility at the magnetic field intensity 1100 Oe is illustrated in Fig. 5. \(\chi_M\) increases with increasing the vacancies on the A and B sites. The reasons for the increase of \(\chi_M\) are:

1. Some of the \(Fe^{3+}\) ions convert to \(Fe^{4+}\) ions, which create the three magnetic interactions (antiferromagnetic between \(Fe^{3+}-Fe^{3+}\) and \(Fe^{4+}-Fe^{4+}\), ferromagnetic between \(Fe^{3+}-Fe^{4+}\)).

2. The tilting of \(<FeO_6>\) octahedron affects the bond length and strength between Fe–O ions.

The Curie–Weiss law is satisfied in the investigated samples. The straight lines in the paramagnetic region of \(LaFeO_3\) sample at 1100 Oe in the temperature range of 850–910 K are shown in Fig. 6.[15] The values of the Curie constant \((C)\), Curie–Weiss constant \((\theta)\), and the effective magnetic moment \((\mu_{eff})\) are calculated from the reciprocal of magnetic susceptibility with absolute temperature and reported in Table 3 using the following equations:

\[
C = \frac{1}{\text{slope}} \quad (7)
\]

\[
\mu_{eff} = 2.83\sqrt{C}. \quad (8)
\]
The presence of a ferromagnetic component in the samples was illustrated by the positive values of $\theta$. The Néel temperature of the samples was determined from the plots of $(dM/dT)$ vs $T$ where $M$ is the magnetization.

Figure 7 illustrates the hysteresis loops of the samples $\text{La}_{1-x}\square_x\text{Fe}_{1-y}\square_y\text{O}_3$, $0.0 \leq x, y \leq 0.02$, step 0.01) at room temperature. The S-shape of the hysteresis loops indicates the presence of a weak ferromagnetic component in addition to the main antiferromagnetic order in the samples. The
magnetic parameters such as saturation magnetization \( M_s \) and remnant magnetization \( M_r \) are listed in Table 4. The value of saturation magnetization \( M_s \) of LaFeO\(_3\) agrees with the data published by Gabala et al. [24]. The magnetization of the LaFeO\(_3\) sample was enhanced by vacancy doping. The value of \( M_s \) of the sample La\(_{0.98}\)Fe\(_{0.02}\)O\(_3\) increased by the factor 1.9 compared with the sample LaFeO\(_3\). The improvement of magnetic parameters for vacancy doped samples can be ascribed to several reasons as follows: (i) The tilting of \( <\text{FeO}_6> \) induces a variation in the Fe–O–Fe bond angle and distance; (ii) The existence of Fe\(^{3+}\) (HS) \((t_2^g \epsilon_g^2)\) and Fe\(^{4+}\) ions in high spin state (HS) Fe\(^{4+}\) \((t_2^g \epsilon_g^3)\) [7].

The inset in Fig. 7 illustrates the hysteresis loop of the parent sample (LaFeO\(_3\)) has a clear shift from the origin due to the exchange bias effect. The exchange bias field \( (H_{EB}) \) was calculated using Eq. (9):

\[
H_{EB} = - (H_{left} + H_{right})/2.
\]  

where \( H_{left} \) and \( H_{right} \) are the intercept of the magnetization on the −ve and +ve on the \( H \)-axis. The values of exchange bias were reported in Table 4. The exchange bias is present due to the exchange coupling between the ferromagnetic-like shell and the antiferromagnetic core in the nanoparticle [25].

Figure 8 illustrates the dependence of the dielectric constant on the absolute temperature of the sample La\(_{0.99}\)Fe\(_{0.01}\)O\(_3\). The trend of \( \varepsilon' \) of the sample is the general trend of dielectric materials where \( \varepsilon' \) increases with increasing the temperature and decreases with increasing the frequency.

Figure 9 shows the dependence of \( \ln\sigma \) on the reciprocal of absolute temperature \((1000/T)\) as a function of frequencies for the sample La\(_{0.98}\)Fe\(_{0.02}\)O\(_3\). The trend data obeys the well-known Arrhenius equation [26]:

\[
\sigma = \sigma_0 \exp (-E/kT),
\]  

where \( E \) is the activation energy, \( k \) is the Boltzmann’s constant and \( T \) is the absolute temperature. The presence of two different straight lines indicates the presence of two conduction mechanisms in the investigated samples. The activation energies were calculated and reported in Table 5 using the Arrhenius equation at frequency 5 MHz. The activation energy in the high temperature region \((E_{II})\) is greater than that of low temperature \((E_I)\). The presence of two activation energies is due to the presence of two conduction mechanisms, which are the small polaron (SP) tunneling and the correlated barrier hopping (CBH) as shown in the next section.

