Role of B-site cation on the structure, magnetic and dielectric properties of nanosized \( \text{La}_{0.7}\text{Sr}_{0.3}\text{Fe}_{1-x}\text{M}_x\text{O}_3 \) (\( M = \text{Mn}; \text{Co} \) and \( x = 0, 0.5 \)) perovskites

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Abstract

The easiness of preparation and tailored properties of perovskite nanoparticles rendered them an important class of materials in the last decade. In this work, \( \text{La}_{0.7}\text{Sr}_{0.3}\text{Fe}_{1-x}\text{M}_x\text{O}_3 \) (\( M = \text{Mn}, \text{Co} \) and \( x = 0, 0.5 \)) orthoferrites were synthesized using combustion method and examined using X-ray diffraction. The orthorhombic structure was clearly obvious with Pbnm space group without the need of any thermal treatment. Field emission scanning electron microscopy (FESEM) accompanied by Energy-dispersive spectroscopy studies were also performed, evidencing the similarity of both nominal and chemical compositions for the studied orthoferrites. The thermal dependence of the dielectric properties was investigated (from room temperature to 698 K) in the frequency range (70 Hz–5 MHz). Magnetic properties were investigated at room temperature and discussed.

Introduction

Orthoferrite nanoparticles possessing perovskite structure promise potential applications in material science and engineering, owing to their broad range of physico-chemical features. New generation of chemical, optical, electronics and biological devices are based on the use of perovskites either ferroelectric and/or ferromagnetic. However, the properties of these compounds lead to an extensive potential applications in the micro-electronics industry. This modern industry includes computer memories as magnetic and ferroelectric random-access memories (RAMs of computers), multilayer ceramic capacitors (MLCC), pyroelectric detectors, and high temperature piezoelectric beside its use as hydrogen storage materials. The challenge of compromisation between two sides, the first side is size control while the other includes phase purity, size distribution, morphology, crystallinity and shape tailoring [1–3]. To solve this problem, sol-gel combustion particular synthesized routes are utilized.

Magnetically, perovskite at nanoscale has qualitatively new different properties compared with their bulk counterparts. These novel properties include changes in the magnetic transition temperature, the emergence of superparamagnetism, size dependence of the saturation magnetization, coercivity, surface spin glass, large coercivity, low saturation magnetization and low-field magnetoresistance effect [1, 4].

For several years, great effort has been devoted to the study of the mixed ferrite-cobaltites/manganite 50%. However, most of those studies do not take into account the doping substituting at A-site which modifies the average A-site ionic radius \( \langle r_A \rangle \) and introduces disorder \( \langle \sigma^2 \rangle \) which suppress the ferromagnetic phase and effect transport properties. Moreover, the obtained magnetization versus high magnetic field, hysteresis loops
measured below room temperature, but the saturated magnetization didn’t obtain. Otherwise, conductivity and dielectric properties did not be studied [5, 6]. Furthermore, P S J Bharadwaj et al prove that magnetization of YFeO₃ originated entirely from the canting of Fe³⁺ moments, as Y³⁺ being diamagnetic, cannot contribute to the magnetization. Regardless of replacement of Y ion by Sm ion, crystallite sizes are still greater than 100 nm [7]. On another side, where Liying Qi et al prepared Ca₀.₇₅Er₀.₂₅MnO₃ using different technique and doping A-site with different ions, but the effect of such dopants on magnetization and dielectric behavior didn’t studied [8]. Doping of alkaline ion, Sr, in LaMnO₃ improves the average manganese valency to preserve the whole electrical neutrality charge and formally produces Mn⁴⁺ with \( t_2^g (S = 3/2) \) electronic configuration hole. In this case, e.g. electrons of Mn⁴⁺ are assumed to be delocalized and play the role of charge carriers [9]. Many studies concentrated on the substitution of Fe which introduces dramatic effects on the structure, dielectric and magnetic properties of perovskite. The substitution or doping of B site by another one affects the Fe–O network by change Fe³⁺/Fe⁴⁺ ratio and electron carrier energy.

Iron-Fe-containing perovskites are of interest owing of their ability to present oxygen vacancies together with fast surface oxygen exchange kinetics make them convenient electrode materials for the cathode part of the fuel cell [10]. Among different transition elements which can be examined, cobalt Co [11] is such a proper candidate since Co ions can have different oxidation state Co²⁺, Co³⁺, and Co⁴⁺ and multiple spin states: low spin LS: \( t_2^g e_g^0 \), \( S = 1/2 \) for Co²⁺ and \( t_2^g e_g^0 \), \( S = 0 \) for Co³⁺, the intermediate spin IS: \( t_2^g e_g^1 \), \( S = 1 \) for Co⁵⁺ and the high spin HS: \( t_2^g e_g^2 \), \( S = 3/2 \) for Co⁵⁺ and \( t_2^g e_g^2 \), \( S = 2 \) for Co⁶⁺ state. The diversity of spin states of Co ions as a result of competition between Hund’s coupling energy and values of crystal field splitting energy have been extensively studied. Our previous work on orthoferrites demonstrated improvement of magnetization upon Ca substitution [12, 13], while rare earth variation revealed promising pressure and gamma sensing for the orthoferrites keeping the Ca ratio unchanged [14, 15].

