Dielectric properties of calcium-substituted lanthanum ferrite

Refka Andoulsi-Fezei, Nasr Sdiri, Karima Horchani-Naifer and Mokhtar Férid

Physical Chemistry Laboratory of Mineral Materials and Their Applications, National Center of Research in Material Sciences Technopole Borj Cedria, Soliman, Tunisia

ABSTRACT

Among \( \text{La}_{1-x}\text{Ca}_x\text{FeO}_3-\delta \) (\( 0 \leq x \leq 0.5 \)) compounds, the optimal value of the direct current conductivity was registered for a 20% substituted amount. We therefore attempted to study the impedance and dielectric properties of 20% calcium-substituted lanthanum ferrite. We investigated the electric properties in depth between 5 Hz and 13 MHz from 350 to 800°C. The results reveal interesting properties. Indeed, the perovskite shows a huge dielectric constant which promotes its utilization in high-performance dielectric material applications. At a given temperature, \( \varepsilon' \) and \( \tan(\delta) \) decrease with increases in frequency. This trend was explained based on the Maxwell Wagner polarization model. The variations in dielectric loss (\( \varepsilon'' \)) with frequency obey the Giuntini theory based on the hopping model. As the temperature increases from 350 to 800°C, the binding energy increases from 0.22 to 0.34 eV, while the minimum hopping distance decreases from 2.16 to 0.12 pm. Consideration of the electric modulus analyzes showed that the relaxation mechanism is dominated at below 400°C by a short-range movement of charge carriers, whereas at above that temperature, a long-range movement of charge carriers is dominant. This study presents a solid foundation for the polarization and dielectric properties of lanthanum ferrite, which is a lead-free, environmentally friendly material and a promising candidate for use in nonlinear optical applications and microwave devices.

1. Introduction

Semiconducting materials have been the focus of many studies due to their integral role in the micro-electronic industry [1]. Among these, lanthanum ferrite, \( \text{LaFeO}_3 \), is an important inorganic compound known for its diverse applications in the field of electronics. It crystallizes into an orthorhombic distorted perovskite structure and is characterized by its rich properties and potential applications in solar cells, capacitors and sensors [2–4]. Over the past few years, increased efforts have been devoted to the synthesis and characterization of this ferrite [5–7]. In fact, researchers have emphasized the importance of the experimental parameters and their preponderant role in obtaining functional lanthanum ferrite. At the same time extensive research has proposed various
alternatives to not only improve the electrical properties of LaFeO$_3$ but also of others such as its magnetic and optical properties. Among the methods adopted, we can mention the isostructural or isovalent substitution of lanthanum or iron ions. In fact, a thorough survey of the literature revealed that Na$^+$, Al$^{3+}$, Pb$^{2+}$, Zn$^{2+}$ constitute suitable substituents in LaFeO$_3$. Indeed, the introduction of Na$^+$ resulted in a great enhancement of the dielectric constant ($\varepsilon'$) to $10^2$ at 100 Hz. However, high loss was registered [8]. In other studies, the effect of antimony doping was investigated by Berchmans et al. [9]. The authors proved that for each Sn$^{2+}$ amount, the samples showed a decreasing trend of $\varepsilon'$ with increases in frequency. Furthermore, bismuth was successfully incorporated into the LaFeO$_3$ lattice. $\varepsilon'$ and $\sigma_{ac}$ decreased with increases in the Bi content up to 10% and then increased. The authors suggested that the La$_{0.9}$Bi$_{0.1}$FeO$_3$ compound is promising for its electric properties [10]. Other studies have paid attention to Al$^{3+}$-substituted LaFeO$_3$. It was shown that both $\varepsilon'$ and $\varepsilon''$ increase with increases in temperature and that there is no anomaly in these variations [11]. Further, it was also demonstrated that Pb$^{2+}$ substituted compounds exhibit colossal dielectric permittivity and multiple relaxations [12].

Apart from lanthanum substitution, the introduction of isovalent or heterovalent cations to the iron site seems to be interesting. In fact, we have already studied the influence of zinc incorporation in a previous work. Promising results were obtained and a significant conductivity improvement with the substitution reported [13]. Titanium-substituted ferrites, on the other hand, exhibit an enormous dielectric constant of between $5.10^3$ and $11.10^3$ at 100 Hz [14]. Likewise, Idrees et al. [15] investigated the conduction and relaxation phenomena of LaFe$_{0.9}$Ni$_{0.1}$O$_3$ between 1 Hz and 10 MHz. They proved that at below 296 K, variable-range hopping is adequate to describe the conductivity. However, small polaron hopping becomes a suitable parameter at above that temperature.

La$_{1-x}$Ca$_x$FeO$_{3-\delta}$ compounds are of great interest due to their various and interesting properties. In fact, many reports on their magnetic and catalytic properties are available in the literature [16–18]. However, their dielectric properties have been less investigated. In our previous work, we studied the structural and electrical properties of La$_{1-x}$Ca$_x$FeO$_{3-\delta}$ (0 ≤ x ≤ 0.5) compounds and determined motivating results [19,20]. Of particular note, the direct current conductivity optimal value was registered for the 20% substituted amount. In this regard, we attempted in the present work to study the dielectric behavior of La$_{0.9}$Ca$_{0.1}$FeO$_{3-\delta}$ using complex impedance spectroscopy. The variations in their dielectric parameters with temperature and frequency are reported, in particular. The investigation of the dielectric properties of Ca$^{2+}$-substituted ferrites is intriguing due to the fact that these compounds are lead-free, environmentally friendly materials and easily synthesized in their pure form.

