Investigation on electrical conductivity and dielectric property of $\text{La}_{0.8}\text{Pb}_{0.2}(\text{Fe},\text{Ti})_{0.5}\text{O}_3$ ceramic nanoparticles

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The modification of the structure lanthanum orthoferrites (LaFeO_3) to obtain ceramic materials with enhanced structural, optical, and electrical properties constitutes an active area of research. The preparation of $\text{La}_{0.8}\text{Pb}_{0.2}(\text{Fe}, \text{Ti})_{0.5}\text{O}_3$ (LPFTO) ceramic nanoparticles by following a cation substitution approach from LaFeO_3 using sol–gel and sintering methods is described. The electrical and dielectric properties of the obtained material are investigated. The contribution of grain and grain boundary in the conduction mechanism is demonstrated by complex impedance analysis. The LPFTO ceramic nanoparticles exhibit a giant dielectric constant of the order of 10^8 . The conductivity analysis suggests the occurrence of thermally activated semiconductor behavior. Moreover, the ferromagnetic–paramagnetic semiconductor transition temperature is observed at 385 K. The ac conductivity behavior satisfies the nonoverlapping small-polaron tunneling (NSPT) model.

Keywords: $\text{La}_{0.8}\text{Pb}_{0.2}(\text{Fe}, \text{Ti})_{0.5}\text{O}_3$; impedance spectroscopy; dielectric; conductivity; NSPT model.

1. Introduction

Lanthanum orthoferrites (LaFeO_3) are an attractive class of research materials because of their comprehensive physical properties and application in advanced technology.^{1–3} Modification of their structure has been shown to play an important role in the optimization of their structural, optical and electrical properties.^{2–5} In this context, cation substitution has been reported to produce cation displacement, which in turn contributes to the structural changes that result in the generation of dielectric dipoles.^{1–4} Thus, Ti-substitution on the Fe site of LaFeO_3 introduced weak ferromagnetic ordering correlated with the $3d^0$ valence electron of Ti-ions, resulting in a dielectric constant in the range of $\sim 10^3$.² Pb-substitution on the La site of $\text{La}_{1-x}\text{Pb}_x\text{FeO}_3$ demonstrated typical colossal dielectric constant (higher than 10^4) behavior for $x > 0.1$ in the temperature range of 300–450 K, and the highest dielectric constant was found to be $\sim 30,000$ for the sample with $x = 0.2$.^{3,4} Moreover, the presence of a hopping polaron as the charge carrier was detected in the relaxation and conduction process.³

Motivated by the magnetic ordering and high dielectric constant introduced by Ti- and Pb-substitution, we decided to modify LaFeO_3 by simultaneously substituting the La and Fe sites with Ti- and Pb-ions. The resulting $\text{La}_{0.8}\text{Pb}_{0.2}(\text{Fe}, \text{Ti})_{0.5}\text{O}_3$ (LPFTO) material was synthesized by sol–gel and sintering methods. A detailed study of its electrical and dielectric properties was carried out by impedance spectroscopy.

Furthermore, the magnetic transition and mobility of charge carriers in the conduction mechanism were demonstrated.

2. Experimental Details

The ceramic nanoparticles were produced by sol–gel and sintering methods. The sol–gel method, which afforded the nanoparticles in powder phase, consisted of dissolving the precursors in the form of nitrate and oxide compounds (La_2O_3 , TiO_2 , PbO and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, all of the analytical grade) with citric acid monohydrate in an aqueous solution. The resulting solution was stirred and heated under certain conditions to form the gel phase. Then, the gel obtained was dried at 200°C and calcined at 900°C to form the material in the powder phase. The resulting sample was carefully ground, compressed into a compacting system with a pressure of 5 kPa for 3 min, and sintered at 1300°C for 3 h to obtain the ceramic material.