In the present piece of work, we prolonged our investigations on the orthoferrite with perovskites structure. We decided to shed light on the variation of B-site cation radius on the physical behavior of \( \text{La}_0.7\text{Sr}_{0.3}\text{FeO}_3, \text{La}_0.7\text{Sr}_{0.3}\text{Fe}_{0.5}\text{Mn}_{0.5}\text{O}_3 \) and \( \text{La}_0.7\text{Sr}_{0.3}\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_3 \) namely Fe, FeMn and FeCo respectively polycrystalline samples were synthesized by combustion technique [16–18]. To check the structure and phase purity, powder x-ray diffraction (XRD) (Bruker D8—USA) using CuK\( \alpha \) radiation (k = 1.5418 Å) was performed at room temperature in the 2θ range 20°–80° with a step size of 0.02°. The microstructure was investigated using scanning electron microscope (SEM) using a Philips XL30, and a semi-quantitative analysis was achieved at 15-kV accelerating voltage using energy dispersive X-ray analyses (EDX). The dependence of magnetization (M) on magnetic field (H) at room temperature was measured using a vibrating sample magnetometer (VSM; Lake Shore -7410-USA). To measure the dielectric properties, the powder was pressed into pellet forms under 5 ton cm⁻² with dimension of 13 mm diameter. Carbon conductive adhesive is used to make good ohmic contact on both surfaces of pelletized samples and the rod conductor. Using Automatic LCR meter (HIOKI 3532-50 LCR HD TESTER), ac resistance, dielectric constant and dielectric loss tangent data were collected from room temperature to 425 °C, and frequency range 70 Hz–5 MHz.

**Experimental techniques**

\( \text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_3, \text{La}_{0.7}\text{Sr}_{0.3}\text{Fe}_{0.5}\text{Mn}_{0.5}\text{O}_3 \) and \( \text{La}_{0.7}\text{Sr}_{0.3}\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_3 \) namely Fe, FeMn and FeCo respectively polycrystalline samples were synthesized by combustion technique [16–18]. To check the structure and phase purity, powder x-ray diffraction (XRD) (Bruker D8—USA) using CuK\( \alpha \) radiation (k = 1.5418 Å) was performed at room temperature in the 2θ range 20°–80° with a step size of 0.02°. The microstructure was investigated using scanning electron microscope (SEM) using a Philips XL30, and a semi-quantitative analysis was achieved at 15-kV accelerating voltage using energy dispersive X-ray analyses (EDX). The dependence of magnetization (M) on magnetic field (H) at room temperature was measured using a vibrating sample magnetometer (VSM; Lake Shore -7410-USA). To measure the dielectric properties, the powder was pressed into pellet forms under 5 ton cm⁻² with dimension of 13 mm diameter. Carbon conductive adhesive is used to make good ohmic contact on both surfaces of pelletized samples and the rod conductor. Using Automatic LCR meter (HIOKI 3532-50 LCR HD TESTER), ac resistance, dielectric constant and dielectric loss tangent data were collected from room temperature to 425 °C, and frequency range 70 Hz–5 MHz.

**Results and discussion**

**XRD characterization**

Figure 1 shows the XRD patterns of \( \text{La}_{0.7}\text{Sr}_{0.3}\text{Fe}_{1-x}\text{M}_x\text{O}_4 \) (\( M = \text{Mn}, \text{Co} \) and \( x = 0, 0.5 \)). The XRD pattern of three specimens looked similar, despite the difference in the B-site cation and effective radius and electronic configuration. However, a slight difference in peak width and position appeared. The peaks are shifted towards higher two theta angle for doped samples.

The XRD patterns showed strong peaks for all samples, with no separation of additional phases except for a minor Sr₃FeO₆ in the undoped sample. Such clear reflections indicate that this preparation technique is the best optimum route for obtained perovskite with single phase without subsequent heat treatment. The diffraction data shows orthorhombicity perovskite structurally with space group pbnm No. 62 for all samples and matched well with the [JCPDS card No. 01-089-1269, card No. 01-087-2015 and card No. 01-089-1268] for the Fe, FeMn and FeCo samples respectively. From the following formula (1) for the orthorhombic symmetry, the lattice
parameters a, b and c were calculated and reported in table 1 where (hkl) are Miller indices and d is interplanar distance:

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

Regardless of the various oxidation states, the unit cell volume of Co doped sample increases slightly than other samples which is ascribed to the preferential high spin of Co cation \((r_{Co^{3+}} = 0.61 \text{ Å})\) rather than low spin one \((r_{Co^{3+}} = 0.545 \text{ Å})\). However, the unit cell of undoped sample is greater than that of Mn doped one where the Fe radius at the sample 6-f coordination is smaller than that of Mn. Tolerance factor values are calculated using cation radii, taking into consideration that La/Sr are in 9-f coordination while Fe, Mn and Co are 6-f coordinated in the perovskite structure.