2. Experimental

La$_{0.9}$Ca$_{0.2}$FeO$_{3-\delta}$ powder was synthesized by the polymerizable complex method. We have already detailed the experimental procedure for lanthanum ferrite preparation in a previous report [21]. Lanthanum nitrate (La(NO$_3$)$_3$.6H$_2$O, FLUKA, 99%), iron nitrate (Fe(NO$_3$)$_3$.9H$_2$O, MERCK, 99%), calcium nitrate (Ca(NO$_3$)$_2$.4H$_2$O, FLUKA, 99%), anhydrous citric acid (C$_6$H$_8$O$_7$.2H$_2$O, Renal Budapest, 99.8%) and ethylene glycol (C$_2$H$_4$O$_2$, Prolabo, 99.8%) were used as raw materials. Stoichiometric amounts of the nitrates were dissolved in distilled water. Citric acid and ethylene glycol were added, and the resulting solution was heated at 130°C, dried at 300°C and calcined at 900°C.

The powder was identified using an X-ray diffractometer (Siemens D500) operating with CuK$\alpha$ radiation at room temperature from 5 to 80°.

For the electrical measurement, the calcined powder was pressed into pellets using a uniaxial pressure system under 8 t. The pellets' diameter was 13 mm and their thickness was 2 mm. They were then sintered at 900°C for 2h in atmospheric air and cooled down to room temperature. After sintering, both sides of the pellets were polished and two platinum plates were used as electrodes. Impedance measurements were then carried out using a computer-controlled impedance analyzer (HP4192A) operating at between 5 Hz and 13 MHz. The temperature was varied from 350 to 800°C.

3. Results and discussion

3.1. XRD analyses

Figure 1 presents an X-Ray diffractogram of the synthesized powder. A single perovskite phase was obtained at 900°C. The XRD pattern was analyzed using X’Pert High Score Plus software. The objective was to determine the lattice parameters of the perovskite phase and the adequate space group. The first step consisted of determination of the peak positions and both the absolute and relative maximum intensities of the reflections. The experimental diffractogram was then compared with the ICDD (International Center for Diffraction Data) reference base data. All the diffraction peaks in Figure 1 matched well with the ICDD PDF 74–2203. The next step was indexation of the reflections and determination of the lattice parameters. For this purpose, we used the DICVOL program integrated into the X’Pert High Score Plus software. The results thus obtained revealed that the Ca$^{2+}$-substituted
lanthanum ferrite crystallized into an orthorhombic unit cell with the Pbnm space group No. 62 and the cell parameters a = 5.501 Å, b = 5.511 Å and c = 7.822 Å.

3.2. Impedance spectroscopy analyses

3.2.1. Variations in the impedance real part with frequency and temperature

Figure 2(a) reports the evolution of the impedance real part $Z'$ with frequency. For each studied temperature, we can identify three distinct parts: one frequency-dependent part and two frequency-independent parts. As concerns the frequency-independent part, the $Z'$ behavior can be explained by pure resistance of the grains. For the frequency-dependent part, however, the resistance and capacitance of the grains contribute simultaneously to the observed response [22].

As regards the temperature effect, the $Z'$ values decreased with increases in temperature in both the low- and high-frequency ranges. This behavior was attributed to thermally activated conductivity. At above 400 Hz, the $Z'$ values merged out regardless of temperature. This can probably be explained by a release of the space charge. The latter resulted from a reduction in the material barrier properties with increases in temperature [23].

3.2.2. Variations in the imaginary impedance part with frequency and temperature

Figure 2(b) illustrates the evolution of the impedance imaginary part $Z''$ with frequency. For each temperature studied, $Z''$ increased with increases in frequency until attaining a maximum value ($Z''_{\text{max}}$), after which it decreased. The observed trend reveals an electrical relaxation phenomenon. As regards the temperature

Figure 1. XRD pattern of La$_{0.8}$Ca$_{0.2}$FeO$_{3-\delta}$ oxide.

Figure 2. (a) Variations in the real part of impedance with frequency at different temperatures (b) Variations in the imaginary part of impedance with frequency at different temperatures.
effect, every peak intensity decreased with increases in temperature. The reason behind this behavior was a decrease in the samples’ resistance with increases in temperature. On the other hand, the relaxation peak was observed to broaden with increases in temperature, revealing a thermal relaxation process [24].

Figure 3(a) displays the normalized spectra ($Z'/Z''_{\text{max}}$) as a function of frequency at different temperatures. The results reveal a clear overlapping of all the curves, suggesting that the relaxation dynamics are not affected by the temperature. This behavior implies that the same relaxation mechanism is occurring in the perovskite lattice. The fusion of all the spectra reveals a possible release of the space charge [25].

The activation energy of the relaxation units ($E_r$) can be calculated from the linear fit of the experimental data in Figure 3(b) using the following Arrhenius relation [26]:

$$f_{\text{max}} = f_0 \exp \left( - \frac{E_r}{k_B T} \right)$$ (1)

where $f_0$ is a pre-exponential factor, $T$ the temperature and $k_B$ the Boltzmann constant.