The samples have semiconducting like behavior as clear from the increase in the conductivity with an increase of temperature. The values of activation energies confirm the semiconducting trend of the samples. The cation deficient in perovskite LaFeO\(_3\) played an important role in the enhancement of the conductivity. Introducing of vacancies in LaFeO\(_3\) leads to formation oxygen deficiency and converting

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**Table 3** Values of the Curie constant (C), the Curie–Weiss constant \( (\theta) \), the effective magnetic moment \( (\mu_{\text{eff}}) \) and the Neel temperatures of the samples La\(_{1-x}\)Fe\(_x\)O\(_3\) at magnetic field intensity of 1100 Oe

| Samples | C (emu/g·mol K\(^{-1}\)) | \( \theta \) (K) | \( \mu_{\text{eff}} \) (B.M.) | \( T_N \) (K) |
|---------|----------------|----------------|-----------------|------------|
| LaFeO\(_3\) (parent) | 5.42 | 655 | 6.58 | 845 |
| La\(_{0.99}\)Fe\(_{0.01}\)O\(_3\) | 2.92 | 800 | 4.83 | 833 |
| La\(_{0.98}\)Fe\(_{0.02}\)O\(_3\) | 5.88 | 770 | 6.86 | 824 |

Fig. 6 Dependence of the reciprocal molar magnetic susceptibility in paramagnetic region for LaFeO\(_3\) at magnetic field intensity 1100 Oe

**Table 4** Values of the saturation magnetization \( (M_s) \), the coercive field \( (H_c) \), the remanence magnetization \( (M_r) \) and the exchange bias field \( (H_{EB}) \), for the samples

| Samples | Positive \( M_s \) (0.01) (emu/g) | Negative \( M_s \) (0.01) (emu/g) | Positive \( H_c \) (Oe) | Negative \( H_c \) (Oe) | Positive \( M_r \) (0.01) (emu/g) | Negative \( M_r \) (0.01) (emu/g) | \( H_{EB} \) (0.01) |
|---------|---------------------------------|---------------------------------|----------------|----------------|---------------------------------|---------------------------------|-------------|
| \( x=y=0.00 \) (parent) | 1.52 | 0 | 1.60 | 0 | 295.78 | 0 | -70.79 | 0.14 | -0.23 | -112.49 |
| \( x=y=0.01 \) | 2.54 | 0 | 2.54 | 0 | 143.34 | 0 | -145.61 | 0.33 | -0.33 | 1.13 |
| \( x=y=0.02 \) | 2.84 | 0 | 2.83 | 0 | 159.28 | 0 | -162.95 | 0.43 | -0.42 | 1.84 |
some of Fe$^{3+}$ ions to Fe$^{4+}$ ions (t$_{2g}$ 3 e$_{g}$ 1 configuration). This will bring a localized electronic structure and lead to an inherent semiconductor nature [16].

Figure 10 illustrates the dependence of ln$\sigma$ on ln$\omega$ at different temperatures. The relation between ln$\sigma$ and ln$\omega$ obeys the universal power law. [27]

$$\sigma_{ac}(\omega) = A\omega^S,$$  \hspace{1cm} (11)

where $\sigma_{ac}$ is the ac conductivity, $\omega = 2\pi f$ is the angular frequency, $A$ is a temperature dependent constant and $S$ is the frequency dependent exponent. Figure 11 shows the relation between the frequency exponent factor ($S$) and $T$. In the 1st temperature region (300–450 K), the increase of $S$ with $T$ which indicates the small polaron (SP) tunneling in this region. This originated from converting some of the Fe$^{3+}$ to Fe$^{4+}$ ions, also, the electron conduction in perovskite-type ferrites takes place through Fe$^{4+}$–O–Fe$^{3+}$ [28]. While in the 2nd temperature region (450–800 K), $S$ decreases with $T$ which illustrates that the correlated barrier hopping (CBH) is the main mechanism. The electrons accept enough energy to hop between the O 2p and the Fe 3d orbitals. The hopping of electrons is affected by the Fe–O distance and the Fe–O–Fe angle. The values of the activation energy ($E_{II}$) increased in the off-stoichiometric samples owing to the presence of oxygen vacancies [13].

Table 5 Values of the activation energy $E_{II}$ (at high temperature region) and $E_I$ (at low temperature) of the samples La$_{1-x}$□$_x$Fe$_{1-y}$□$_y$O$_3$ at frequency 5 MHz

| Samples                  | $E_I$ (eV) (0.01) | $E_{II}$ (eV) (0.01) |
|--------------------------|-------------------|----------------------|
| LaFeO$_3$                | 0.17              | 1.05                 |
| La$_{0.99}$□$_{0.01}$Fe$_{0.99}$□$_{0.01}$O$_3$ | 0.16              | 1.57                 |
| La$_{0.98}$□$_{0.02}$Fe$_{0.98}$□$_{0.02}$O$_3$ | 0.16              | 1.70                 |
**Conclusion**

Orthoferrite of formula La$_{1-x}$□$_x$Fe$_{1-y}$□$_y$O$_3$, (0.0 ≤ $y$, $x$ ≤ 0.02, step 0.01) were well synthesized using the citrate combustion technique. XRD revealed that the investigated samples crystallized in a single phase orthorhombic structure with space group Pbnm. The particle size of LaFeO$_3$ increased gradually with increasing the vacancy content. The magnetic hysteresis loops indicate the antiferromagnetic properties of the samples. $\chi$M of La$_{0.98}$□$_{0.02}$Fe$_{0.98}$□$_{0.02}$O$_3$ increased by a factor 1.7 times more than of LaFeO$_3$ sample. The investigated samples have semiconducting-like behavior as clear from the increase in the conductivity with the temperature and the values of activation energies. The small polaron tunneling (SP) and the correlated barrier hopping (CBH) are the main conduction mechanisms in the samples.

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**Declarations**

**Conflict of interest** All authors declare that they have no conflict of interest.

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