The perovskite structure is governed by the Goldschmidt tolerance factor \(t = (r_A + r_O) / \sqrt{2} (r_B + r_O)\). Here, \(r_A\), \(r_B\) and \(r_O\) are the cation/anion radii with nine and six fold coordination numbers respectively. The condition \(t < 1\) is appreciated by cooperative rotations of the \((BO_6)/_2\) octahedra [15].

From the x-ray diffraction peak broadening, the crystallite size \(D_{\text{XRD}}\) and microstrain \(\varepsilon\) were determined using Scherrer’s equation (2) and Williamson and Hall equation (3) and reported in table 1

\[ D_{\text{XRD}} = \frac{k\lambda}{\beta \cos \theta}, \]
\[ \frac{\beta \cos \theta}{\lambda} = \frac{1}{D_{\text{XRD}}} + 4\varepsilon \frac{\sin \theta}{\lambda}, \]

Where \(k = 0.94\) is the particle shape factor given the nanoparticles are of spherical shape, \(\theta\) is diffraction angle, \(\lambda = 1.5404 \text{ Å}\) is the wave length of incident radiation and \(\beta\) is corrected full width at half maximum (FWHM) of the most intense peak. X powder software performs this function and using the Scherrer’s and W-H formula [19, 20] as represented in figure 2. The relatively low formation temperature of such compositions phases represents the greatest contribution to the nanosized powders.

The morphology is depicted by electron microscopy scanning as revealed in figures 3(a)–(c). The grain size and morphology of the surface are ambiguous and irregularly coagulated with different shape and size which may be ascribed to the absence of surfactant during preparation and single phase formation without annealing. Determination of grain size is based on ImageJ software program which is 55.7, 47.4 and 53.5 nm for Fe, FeMn and FeCo respectively. Energy dispersive x-ray analysis has conducted the qualitative study of the constituent

![Figure 1. XRD patterns of La0.7Sr0.3Fe1-xMxO3 (M = Mn, Co and x = 0, 0.5).](image)

### Table 1. Structural parameters of the orthoferrite nanoparticles.

| Sample   | t | Scherrer | W-S | SEM | \(\varepsilon\) %a | a(Å) | b(Å) | c(Å) | V,(Å)³ |
|----------|---|----------|-----|-----|---------------------|------|------|------|--------|
| Fe       | 0.9537 | 26 | 52.90 | 55.7 | 0.328 | 5.5352 | 5.5208 | 7.8533 | 239.9869 |
| FeMn     | 0.9526 | 17 | 45.95 | 47.41 | 0.371 | 5.4087 | 8.0010 | 5.5442 | 239.9253 |
| FeCo     | 0.9585 | 29 | 95.20 | 53.56 | 0.244 | 5.1485 | 5.5922 | 7.9218 | 240.0411 |
elements and the elements found in the three compositions are in accordance with those in nominal compositions. As shown in table 2, Scherrer’s formula and Williamson Hall measure the crystallite size to determine the microstrain’s contribution. Besides, all grains are below 100 nm. The grain size detected by FESEM is larger than that assessed by Scherrer formula. This was obviously described by fact that each grain detected by FESEM contains many crystallites [21].

**Dielectric properties**

**Conduction mechanism**

The resistance (R), The capacitance (C) and dielectric loss tangent (tan δ), of the specimens were measured in the frequency range from 70 Hz to 5 MHz and temperature range from 300 to 700 K. AC conductivity (σ\(_{ac}\)) was calculated using the formula:

\[
σ_{ac} = \frac{l}{RA},
\]

where l is the thickness, A is the cross section area of the pellet and R is the resistance. Dielectric constant \(\varepsilon_r(\omega)\) also called relative permittivity is a complex quantity, i.e., \(\varepsilon_r(\omega) = \varepsilon'_r(\omega) - i\varepsilon''_r(\omega)\), where \(\varepsilon'_r(\omega)\) is real and \(\varepsilon''_r(\omega)\) (ω) is imaginary part of \(\varepsilon_r(\omega)\). \(\varepsilon'_r(\omega)\) is calculated by using the relation:

\[
\varepsilon'_r(\omega) = \frac{C}{C_0},
\]

where C is the capacitance measured experimentally and \(C_0\) is the geometrical capacitance \(C_0 = \frac{A\varepsilon_0}{l}\), where \(\varepsilon_0\) is the permittivity of free space = 8.85 \(\times\) 10\(^{-12}\) F/m.