From the slope of $\ln(f_{\text{max}})$ versus $(1/T)$ plot given in Figure 3(b), we determined $E_r$ to be 77 meV.

On the other hand, it is known that the activation energy values indicate the nature of the charge carriers involved in the dynamics of relaxation and conduction. In fact, when n-type polarons contribute to the process, the activation energy is lower than 0.2 eV. For p-type polarons, however it is higher than 0.2 eV [27]. As concerns the ionic contribution generally occurring via oxygen ions and vacancies, the activation energy is higher than 1 eV [28,29].

The value obtained for the activation energy in the present study indicated the existence of n-type polarons within the perovskite lattice. Electrons were therefore hopping between mixed valence state iron cations in octahedral coordination via oxygen vacancies. This process requires low activation energy. In fact, the energy barrier of electron hopping between mixed valence state iron cations was significantly lowered by the bridging effect of the ionized oxygen vacancies [30]. Similar behavior was reported by Mahato et al. [31].

### 3.3. Dielectric study

The impedance data were used to evaluate the dielectric behavior of the lanthanum ferrite using the following relations:

$$\varepsilon' = -\frac{z''}{\omega C_0 (z'^2 + z''^2)}$$ (2)

$$\varepsilon'' = -\frac{z'}{\omega C_0 (z'^2 + z''^2)}$$ (3)

where $\varepsilon'$ is the real permittivity part known as the dielectric constant and $\varepsilon''$ is the imaginary part known as dielectric loss, $\omega$ is the angular frequency and $C_0 = \varepsilon_0 \frac{A}{e}$ is the empty cell capacitance ($\varepsilon_0$ is the vacuum permittivity, $A$ the cross-sectional area of the pellet surface and $e$ its thickness).

#### 3.3.1. Variations in $\varepsilon'$ with frequency and temperature

The dielectric constant values are plotted as a function of frequency at different temperatures in Figure 4(a). At 350°C, $\varepsilon'$ varied between 22527 (at 5 Hz) and 350 (at 13 MHz). For any given temperature, it is seen that $\varepsilon'$ decreased slowly with increases in frequency up to 200 Hz. At above this frequency value, a very sharp decrease is recorded. Thereafter, $\varepsilon'$ attained a constant value. A similar trend was observed for all the temperatures studied.

---

**Figure 3.** (a) Normalized spectra ($Z'/Z''_{\text{max}}$) as a function of frequency at different temperatures (b) Plot of $\ln(f_{\text{max}})$ versus $1/T$ for $\text{La}_{0.8}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$. 

---

**Figure 4.**
At low frequencies, high dielectric constants were obtained. These probably emanated from the space charge and the Maxwell Wagner polarization processes. The first type of polarization originates from the presence of free charges built up at the interface between the sample and the electrodes, while the second is created by the free charges present at the interface within the sample bulk [32,33]. To further support these observations, we replotted our data based on the universal dielectric response model [33]. Under these conditions, the charge carriers’ hopping between spatially fluctuating lattice potentials not only produces conductivity but also gives rise to the dipolar effect. We therefore plotted $\ln(f'\varepsilon')$ versus $\ln(f)$ for some selected temperatures in Figure 4(b). As shown, the fitting curves follow a linear behavior in the studied frequency range. On the basis of the results obtained, we can conclude that Maxwell-Wagner polarization and space charges are the main factors contributing to the high $\varepsilon'$ observed at low frequency.

Hence, the observed trend in Figure 4(a) can be understood as follows: in the low frequency region, dipoles align themselves with the applied field direction and polarize the studied lanthanum ferrite. When the frequency increases, variations in the electric field become so rapid that the dipoles cannot follow them and the polarization is decreased [34]. This behavior is reflected in Figure 4(a) by the decrease in $\varepsilon'$ in the high-frequency range. At above 3 kHz, all the dielectric curves merge out irrespective of temperature and $\varepsilon'$ tends toward zero.

It is interesting to note that an immense dielectric constant ($\varepsilon' > 10^3$) is obtained over a broad temperature range for the $La_{0.8}Ca_{0.2}FeO_{3.4}$ perovskite. Since the dielectric constant is proportional to the refractive index squared ($n^2$) [35,36], lanthanum ferrite is clearly a promising candidate in the field of nonlinear optics such as optical fibers [37] and Simulated Raman Scattering devices [38].

It is worth noting, moreover, that the immense dielectric constant obtained in this study is much larger than that reported in our previous study on pristine $LaFeO_3$ [39]. Indeed, for the substituted compound, $\varepsilon'$ is 18 times higher than that measured for the parent oxide. A possible explanation of this behavior is that calcium substitution produces more mixed valence state ions and defects and that these contribute to enhancement of $\varepsilon'$.

To investigate the dielectric behavior further, we attempt to propose the most likely dipole formation mechanism in $La_{0.8}Ca_{0.2}FeO_{3.4}$. In fact, understanding the polarization origin remains an important tool. Our efforts were therefore focused on funding an explanation for the electron exchange contributing to the observed dielectric trend.