The crystal structure of the ceramic phase was elucidated using a PANalytical-XPert PRO X-ray diffractometer with a $\text{Cu K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation source in the Bragg's angle range of $10\text{--}80^\circ$. The structural analysis of the experimental pattern was further analyzed using the HighScore Plus and VESTA software. Scanning electron microscopy (SEM) images were obtained by using an SEM FEI QUANTA 650 instrument. The ceramic sample was coated with carbon using a Quorum K975x Turbo Evaporator. The electrical

impedance spectra were deduced in the frequency range of 100 Hz to 1 MHz and the temperature range of 50–300 °C using an RLC meter FLUKE-PM6303 to obtain the impedance data as a function of frequency for each varying temperature. The impedance data were fitted using Zsimpwin 7.0 software to identify the equivalent circuit model in order to describe the electrical response of the system. Then, the impedance data were transformed into the real and imaginary part of impedance which were further transformed into dielectric constant, dielectric loss, and complex conductivity data.

2.1. Results and discussion

2.1.1. Structural analysis

Figure 1 presents the X-ray diffraction (XRD) pattern of the LPFTO ceramic nanoparticles. Well-defined diffraction peaks were identified, which confirmed that LPFTO crystallized in

Table 1. The structural parameters for LPFTO ceramic.

Parameters	
Lattice parameter (Å)	
<i>a</i>	5.543
<i>b</i>	7.824
<i>c</i>	5.519
Volume unit cell (Å ³)	239.4
Average crystallite size (nm)	76.2
Bond distance (Å)	
Fe/Ti–O1 × 2 (s)	1.913
Fe/Ti–O1 × 2 (l)	2.077
Fe/Ti–O2 × 2 (m)	2.007
<Fe/Ti–O>	1.999
Bond angle (°)	
Fe/Ti–O1–Fe/Ti	157.06
Fe/Ti–O2–Fe/Ti	154.13
Tilt angle (°)	14.904

Fig. 1. The XRD pattern of the LPFTO ceramic.

(a)

(b)

Fig. 2. (a) SEM image and (b) EDX spectrum of the LPFTO ceramic.

a single phase with orthorhombic structure and the *Pnma* space group. The detailed structural parameters are summarized in Table 1. The cell parameters follow the trend $a \approx c \approx b/\sqrt{2}$ (the $b/\sqrt{2} = 5.587$), indicating the presence of Jahn–Teller distortion.¹

The morphology of the LPFTO ceramic was observed by using SEM. The corresponding SEM micrograph is displayed in Fig. 2(a), in which a polycrystalline nature can be seen. The grains are distributed inhomogeneously throughout the sample surface with different sizes and shapes. The average grain size of the LPFTO ceramic nanoparticles was found to be 300 nm. To confirm the composition and purity of the LPFTO compound, energy-dispersive X-ray microanalysis (EDX) was performed, and the corresponding spectrum is shown in Fig. 2(b). As can be seen, all the expected elements (La, Pb, Fe, Ti and O) are present in the sample.

Fig. 3. Complex impedance plot at different temperatures for the LPFTO ceramic.

3. Complex Impedance Analysis

To determine the conduction mechanism occurring in this compound, the complex impedance spectrum, i.e., the Nyquist plot at different temperatures, was obtained (Fig. 3). The impedance is characterized by the formation of a semicircle and is strongly affected by the changes in the temperature. As can be seen, the diameter of the semicircle decreases when the temperature is increased, which is consistent with semiconducting behavior.⁵

The impedance data were modeled by an equivalent circuit using Zsimpwin 7.0 software to describe the electrical response of the system. The best fit was obtained for the two parallel combinations of grain/bulk resistance (R_b) — constant phase element (Q_b) and grain boundary resistance (R_{gb}) — constant phase element (Q_{gb}). The Q value is known as the nonideal capacitor and expressed as^{6–8}:

$$Z_{CPE} = [Q(i\omega)^n]^{-1}, \quad (1)$$

where Q is the capacitance value, ω is the angular frequency and n represents the magnitude of electrical response from the ideal behavior (Debye relaxation).

Next, the frequency dependence of the phase θ of the complex impedance at different temperatures (Fig. 4) was evaluated to directly determine the different contributions in the conduction process. Two peaks are clearly distinguishable at 50°C; the peak at higher frequency can be assigned to the grain contribution, whereas that at lower frequency is attributable to the grain boundary contribution. The peaks shift toward higher frequency with increasing temperature, resulting in gradual suppression of the peak at a higher frequency.