Figures 4(a)–(c) shows the relation between electrical conductivity (ln σ) and frequency at various temperatures for the examined compositions. Unlike behavior of the electrical conductivity with variations of frequency and temperature was observed. These curves show a plateau in the frequency range from 70 Hz to 10\(^5\) Hz, the conductivity is frequency independent \(σ_{dc}\). At the frequency beyond 10\(^5\) Hz, the conductivity increases with frequency. In dispersive region, the conductivity is explained by the power law [22]:

![Diagram](image-url)
Figure 3. (a)–(c). Morphology from FESEM micrographs and EDX of samples (a) La$_{0.7}$Sr$_{0.3}$FeO$_3$; (b) La$_{0.7}$Sr$_{0.3}$Fe$_{0.5}$Mn$_{0.5}$O$_3$; (c) La$_{0.7}$Sr$_{0.3}$Fe$_{0.5}$Co$_{0.5}$O$_3$.

Table 2. (a) Activation energy values at different frequencies. (b) Room temperature values of the ac conductivity ($\sigma$), dielectric constant ($\varepsilon'$), and quality factor of the samples ($Q$) at selected frequencies.

| $\nu$, Hz | $1 \times 10^2$ | $1 \times 10^4$ | $5 \times 10^3$ | $7 \times 10^5$ | $1 \times 10^6$ |
|-----------|-----------------|-----------------|-----------------|-----------------|-----------------|
| (a) $E_a$ (eV) | | | | | |
| Fe | 0.36 | 0.33 | 0.28 | 0.28 | 0.26 |
| FeMn | 0.29 | 0.27 | 0.23 | 0.22 | 0.21 |
| FeCo | 0.35 | 0.33 | 0.29 | 0.29 | 0.28 |
| (b) Sample | $\sigma$ ($\Omega^{-1} \text{m}^{-1}$) | $\varepsilon'$ | | | |
| 100 kHz | 1 MHz | 100 kHz | 1 MHz | 100 kHz | 1 MHz |
| Fe | 0.105 | 0.157 | 3525.5 | 834.3 | 0.18 | 0.29 |
| FeCo | 0.012 | 0.016 | 355.3 | 115.3 | 0.16 | 0.40 |
| FeMn | 0.006 | 0.009 | 325.6 | 111.6 | 0.30 | 0.65 |
Universal Dynamic Response (UDR) dependent temperature, $A$, indicates the strength of polarization. The slope of the $\ln(\sigma_{ac})$ as a function of $\ln(\omega)$ in the frequency dependent region gives the difference of the conductivity exponent $s$. The later indicates the degree of interaction between mobile ions and lattice. It is related to the degree of association between moving ions showing the conductivity due to energy stored in the collective ion short-range motion. The frequency dependence of $\sigma_{ac}$ indicates that the small polaron hopping mechanism is responsible for conduction. The lines approach each other at high frequencies indicating the possibility of presence of space charge. Globally, the action of conductivity in all temperature range is defined by the universal power law of Jonscher governed by the well known relationship \[23-25].

$$\sigma_{ac}(\omega) = A\omega^s \quad (0 < s < 1),$$  \hfill (6)

The conductivity revealed a peak from $10^5$ Hz to $2 \times 10^6$ Hz frequency range. Beyond this peak, it decreases with frequency, which is consistent with the literature published \[26]. The plot (In $\sigma$) versus (In $\omega$) is presented in figures 4(a)-(c) where $\omega$ is the angular frequency. The variation of the exponent $s$ over the entire temperature range can be expected if a simple hopping process between two site depends on the polarizability of the material involved. The value of $s$ less than one is considered to have a physical meaning. In our case, $s \leq 1$, the hopping process involves a translation motion with a sudden hopping whereas if it involves localized hopping without the species leaving the neighborhood. The frequency where the alteration in slope appeared was recognized as the hopping frequency ($\omega_p$). It seems, from figure 4(d) that $s$ depends on temperature with a characteristic move towards the high frequency region with rising temperature. This frequency confers to polaron hopping of charges species. At high temperature, the charge species at grain boundaries have enough energy to hope over the barrier in turn increasing conductivity \[24]. Clearly, it decreases while temperature increases from 300 to 473 K, Cherif et al indicated that this behavior suggests that the conduction mechanism is triggered thermally and that hopping is the dominant mechanism in this temperature range, which agree with Mott's theory commonly presented in perovskite materials \[26]. This parameter increases at $T = 500$ K to reach maximum value at $T = 573$ K beyond that temperature it decreases again. The increasing parameter $s$ with increasing temperature shows that compositions evolve from metallic to semiconductor regime, which is in good agreement with increasing conductivity with higher temperatures as shown in figures 5(a)-(c). The discrepancy of $s$ for three

Figure 4. (a)–(d). Frequency dependence of conductivity for the investigated samples at selected temperatures- d: exponential factor dependence on temperature (a) Fe; (b) FeMn; (c) FeCo.

\[ \sigma_{ac} = \sigma_0 + A\omega^s, \]  \hfill (7)
compounds is ascribed to the variety of conductivities as revealed in figure 6. In addition, A. Ben Jazia Kharrat describes the increase in $\sigma$ with temperature using the non-overlapping small polaron tunneling (NSPT) model where $s$ is calculated using the relation (8) [27].

$$s = 1 + \frac{4k_B}{W_H},$$

(8)

Where, $W_H$ represents the polaron hopping energy, $k_B$ is the Boltzmann constant.