In fact, ferrites are generally prepared at high temperatures. During the calcination stages, only a very small number of oxygen anions can be lost. This results in the creation of positively charged oxygen vacancies. These intrinsic defects are presented in the Kroger-Vink [40] notation according to the following equation:

$$O_0^+ \rightarrow \frac{1}{2} O_2 + V_0^- + 2e \quad (4)$$

where $O_0^+$ is an oxygen occupying the oxygen site in the lattice, $O_2$ oxygen gas and $V_0^-$ a doubly positively charged oxygen vacancy.

Additionally, electrons generated from Equation (4) may partially reduce the number of $Fe^{3+}$ cations, giving rise to $Fe^{2+}$ ions (Equation (5)).

$$Fe_{Fe}^{3+} + 1e \rightarrow (Fe_{Fe}^{2+}) \quad (5)$$

where $Fe_{Fe}^{3+}$ is a trivalent iron cation occupying the iron site in the lattice and $(Fe_{Fe}^{2+})$ an iron site carrying an effective negative charge due to the presence of $Fe^{2+}$.

The same $Fe^{3+}$ reduction mechanism was reported in our previous study on $LaFeO_3$ electric properties [39].

Apart from intrinsic oxygen vacancies, the lanthana num substitution would probably cause the formation of oxygen defects and iron ions in a tetravalent state. Indeed, to preserve electroneutrality, the substitution of a given cation by one with a lower valence can either decrease the number of oxygen anions, increase
Oxygen vacancies can arise from the substitution as follows:

$$2\text{CaO} + 2\text{La}^{3+} + \text{O}_2^x \leftrightarrow 2(\text{Ca}^{2+}) + V_0^x + \text{La}_2\text{O}_3$$

(6)

where \((\text{La}^{3+})\) is a trivalent lanthanum cation occupying the lanthanum site in the lattice and \((\text{Ca}^{2+})\) a lanthanum site carrying an effective negative charge due to the presence of \(\text{Ca}^{2+}\).

The oxygen vacancies formed according to Equation (6) are, moreover, in equilibrium with the atmospheric oxygen. This probably results in hole formation, as given by the following equation:

$$V_0^x + \frac{1}{2}\text{O}_2 \leftrightarrow 2\text{h}^* + \text{O}_2^x$$

(7)

Alternatively, the holes formed in the perovskite lattice may partially oxidize the trivalent iron cations to form \(\text{Fe}^{4+}\) ions. Equation (8) summarizes the reaction leading to tetravalent iron creation:

$$\text{Fe}^{3+} + \text{h}^* \leftrightarrow (\text{Fe}^{4+})^\gamma$$

(8)

where \((\text{Fe}^{4+})^\gamma\) is an iron site carrying an effective positive charge due to the presence of \(\text{Fe}^{4+}\).

In a similar fashion, we have proposed a mechanism for \(\text{Fe}^{3+}\) and oxygen vacancy formation in \(\text{Zn}^{2+}\)-substituted lanthanum ferrite [13]. As mentioned earlier, both \(\text{Fe}^{4+}\) and \(\text{Fe}^{3+}\) are present in the perovskite lattice. In these circumstances, one can determine the most probable dipoles that might be formed in the oxide. In fact, the presence of \(\text{Fe}^{2+}\) in \(\text{Fe}^{4+}\) sites creates a doubly negatively charged iron site noted as \((\text{Fe}^{4+})^\gamma\). The divalent iron in the \(\text{Fe}^{2+}\) sites will carry, in a similar way, one effective negative charge as \((\text{Fe}^{3+})^\gamma\). Consequently, the negatively charged sites may form dipoles with vacant oxygen sites as \((\text{Fe}^{4+})^\gamma - (\text{O})^\gamma\) and \((\text{Fe}^{3+})^\gamma - (\text{O})^\gamma\).

It is interesting to note that the singly ionized oxygen vacancies are formed during the sintering process. They are also retained in the structure even at room temperature [42]. The equation for \(V_0^x\) formation is given below:

$$V_0^x + \text{1e} \leftrightarrow V_0^\gamma$$

(9)

Kumar et al. [43] have also reported a similar mechanism of electric dipole formation in the case of lanthanum chromite.

With the application of the AC signal, the dipoles, already cited, can change their orientation. This is probably due to an electron exchange between divalent, trivalent and tetravalent iron cations \((\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+} \leftrightarrow \text{Fe}^{4+})\) or to hopping of oxygen ions between oxygen vacancies. When the applied field frequency increases, the electron exchange speed slows down and the charge carriers become increasingly localized. This results thereby in a decrease in the dielectric constant.

As concerns the temperature effect, Figure 5 shows an increase in \(\varepsilon'\) with temperature at 8 Hz. In fact, the dielectric constant increases from 2500 to 303,034 when the temperature rises from 350 to 800°C. The reason behind this behavior may be that the dipoles mentioned previously dissociate with increases in temperature. Charge carriers are then intercepted at the
grain boundaries due to their high resistance. As a result, barriers are formed at the grain-grain boundary interfaces, giving rise to a high dielectric constant.

On the other hand, the increase in the dielectric constant with temperature is due to the effect of the mixed valence occupation (Fe$^{3+}$, Fe$^{4+}$) of the B site of the perovskite lattice. This behavior induces a disturbance of the polar order at long distance (ferroelectric) resulting in the formation of polar nano regions [44,45].