The frequency dependence of the real part of the impedance (Z') at different temperatures is plotted in Fig. 5. As can be seen, the Z' value decreases on increasing both the frequency and the temperature. The decrease in the Z' value

Fig. 4. Bode plot of phase angle as a function of frequency at different temperatures for the LPFTO ceramic.

with increasing temperature indicates an increase in the ac conductivity in the LPFTO sample.⁹ This behavior changes completely in the high-frequency region, in which the Z' value merges for all the temperatures above a certain fixed frequency, indicating a possible release of space charge polarization.⁹ At high temperatures, the Z' value is not affected by the frequency increase, which suggests the existence of a relaxation mechanism in this compound. Figure 6 displays the evolution of the imaginary part (Z'') of the impedance with frequency at different temperatures. The Z'' value varies with frequency and reaches the maximum value at a particular frequency known as electrical relaxation frequency. The spectrum of Z'' presents the shifting of the relaxation peak toward higher frequency with rising temperature, which constitutes further evidence of the presence of relaxation

Fig. 5. Frequency dependence of the real part of impedance (Z') at different temperatures for the LPFTO ceramic.

Fig. 6. Frequency dependence of the imaginary part of impedance (Z'') at different temperatures for the LPFTO ceramic.

mechanisms in the material. The magnitude of the Z'' peak also decreases gradually on increasing the temperature, indicating the accumulation of space charge in the system.^{9,12} The broadening of the Z'' peak in the high-frequency region with increasing temperature suggests that the relaxation mechanism in this system is thermally activated. The relaxation mechanism might be due to the presence of charge carriers at low temperature and vacancies/defects in the high-temperature region.¹²

4. Dielectric Results

Figure 7 shows the frequency dependence of the dielectric constant (ϵ') at different temperatures for the LPFTO ceramic.

Fig. 7. Frequency dependence of the dielectric constant (ϵ') at different temperatures for the LPFTO ceramic.

Fig. 8. Frequency dependence of the dielectric loss (ϵ'') at different temperatures for the LPFTO ceramic.

The ϵ' values become larger at low frequency, until approaching $\sim 10^8$ at 10^2 Hz, and decrease with increasing frequency for all temperatures, reaching a constant value at a higher frequency range. However, ϵ' increases with temperature. It is known that, in the polarization responsible for the dielectric behavior of materials, four polarization mechanisms are involved: space charge polarization that occurs in the range of 10^0 – 10^3 Hz, dipolar polarization up to 10^{10} Hz, ionic polarization up to 10^{13} Hz, and electronic polarization up to 10^{16} Hz.^{9–11} At low-frequency, because all the polarization mechanisms participate in the system, ϵ' reaches its maximum value. In contrast, the contributions from space charge, dipolar and ionic polarization will be reduced with increasing frequency, which explains the decrease in ϵ' . Figure 8 presents the frequency dependence of the dielectric loss (ϵ'') at different temperatures for the LPFTO ceramic. The ϵ'' value decreases with increasing frequency. The highest value was observed at low frequency, confirming the contribution of all the polarization effects.¹¹ The ϵ'' value also increases with temperature, suggesting the appearance of ionic conductivity, which is related to the loss of oxygen during the sintering process.^{11,12} In this case, the conductivity starts to dominate and is responsible for the increase in the ϵ'' value. The higher value of ϵ'' obtained at high temperatures might be due to the space charge polarization and the ferroelectric domain wall contribution.¹² A relaxation peak is observed for each temperature, which confirms the relaxation process occurring in this system. The peaks shift toward higher frequency with increasing temperature, suggesting that the relaxation process is thermally activated, in accord with the result of the complex impedance analysis.

5. Electrical Conductivity Analysis

Figure 9 displays the total conductivity σ as a function of frequency at different temperatures for the LPFTO ceramic.

Fig. 9. Frequency dependence of total conductivity σ at different temperatures for the LPFTO ceramic.

As can be seen, the conductivity of LPFTO consists of two parts: dc conductivity, which is independent of frequency and appears at the low-frequency region, and ac conductivity, which depends on the frequency and appears at the high-frequency region.

The frequency dependence of the total conductivity suggests the occurrence of relaxation phenomena in the system and follows the Jonscher model. The Jonscher equation can be used to explain the conductivity behavior as follows^{12,13}:

$$\sigma(\omega) = \sigma_{dc} + B\omega^s,$$

where $\sigma(\omega)$ is the total conductivity, σ_{dc} is the dc conductivity, and s is the frequency exponent. Values of s below unity are indicative of the translational motion of charge carriers; however, for $s > 1$, the motion of charge carriers is localized in the lattice.¹² The conductivity parameters are given in Table 2.