However, in the region between 30 kHz and 5 MHz, $\sigma_{AC}$ decreases with both of frequency and temperature and the conductivity contribution of the electrodes might be ignored. However, for higher frequency ($f > 7 \times 10^5$ Hz), it depends on frequency only. It can be verified that such specimens exhibit a metallic behavior at this temperature range. The evolution of $\sigma_{AC}$ follows the Drude model suggesting existence of a high
free carrier density and following simplified expresses $\sigma_{AC}$ well [27]:

$$\sigma_{AC}(\omega) = \frac{\sigma_0 e^{r_\ell}}{(1 + \omega^2 r_\ell^2)},$$

(9)

Where $r_\ell$ represents the relaxation time describing the electron-phonon scattering. Finally, the temperature behavior of $s$ may suggest the appropriate model of conduction mechanism in the light of the various theoretical models that correlate the conduction mechanism with behavior $s$ versus $(T)$. According to the literature, the exponent $s$ decreases with higher temperature in the correlated Barrier Hopping (CBH) model.

In the Overlapping Large Polaron Tunneling (OLPT), the exponent $s$ decreases with increasing temperature to a minimum value and then begins to rise with rising temperature. The exponent $s$ is nearly equal to 0.8 in the Quantum Mechanical Tunneling Model (QMT) and increases with increasing temperature or is independent of temperature. The exponent $s$ increases with increasing temperature in the Nonoverlapping Small Polaron tunneling (NSPT). From figure 4(d), in the first section, $s$ decreases with increasing temperature, which shows that the Correlated Barrier Hopping (CBH) is the most suitable model to characterize electrical conduction. In the second region, with increasing temperature, $s$ decreases to the minimum value, demonstrating that Overlapping Large Polaron Tunneling (OLPT) is the most suitable method for conduction. However, Quantum Mechanical Tunneling Model (QMT) explains the third region where the temperature increases and last stage is similar to first one [28]. To understand the transport properties for La$_{0.7}$Sr$_{0.3}$FeO$_3$, La$_{0.7}$Sr$_{0.3}$Fe$_{0.5}$Mn$_{0.5}$O$_3$ and La$_{0.7}$Sr$_{0.3}$Fe$_{0.5}$Co$_{0.5}$O$_3$ samples, the experimental ln$(\sigma T)$ versus $(1/T)$ curves are fitted according to the following equation [26]: (at high temperatures)

$$\sigma_{AC}T = A \exp \left(-\frac{E_a}{k_B T}\right),$$

(10)

where $A$ is the pre-exponential factor, $E_a$ is the activation energy, $k_B$ is the Boltzmann constant and $T$ is the absolute temperature. Figures 6(a)–(c) shows a linear variation of ln$(\sigma T)$ versus 1000/T at the selected frequencies $f = 100$ Hz, 10 kHz, and 500 kHz. Such behavior proves that conductivity is explained by thermally activated hopping of small polarons. The fitting by VRH model is adequate for the three compounds. The deduced frequency dependent activation energy values were listed in table 2(a).

With rising frequencies, the activation energy values decreases slightly, as shown in figure 6(d). Nevertheless, it falls to low values at high temperature and frequencies, indicating that the sample will switch from a semiconductor to a metallic behavior as reported [27]. On the other hand, relatively low values of activation energy in the low temperature region are clearly shown as compared to counterpart at the high temperature region. The low temperature ($T < 390$ K) electrical conduction with lower activation energy values indicates that the hopping of localized charging carriers governs electrical transport. Whereas the conduction in the higher temperature region ($T > 450$ K), of larger activation energy values, demonstrates the presence of polarons in the conduction process [29].