It is reported, moreover, that the activation of oxygen vacancies in the perovskite lattice is temperature dependent [46]. In fact, the vacancies are blocked at low temperatures. As the temperature rises, however, they are thermally ionized. Therefore, the numbers of charge carriers and defects increase with increases in temperature. The latter are accumulated at the grain boundaries, resulting in enhancement of the interfacial and space charge polarization. This behavior supports the increase in the dielectric constant with temperature. Singh et al. [47] reported similar behavior for KNbO$_3$ perovskite oxide.

Furthermore, it is of interest to note that $\varepsilon''$ increases sharply from 2500 to 250,000 between 350 and 500°C, whereas the dielectric constant shows nearly thermal stability with further rises in temperature from 500 to 800°C. Such feature is important for high performance dielectric materials applications.

### 3.3.2. Variations in $\varepsilon''$ with frequency and temperature

Figure 6(a) depicts the evolution of the imaginary part of permittivity ($\varepsilon''$) with frequency at different temperatures. It is evident that $\varepsilon''$ for any given temperature decreases with increases in frequency. In the high-frequency range, $\varepsilon''$ is found to be almost independent of the AC field frequency. Similar behavior was also registered for pristine LaFeO$_3$. The latter exhibits dispersion in the low-frequency range, followed by a frequency-independent trend in the high-frequency range [39].

It is known that the origins of the dielectric loss are conduction losses, dipole relaxation losses and vibrational losses [48]. A close inspection of Figure 6(a) reveals that high values are obtained for $\varepsilon''$ at low frequencies. This behavior arises mainly from the contribution of charge carrier jumps, conduction loss and dipolar losses, whereas vibrational losses are probably the only source of the observed dielectric loss at high frequencies. Concerning the temperature effect, conduction, dipolar and vibrational losses have minimum values at low temperatures, but these losses increase with increases in temperature. This explains the increase in the $\varepsilon''$ values with temperature.

In order to acquire a deeper insight into the La$_{0.8}$Ca$_{0.2}$FeO$_{3-\delta}$ transport properties, we attempted to evaluate the barrier height to be overcome by charge carriers entering the lattice. As a matter of fact, the dielectric loss $\varepsilon''$ can be described by Giuntini’s law [49] on the basis of the hopping model. It is simplified as follows:

$$\varepsilon''(\omega) = A\omega^m$$

where $A$ is a constant that depends on temperature, $\omega$ the angular frequency and $m$ an exponent describing the degree of interaction between the dipoles in the lattice. The latter is related to the maximum barrier height ($W_M$) in accordance with the following expression:

$$m = -\frac{4K_BT}{W_M}$$

where $K_B$ is the Boltzmann constant and $T$ the temperature.

The Ln($\varepsilon''$) versus Ln($\omega$) plot is displayed in Figure 6(b). This can be used to determine the $m$ values, and the maximum barrier height can then be calculated according to Equation (11). The results obtained reveal that $W_M$ increased from 0.22 to 0.34 eV when the
temperature rose from 350 to 800°C (Figure 7). This is reasonable because with increases in temperature, the dipoles inside the lattice can dissociate and the charge carriers intercept at the grain boundaries to form barriers. The height of these latter increases with increases in temperature.

To proceed further with the investigation of the \( \text{La}_{0.8}\text{Ca}_{0.2}\text{FeO}_{3-\delta} \) electric properties, we have estimated the minimum hopping distance \( R_{\text{min}} \). It is calculated according to Equation (12) using the binding energy values. Figure 7 reports the \( R_{\text{min}} \) evolution with temperature at 50 Hz. The results obtained reveal that \( R_{\text{min}} \) decreases from 2.16 to 0.12 pm when the temperature rises from 350 to 800°C.

\[
R_{\text{min}} = \frac{2e^2}{\pi \varepsilon_0 \varepsilon W_M} \tag{12}
\]

where \( e \) is the electron charge, \( \varepsilon' \) the dielectric constant and \( \varepsilon_0 \) the permittivity of free space.

### 3.3.3. Variations in \( \tan \delta \) with frequency and temperature

\( \tan \delta \) represents the electric energy lost as heat during the polarization process when an alternating current field is applied. The loss values (\( \tan \delta \)) are calculated using the following equation:

\[
\tan \delta = \frac{\varepsilon''}{\varepsilon'} \tag{13}
\]

where \( \delta \) is the phase difference between the applied electric field and the induced current.

The dielectric loss evolution with frequency at different temperatures is depicted in Figure 8. Results for a specified temperature show a decreasing trend for dielectric loss with increases in frequency. In the high-frequency range, \( \tan \delta \) remains frequency independent. This behavior can be explained to some extent based on the grain and grain boundary impedance [50]. In fact, due to the grain boundaries’ contribution, lanthanum ferrites possess high impedance at low frequencies. In the high-frequency range, however, the sample exhibits low impedance due to the grain contribution. Thus, exchanges between iron cations become difficult because of the ferrite’s high impedance. Therefore, high energy is needed for the electron transfer, and a high dielectric loss occurs at low frequencies. In the high-frequency range, however, low energy values are required for electron motion. This is reflected in the low dielectric loss in Figure 8 [51].