The σ_{dc} value increases with increasing temperature, suggesting that the conduction mechanism is thermally activated. On the basis of this observation, the activation energy

Table 2. Jonscher model fitting results of the total conductivity for the LPFTO ceramic.

T (°C)	σ_{dc} (S m ⁻¹)	B	s
50	5.95×10^{-6}	1.11×10^{-5}	0.50
75	6.30×10^{-6}	1.62×10^{-5}	0.53
100	6.95×10^{-6}	6.38×10^{-6}	0.57
125	1.22×10^{-5}	4.56×10^{-7}	0.65
150	3.50×10^{-5}	4.95×10^{-8}	0.81
175	8.81×10^{-5}	1.68×10^{-7}	0.93
200	1.53×10^{-4}	9.31×10^{-8}	0.99
225	2.12×10^{-4}	3.75×10^{-8}	1.09
250	4.14×10^{-4}	1.01×10^{-8}	1.24
275	8.07×10^{-4}	1.42×10^{-9}	1.36
300	1.40×10^{-3}	2.72×10^{-10}	1.49

Fig. 10. The plot of dc conductivity vs. the inverse of temperature. The inset describes the evolution of $\ln \sigma_{dc}$ vs $10^3/T$ for the LPFTO ceramic.

of conduction process can be obtained by using the Arrhenius relation^{9,12} as follows:

$$\ln \sigma = \ln \sigma_0 - \frac{E_a}{k_B} \frac{1}{T},$$

where E_a is the activation energy, k_B is the Boltzmann constant, σ is conductivity, and T is temperature. The activation energy is determined from the slope of the linear fit. The evolution of the dc conductivity as a function of temperature is illustrated in Fig. 10. Two different activation energies are involved in the conduction mechanism: $E_{a1} = 39$ meV for $T > 385$ K and $E_{a2} = 18$ meV for $T < 385$ K. In addition, the Curie temperature, i.e., the transition temperature of a ferromagnetic semiconductor to a paramagnetic semiconductor, was found to be 385 K. When the temperature increases, both the mobility and the density of the charge carriers increase, resulting in low activation energy. Nonetheless, the saturation of σ_{dc} is observed at high temperatures. This is most likely due to the presence of defects in the grain boundary, which become traps for the movement of charge carriers in the lattice.

As can be seen from Table 2, s was found to be < 1 for $T < 200^\circ\text{C}$ and > 1 for $T > 200^\circ\text{C}$ and to increase with temperature. This indicates that the charge carriers have translational motion at $T < 200^\circ\text{C}$ and localized hopping without leaving the neighborhood at $T > 200^\circ\text{C}$.¹² Accordingly, the temperature dependence s parameter satisfies the nonoverlapping small-polaron tunneling (NSPT) model with the relation^{9,12}:

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

where W_H describes the polaron hopping energy.

Figure 11 presents the temperature dependence of $1 - s$ for the LPFTO ceramic. Two different slopes are obtained, resulting in two values of W_H : 246 meV at low temperatures

Fig. 11. Temperature dependence of $1 - s$ for the LPFTO ceramic.

and 75 meV at high temperatures. The W_H value decreases with increasing temperature, which further confirms that the conduction mechanism is thermally activated.

6. Conclusion

Ceramic nanoparticles of LPFTO have been successfully synthesized by sol-gel and sintering methods. The synthesized-ceramic material crystallizes in the orthorhombic structure with the $Pnma$ space group. Its electrical properties are strongly dependent on temperature and frequency. The complex impedance analysis afforded grain and grain boundary contributions, indicating that the two conduction mechanisms are involved. This was also confirmed by electrical conductivity analysis. The activation energies calculated from dc conductivity were found to be 18 meV at low temperature and 39 meV at high temperature, which is consistent with the occurrence of the two different mechanisms in the conduction processes. The ac conductivity was found to obey the NSPT model. By calculating the polaron hopping energy, we have confirmed that the conduction processes in this system are thermally activated.

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