Dielectric constant and dielectric loss

Dielectric frequency response to sinusoidal electrical fields can be expressed by their dynamic relative dielectric permittivity as follows:

$$\varepsilon'(\omega) = \varepsilon_r(\omega) = i \varepsilon''(\omega),$$

(11)

Where $\varepsilon$ is dielectric material permittivity, $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m is free space permittivity. On the other hand, $\omega$ is angular frequency $\varepsilon_r$ is the real component, which is in phase with the applied field and $\varepsilon''(\omega)$ is the imaginary component which is in quadrature with the applied field. Figures 7(a)–(c) shows the dielectric constant variation for the compounds under investigation with respect to the frequency. The dielectric response of these samples shows no related clear peak which clearly indicates the predominance of the hopping mechanism in this process. The dielectric plots can be classified into three regions: low frequency region less than 100 Hz, intermediate region between 10$^3$–10$^7$ Hz and high frequency $>10^8$ Hz. All samples in the low frequency region show high dielectric constant. Which slightly decreases and becomes stable after that as well as declines again in third part. The decrease of dielectric constant at higher frequencies region takes place in many steps, these different steps may arise from contributions of the electrode, grains, and grain boundaries.

The dielectric behavior of these samples at low frequency can be described by the Maxwell-Wagner extrinsic interfacial model [15, 30, 31]. According to this model, the dispersion at low frequencies attributed to the interfacial polarization and the presence of depletion layers near the sample electrode contacts. In addition, the electrical charge imbalance produced by the divalent substitution of the Sr$^{2+}$ ion for the trivalent La$^{3+}$ ions, is balanced by the formation of oxygen vacancies and the conversion of some of the Fe$^{3+}$ to Fe$^{4+}$ at the octahedral sites. It could be suggested that by ionizing oxygen vacancy, electron hopping can participate to the dielectric relaxation process in these samples.

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Samples show a high dielectric constant for frequencies below 10$^3$ Hz. This is clear evidence that two forms of dispersion mechanisms are present within a single material, one of them is dominant at higher frequencies. This behavior is similar to the Debye relaxation and, in this region, $\varepsilon_r$ varies as $(\omega^{-0.5})$. In table 2(b), the room
temperature values of the dielectric constant decreased with Co and Mn doping when compared with the pure sample. Same trend is observed for the conductivity values. The probable explanation is the decrease of the number of dipoles sharing in the polarization process. Moreover, the corresponding valence (Fe$^{3+}$, Fe$^{4+}$) is suppressed ad both Mn$^{3+}$ and/or Co$^{3+}$ ions present on equivalent lattice sites could capture the hopping electrons in this case. This probability couldn’t rule out the existence of oxygen vacancies in the orthoferrites. Additionally, with increasing thermal energy, the valence exchange of this type will be altered. The values of $\sigma$ for the Co doped sample decreased to one tenth while that for the Mn doped one, it reached $1/100$ compared to the undoped one. This fact is due to the critical ratio (50%) substitution of Fe ions which rendered the compound as intermediate orthoferrite-orthocobaltite in case of Co. Similarly, the nanoparticles could be regarded as manganite-orthoferrite simultaneously in Mn doped sample. Dielectric constant values were lowered obviously as polarization and conduction are of the same origin. The quality factor was calculated from the reciprocal of $\tan\delta$ and listed also in table 2(b). The values were found to be enhanced with both Co and Mn substitution. This is a direct consequence of improved resistivity values.

Figures 7(a)–(c) shows high $\varepsilon_r$ at low frequency for three specimens. This behavior may be owing to the contribution of all kinds of polarization, namely mechanical, ionic, orientation and spatial polarizations. $\varepsilon_r$ decreases as frequency increases since the dipoles can not comply with the external field variation and therefore the polarization decreases. Figures 8(a)–(c) shows that the dielectric constant at low frequencies ($<10^3$ Hz) is slight dependent on the temperature. However, for frequencies $>10^3$ Hz, the dielectric constant $\varepsilon_r$ decreases as temperature increases. Essentially, the temperature plays double effect in the present specimens, if polarization of orientation is regulated in the process then it is randomized by the temperature and tends to decrease the dielectric constant. As a consequence, the overall dielectric constant in the system will decrease. Furthermore, when polarization is primarily controlled by space charge polarization, the system’s dielectric constant will increase with increasing the temperature as just the rate of accumulation of interfacial charge decreases, conclusively, the present samples display the orientational polarization is mostly regulated by the space polarization.
Dielectric loss is known as the amount of power loss in dielectric material under the influence of field voltage applied\[25, 30, 32\]. In addition, the current perovskite oxide has a very high dielectric constant at room temperature of around $10^6$. Thus, the La$_{0.7}$Sr$_{0.3}$Fe$_2$O$_3$, La$_{0.7}$Sr$_{0.3}$Fe$_{0.5}$Mn$_{0.5}$O$_3$ and, La$_{0.7}$Sr$_{0.3}$Fe$_{0.5}$Co$_{0.5}$O$_3$ can be known as a substance with a high dielectric constant oxide. Such finding also allow us to suggest such perovskite because of their chemical and thermal stability to be used in double-layer condensers.