An interesting characteristic observed in this study is the low loss values at high frequencies. These losses arise from the Joule effect on the free electrons that are only within skin depth [52]. In this high-frequency range, the electromagnetic field is confined to the material surface. We therefore attempted to explain the results based on the penetration depth \( \delta \), which is expressed as:

\[
\delta = \sqrt{\frac{2}{\omega \mu_0 \sigma}} \tag{14}
\]

where \( \omega \) is the angular frequency, \( \mu_0 \) the free space permeability and \( \sigma \) the conductivity [53].

Equation (14) shows that \( \delta \) is dependent on \( \omega \) and \( \sigma \). As already reported in Figure 2(a), low \( Z' \) values are obtained at high frequencies, a result that reflects high conductivity values. Such high \( \sigma \) values would probably result in low \( \delta \) values at high frequencies. Thus, in this frequency range, the generated heat is confined to the surface. This characteristic makes lanthanum ferrite a potential candidate for applications in high-frequency microwave devices [54].

![Figure 7](image-url) Evolution of \( R_{\text{min}} \) and \( W_M \) as a function of temperature.
3.4. Modulus study

To investigate the electric transport in the sample further, we employed the electric modulus. We also compared the spectroscopic plots the imaginary parts of the impedance $Z''$ and modulus $M''$. In fact, use of the modulus enabled us to analyze the dynamic aspects of the electric transport phenomena. The $M''$ values were therefore calculated at different frequencies for a given temperature according to the following equation:

$$M''(\omega) = \omega C_0 Z$$  \hspace{1cm} (15)

As a matter of fact, the modulus $M''$ is often used together with the impedance $Z''$ in order to distinguish the microscopic process responsible for localized dielectric relaxation and long-range conduction. Indeed, it is known that combining the plots of $Z''$ and $M''$ with respect to frequency is a convenient tool often used to determine whether the short-range or long-range movement of charge carriers dominates the relaxation process. In fact, if the $Z''$ and $M''$ plots overlap, a long-range movement of charge carriers in the lattice is indicated, whereas, their separation reveals that the relaxation process is dominated by short-range transport [54].

In view of the above statements, we compare $Z''$ and $M''$ plots for some selected temperatures in Figure 9. It is evident that there is a significant mismatch between the $Z''$ and $M''$ peaks at 350°C. This behavior reveals that the charge carriers are localized and do not contribute to long-range conduction. At 400°C, however, we note that the $Z''$ and $M''$ peaks occur at the same frequency. This reveals that the charge carriers are delocalized and contributing to long-range conduction. A similar behavior is observed for the other temperatures studied.

In this study, we present our efforts to analyze the dielectric behavior of the lanthanum ferrite. In fact, a thorough understanding of the origins of polarization remains an important tool for use in designing a functional lanthanum ferrite suitable for high-performance nonlinear optical applications and microwave devices.

4. Conclusion

The present work is a contribution to the study of the dielectric properties of $\text{La}_{0.8}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$. As concerns the electric properties, complex impedance spectroscopy analyses were carried out. The dielectric data were analyzed based on the universal dielectric response model. The present study reveals interesting features. In fact, a gigantic dielectric constant is obtained at different temperatures. At low frequencies, both $\varepsilon'$ and $\tan(\delta)$ show a dispersive trend. This behavior was explained based on the Maxwell Wagner polarization model. On the other hand, we proposed the most likely mechanism for explaining the observed dielectric behavior. The variations in $\varepsilon''$ with frequency obey Giuntini’s law. From the dielectric data, we estimated the binding energy ($W_m$). It increases from 0.22 to 0.34 eV when the temperature rises from 350 to 800°C. However, the minimum hopping distance ($R_{\text{min}}$) shows a decreasing
trend from 2.16 to 0.12 pm. As concerns the modulus analyses, the results show that the short-range movement of charge carriers dominates the relaxation process at 350°C, whereas at 400 and 500°C, the long-range movement becomes predominant.

Figure 9. Variations in the imaginary parts of the modulus and impedance ($M^*$ and $Z^*$) with frequency.
Highlights

- The substituted lanthanum ferrite possesses giant dielectric constant.
- Low dielectric loss at high frequency.
- La$_{0.95}$Ca$_{0.05}$FeO$_3$-$_6$ compound is a promising candidate for nonlinear optical applications and microwave devices.

Disclosure statement

No potential conflict of interest was reported by the authors.

References

[1] Ward R. Mixed metal oxides. New York (NY): Oxford Clarendon Press; 1966.
[2] Dai Z, Lee CS, Kim BY, et al. Honeycomb-like periodic porous LaFeO$_3$ thin film chemiresistors with enhanced gas-sensing performances. Appl Mater Interfaces. 2014;6:16217–16226.
[3] Deok Han G, Choi HJ, Bae K, et al. Fabrication of lanthanum strontium cobalt ferrite-gadolinium doped ceria composite cathodes using a low-price inkjet printer. Appl Mater Interfaces. 2017;9:39347–39356.
[4] Taylor FH, Buckenridge J, Catlow CRA. Defects and oxide ion migration in the solid oxide fuel cell cathode material LaFeO$_3$. Chem Mater. 2016;28:8210–8220.
[5] Zheng WJ, Liu RH, Peng DK, et al. Hydrothermal synthesis of LaFeO$_3$ under carbonate containing medium. Mater Lett. 2000;43:19–22.
[6] Liu T, Xu Y. Synthesis of nanocrystalline LaFeO$_3$ powders via glucose–sol–gel route. Mater Chem Phys. 2011;129:1047–1050.
[7] Li F, Liu Y, Sun Z, et al. Facile preparation of porous LaFeO$_3$ nanomaterial by self-combustion of ionic liquids. Mater Lett. 2011;65:406–408.
[8] Cao E, Qin Y, Cui T, et al. Influence of Na doping on the magnetic properties of LaFeO$_3$. Ceram Int. 2017;43:7922–7928.
[9] Berchmans LJ, Sindhu R, Angappan S, et al. Effect of antimony substitution on structural and electrical properties of LaFeO$_3$. J Mater Process Technol. 2008;207:301–306.
[10] Ahmed MA, Azab AA, El-Khawas EH. Structural, magnetic and electrical properties of Bi doped LaFeO$_3$ nano crystals synthesized by auto-combustion method. J Mater Sci. 2015;26:8765–8773.
[11] Acharya S, Chakraborti PK. Some interesting observations on the magnetic and electric properties of Al$^{3+}$ doped lanthanum orthoferrite (La$_{0.95}$Al$_{0.05}$FeO$_3$). Solid State Commun. 2010;150:1234–1237.
[12] Devi CK, Mallesh S, Krishna MJ, et al. Role of defects and oxygen vacancies on dielectric and magnetic properties of Pb$^{2+}$ ion doped LaFeO$_3$ polycrystalline ceramics. Phys B. 2014;448:304–311.
[13] Andoulsi-Fezei R, Horchani-Naifer K, Férid M. Influence of zinc incorporation on the structure and conductivity of lanthanum ferrite. Ceram Int. 2016;42:1373–1378.
[14] Phokha S, Hunpratup S, Pinitsoontorn S, et al. Structure, magnetic, and dielectric properties of Ti-doped LaFeO$_3$ ceramics synthesized by polymer pyrolysis method. Mater Res Bull. 2015;67:118–125.
[15] Idrees M, Nadeem M, Hassan MM. Investigation of conduction and relaxation phenomena in LaFe$_{0.95}$Ni$_{0.1}$O$_3$ by impedance spectroscopy. J Phys D: Appl Phys. 2010;43:155401–155409.
[16] Ahmed MA, El-Deek SI. Extraordinary role of Ca$^{2+}$ ions on the magnetization of LaFeO$_3$ orthoferrite. Mater Sci Eng B. 2006;128:30–33.
[17] Merino NA, Barbero BP, Grange P, et al. La$_{1-x}$Ca$_x$CoO$_3$ perovskite-type oxides: preparation, characterization, stability, and catalytic potentiality for the total oxidation of propane. J Catal. 2005;231:232–244.
[18] Li F, Liu Y, Liu R, et al. Preparation of Ca-doped LaFeO$_3$ nanopowders in a reverse microemulsion and their visible light photocatalytic activity. Mater Lett. 2010;64:223–225.
[19] Andoulsi R, Horchani-Naifer K, Férid M. Structural and electrical properties of calcium substituted lanthanum ferrite powders. Powder Technol. 2012;230:183–187.
[20] Andoulsi R, Horchani-Naifer K, Férid M. Electrical conductivity of La$_{1-x}$Ca$_x$FeO$_3$ solid solutions. Ceram Int. 2013;39:6527–6531.
[21] Andoulsi R, Horchani-Naifer K, Férid M. Preparation of lanthanum ferrite powder at low temperature. Cerâmica. 2012;58:126–130.
[22] Sumi S, Prabhakar Rao P, Mahesh SK, et al. Electrical transport properties of manganese containing pyrochlore type semiconducting oxides using impedance analyses. Mater Res Bull. 2012;47:4365–4375.
[23] Lily K, Kumari K, Choudhary RNP. Impedance spectroscopy of (Na$_{0.5}$Bi$_{0.5}$)$_2$(Zn$_{0.75}$Ti$_{0.25}$)O$_3$ lead-free ceramic. J Alloys Compd. 2008;453:325–331.
[24] Dhak P, Dhak D, Das M, et al. Impedance spectroscopy study of LaMnO$_3$ modified BaTiO$_3$ ceramics. Mater Sci Eng B. 2009;164:165–171.
[25] Debye P. Polar molecules. New York (NY): Chemical catalogue company; 1929.
[26] Li JK, Tang XG, Zhang TF, et al. Impedance response and high temperature dielectric relaxation behavior in lead barium strontium zirconate ceramics. J Mater Sci: Mater Electron. 2016;27:1582–1589.
[27] Ke Q, Lou X, Wang Y, et al. Oxygen-vacancy-related relaxation and scaling behaviors of Bi$_2$O$_3$La$_{0.5}$Fe$_{0.98}$Mg$_{0.02}$O$_2$ ferroelectric thin films. Phys Rev B. 2010;82:024102.
[28] Ming-Ding L, Xin-Gui T, Si-Ming Z, et al. Oxygen-vacancy-related dielectric relaxation behaviours and impedance spectroscopy of Bi(Mg$_{1/2}$Ti$_{1/2}$)$_2$O$_3$ modified BaTiO$_3$ ferroelectric ceramics. J Materiomics. 2018;4:194–201.
[29] Tian-Fu Z, Xin-Gui T, Qiu-Xiang L, et al. Oxygen-vacancy-related high temperature dielectric relaxation in (Pb$_{1-x}$Bi$_x$)$_2$ZrO$_3$ ceramics. J Am Ceram Soc. 2015;98:551–558.
[30] Zhao XZ, Zhang ML, He EJ, et al. Multiferroic property, dielectric response and scaling behavior in aurivillius Bi$_{2.25}$Ga$_{2.75}$Fe$_{0.5}$Co$_{0.5}$Ti$_{0.5}$O$_{15}$ ceramic. J Alloy Compd. 2017;695:2556–2562.
[31] Dev KM, Ato D, Sinha TP. Dielectric relaxation and ac conductivity of double perovskite oxide Ho$_3$ZnZrO$_6$. Phys B Condens Mater. 2011;406:2703–2708.
[32] Kyritsis A, Pissis P, Grammatikakis J. Dielectric relaxation spectroscopy in poly (hydroxyethyl acrylates) water hydrogels. J Polym Sci Polym Phys. 1995;33:1737–1750.
[33] Jonscher AK. Dielectric relaxation in solids. London: Chelsa Dielectric Press; 1983.
Awadhia A, Patel SK, Agrawal SL. Dielectric investigations in PVA based gel electrolytes. Prog Cryst Growth Charact Mater. 2006;52:61–68.