For all substance, the frequency dependence of the imaginary component of the dielectric constant ($\varepsilon''$) is shown in figures 9(a)–(c). It is clear that in three samples $\varepsilon''$ shows higher values except for La$_{0.7}$Sr$_{0.3}$Fe$_2$O$_3$ than other two samples where $\varepsilon''$ decreases with increasing temperature and frequency. Accordingly, these samples show high $\varepsilon''$ as can be seen from the variation of tan $\delta$ versus frequency at various temperatures. All the samples show high $\varepsilon''$ in the low frequency section and $\varepsilon'' (\omega) > \varepsilon'_r (\omega)$. This section of $\varepsilon''$ depends on $\omega^{-1}$ according to the electrodynamics relation $\varepsilon'' (\omega) = \sigma_{dc} / \varepsilon_0 \omega$. Therefore, $dc$ conductivity can dominate in this frequency interval. The conductivity of ionic solids [33] and the dielectric losses increase with increasing temperature as seen from figures 9(a)–(c) that illustrates $\varepsilon''$ versus frequency.

### Magnetic properties

Magnetization field dependence (M-H) loops of samples at room temperature (293 K) and magnetic field up to $\pm 20$ kOe are shown in figures 10(a)–(d). The magnetization is improved by increasing the magnetic field and does not saturate completely in magnetic field even until 20 kOe. Surface spin disorder is likely to play a role in preventing saturation [34]. The magnetization has an antiferromagnetic behavior with a large hysteresis loop area for pure La$_{0.7}$Sr$_{0.3}$Fe$_2$O$_3$ and small hysteresis loop for La$_{0.7}$Sr$_{0.3}$Fe$_{0.5}$Mn$_{0.5}$O$_3$ and La$_{0.7}$Sr$_{0.3}$Fe$_{0.5}$Co$_{0.5}$O$_3$ compounds. The weak ferromagnetic component here originated from the canted spin order as LaFeO$_3$ is considered as G-type antiferromagnet. The magnetization reaches 1.29, 1.32 and 1.15 emu g$^{-1}$ for Fe, FeMn and FeCo respectively. The coercivity is 4840.5, 158.79 and 480.28 for Fe, FeMn and FeCo samples respectively. Interestingly, there is huge variety in the coercivity of three samples. The plausible reason here is the magnetocrystalline anisotropy that is always positive for the Co ions in which gives the Co doped nanoparticles triple coercivity as compared with that Mn doped. In this situation, for the pure LCFO, the existing exchange interaction is that the superexchange interaction $Fe^{3+}–O^{2–}–Fe^{3+}$, $Fe^{4+}–O^{2–}–Fe^{3+}$, $Fe^{4+}–O^{2–}–Fe^{4+}$, which results in the canted antiferromagnet with weak ferromagnetic component. Doping with Co or Mn initiated new exchange interactions like that between different pairs of cations either of similar or different valences through the intervening oxygen anions. It is always probable that the double exchange interaction occurs between (Mn$^{3+}$, Mn$^{4+}$); (Co$^{3+}$, Co$^{4+}$); as ferromagnetically coupled.

This will in turns enhances the ferromagnetic character by increasing $M_s$ and shrinking the loop area as well as decreasing the coercive field and remanence values. More investigations concerning the thermal variation of magnetization is needed to deeply understand the 50% doping effect on the magnetic ordering of the orthoferrite and the diversity of interactions or possibly of spin reorientation. Also, one will try to depict the Neel temperature in all samples in our future work by measuring magnetic susceptibility.

According to Banerjee criterion, the sign of the slope of Arrott curves ($M^2$ versus $H/M$) allowed us to check the order of magnetic phase transition. In this circumstance, the observed slope is positive for all the temperatures range, indicating that the magnetic transition between FM and PM phase is of a second order.

![Figure 9](image-url) (a)–(c). Frequency dependence of dielectric loss (a) Fe; (b) FeMn; (c) FeCo.
Otherwise, the hysteresis loop has a very small area. As a result, we have a little energy loss through the
magnetization-demagnetization cycle.

Trials to improve the magnetization of such compounds and decreasing their Neel temperature could
recommended them to be used in magnetic refrigeration applications [35–37]. In memory storage devices, field
\((H_C)\) is important for the writing and overwriting of tap media, together with long-term thermal stability of
antiferromagnetic materials. As shown in figure 10, hysteresis loops are not a typical (s-shape) type of
ferromagnetic behavior, i.e., the hysteresis curves lack saturation. Also, total magnetization \((M_s)\) is composed of
two parts: paramagnetic part as linear contribution, and weak ferromagnetic part as loop. In this situation, the
spontaneous magnetization could be accomplished by extrapolating the linear part of the M-H curves to
\(H = 0\) [15]. This residual magnetization was found to be small.

Such results are consistent with the presence of a glass state. The high \(H_c\) value for La0.7Sr0.3FeO3 could also
be attributed to an increase in intragranular porosity due to the average particle size of sample. To explain that,
the particle comprises several grains inside the magneto crystalline anisotropy is average over many grains
and various orientation. Large anisotropy results in an increase in coercivity with an increase in particle size [38].