Sdiri N, Elhouichet H, Dhaou H, et al. Effects of the substitution of P$_2$O$_5$ by B$_2$O$_3$ on the structure and dielectric properties in (90 – x) P$_2$O$_5$·x B$_2$O$_3$·10 Fe$_2$O$_3$ glasses. Spectrochim Acta A. 2014;117:309–314.

Sdiri N, Boukhachem A, Dhahri E. Optical investigations of La$_{0.7}$Ca$_{0.3}$-$x$K$_x$MnO$_3$ (x= 0.00, 0.05 and 0.10) probed by spectroscopic ellipsometry. Ceram Silik. 2012;56:95–101.

Shelby RM, Levenson MD, Perlmutter SH, et al. Broad band parametric deamplification of quantum noise in an optical fiber. Phys Rev Lett. 1986;57:691–694.

Boyd R. Nonlinear optics. New York (NY): Academic Press; 1992.

Andoulsi-Fezei R, Sdiri N, Horchani-Naifer K, et al. Effect of temperature on the electrical properties of lanthana-num ferrite. Spectrochim Acta A. 2018;205:214–220.

Rahman MN. Ceramic processing and sintering. United States of America (USA): CRC Press; 2003.

Barbero BP, Cadús LE, Marchetti SG. Determination of Fe (IV) species in partially substituted perovskite La$_{0.6}$Ca$_{0.4}$FeO$_3$. Hyperfine Interact. 2009;194:367–379.

Moss R, Hardtl KH. Electronic transport properties of Sr$_{1.4}$La$_{0.6}$TiO$_3$ ceramics. J Appl Phys. 1996;80:393.

Kumar P, Kumar SR, Sinha ASK, et al. Effect of isovalent ion substitution on electrical and dielectric properties of LaCrO$_3$. J Alloy Compd. 2013;576:154–160.

Wang HC, Schulze WA. The role of excess magnesium oxide or lead oxide in determining the microstructure and properties of lead magnesium niobate. J Am Ceram Soc. 1990;73:825–832.

Bokov A, Ye ZG. Frontiers of ferroelectricity. Boston: Springer; 2007.

Lina L, Chunchang W, Xiaohong S, et al. Oxygen-vacancy-related relaxations of Sr$_2$CuNb$_2$O$_9$ at high temperatures. J Alloy Compd. 2013;552:279–282.

Gurvinderjit S, Tiwari VS, Gupta PK. Role of oxygen vacancies on relaxation and conduction behavior of KNbO$_3$ ceramic. J Appl Phys. 2010;107:064103.

Abdel Aziz MM, Afif MA, Labib HH, et al. Electrical and dielectric properties of amorphous Ge$_{1.35}$Ti$_{0.15}$ films. Acta Phys Pol A. 2000;98:393–399.

Giuntinin JC, Zanchetta JV, Jullien D, et al. Temperature dependence of dielectric losses in chalcogenide glasses. J Non-Cryst Solids. 1981;45:57–62.

Koop CG. On the dispersion of resistivity and dielectric constant of some semiconductors at audio frequencies. Phys Rev. 1951;83:121.

Sindhu M, Ahlawat N, Sanghi S. Rietveld refinement and impedance spectroscopy of calcium titanate. Curr Appl Phys. 2012;12:1429–1435.

Li Z, Meng Z. A Review of the radio frequency non-destructive testing for carbon-fibre composites. Meas Sci Rev. 2016;16:68–76.

Bhalla AS, Guo-Rustum Roy R. The perovskite structure - a review of its role in ceramic science and technology. Mater Res Innovations. 2000;4:3–26.

Wang CC, Lei CM, Wang GJ, et al. Oxygen vacancy related dielectric relaxations in SrTiO$_3$ at high temperatures. J Appl Phys. 2013;113:094103.