Table 3 demonstrates a comparative study between our prepared samples and those recorded in the
literature in view of their magnetic properties. The data revealed small particle sizes with superior properties.
The coercivity values are much larger than that for other doped LaFeO3. These results recommend further
studies on different doping levels and on downsizing the orthoferrites to promote memory devices and
spintronics applications.

**Conclusion**

The orthoferrite nanoparticles La0.7Sr0.3Fe0.3M0.3O3 were successfully prepared using citrate-nitrate
combustion technique without subsequent heat treatment. Single phase orthorhombic structure was identified
for the undoped, Mn and Co doped samples. From the ac conductivity measurements, the conduction process
was dominated by small polaron hopping. The exponent \(s\) variation was in good agreement with Mott theory.

Figure 10. (a)–(d). Magnetization versus magnetic field (a) Fe; (b) FeMn; (c) FeCo; (d) for three samples.
Table 3. Values for the remanence magnetization (\(M_r\)), saturation magnetization (\(M_s\)), squareness ratio (SQR) and coercivity (\(H_c\)) for reported orthoferrites, O; orthorhombic, R; rhombohedral.

| Composition                          | Synthesis method          | Phase structure | Crystallite size, nm | \(M_r\), emu g\(^{-1}\) | \(M_s\), emu g\(^{-1}\) | (SQR = \(M_r/M_s\)) | \(H_c\), (Oe) | References |
|--------------------------------------|---------------------------|-----------------|----------------------|--------------------------|--------------------------|----------------------|----------------|------------|
| La\(_{0.7}\)Sr\(_{0.3}\)FeO\(_3\)     | Auto-combustion           | Orth            | 26                   | 0.458                    | 1.29                     | 0.35                 | 4840.5         | Present work |
| La\(_{0.7}\)Sr\(_{0.3}\)Fe\(_0.5\)Mn\(_0.5\)O\(_3\) | Auto-combustion           | Orth            | 17                   | 0.080                    | 1.32                     | 0.06                 | 158.79         | Present work |
| La\(_{0.7}\)Sr\(_{0.3}\)Fe\(_0.5\)Co\(_0.5\)O\(_3\) | Auto-combustion           | Orth            | 29                   | 0.16                     | 1.15                     | 0.14                 | 480.28         | Present work |
| La\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\)     | Citrate-gel (1200 °C)     | Orth            | 29                   |                          |                          | 44                   | 10             | 39         |
| La\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\)     | Solution combustion/600 °C | R               | 20                   |                          |                          |                      | 16.46          | 40         |
| La\(_{0.7}\)Sr\(_{0.3}\)Mn\(_{0.96}\)\(^{37}\)Fe\(_{0.04}\)O\(_{5+\delta}\) | Co-precipitation          | Orth            | 63.26                | 1.09                     | 16.9                    | 0.06                 | 58.27          | 41         |
| La\(_{2/3}\)Ca\(_{1/3}\)MnO\(_3\)     | Solid-state reaction/1350 °C | Orth           | 0.04                 |                          |                          | 3.61                 | 0.01            | 3.3         |
| La\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\)     | Sol-gel/1450 °C           | Orth            | 10 000 nm            | 1.87                     | 59.15                   | 0.03                 | 22.95          | 35         |
| La\(_{2/3}\)Ca\(_{1/3}\)MnO\(_3\)     | Solid-state/800 °C        | Orth            | 100 nm               | 0.32                     |                          |                      | 770            | 43         |
| La\(_{0.67}\)Ca\(_{0.33}\)MnO\(_3\)   | Solid-gel/1450 °C         | Orth            | 2                    |                          | 100                     | 50                   | 30             | 44         |
| La\(_{0.67}\)Ca\(_{0.33}\)MnO\(_3\)   | Co-precipitation/600 °C   | Orth            | 36.5                 | 0.47                     | 2.11                    | 0.22                 | 503.76         | 45         |
| La\(_{0.7}\)Ca\(_{0.3}\)FeO\(_3\)     | Auto-combustion           | Orth            | 30.4                 | 0.3                      | 1.9                     | 0.157                | 192.7          | 46         |
| La\(_{0.65}\)Gd\(_{0.4}\)FeO\(_3\)    | Co-precipitation/1200 °C  | Orth            | 30                   | 0.01                     | 0.33                    | 0.04                 | 66.7           | 15         |
The computed activation energies were found to be 0.29–0.36 eV. Room temperature ac conductivity for the Co doped sample decreased to one tenth while that for the Mn doped one, it reached 1/100 the original value for the undoped one. The dielectric constant reflected the trend of the conductivity. The M-H loops assured the G-type antiferromagnetic character with the presence of small remnant magnetization and considerable coercive field strongly dependent on the dopant transition metal ion. Extended future work must be carried out to explore the behavior of different substituents and their corresponding physical properties as a function of temperature.

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