Effect of Sr-substitution on the structural and dielectric properties of LaFeO_3 perovskite materials

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Received 2 July 2018; Revised 11 September 2018; Accepted 29 September 2018; Published 1 November 2018

The study aims to investigate the structural and dielectric properties of perovskite $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0.1, 0.2, 0.3$, and 0.4) synthesized by sol-gel and sintering methods. X-ray diffraction (XRD), transmission electron microscopy (TEM), and LCR-Meter were used to identify the phase, crystallography parameters, morphology, particle size, and electrical behavior of the synthesized perovskite materials. The samples showed a single-phase orthorhombic crystal structure with $Pbnm$ space group. Sr-substitution induced the volume unit cell and crystallite size to decrease. The synthesized nanoparticles were uniform and homogeneous with the particle size less than 200 nm. Impedance spectroscopy (IS) was used to explain the electrical behavior as a function of frequency (100 Hz to 1 MHz) at various temperatures (300–373 K). The presence of small polarons as charge carriers within the grain and grain boundary were elucidated from the electrical conductivity experiments. Sr-substitution caused the dielectric constant and electronic conductivity to increase with the highest values obtained from $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0.4$).

Keywords: $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$; impedance spectroscopy; conductivity; dielectric.

1. Introduction

The perovskite structure has the chemical formula ABX_3 , where X is usually the O^{2-} anion. Generally, perovskite oxides have high oxygen mobility and they can become partially substituted, causing ion conductivity (from the O^{2-} anion) and electronic conductivity (from the charge carrier, either electron or hole).^{1,2} One of the well-known perovskite structures is LaFeO_3 . Stoichiometrically, this material is composed of La^{3+} cations in the A-sites, Fe^{3+} cations in the B-sites, and O^{2-} anions in the X-sites. LaFeO_3 is a potential electrode material for solid oxide fuel cells and gas sensors.³ Several LaFeO_3 studies have shown the possibility of increasing LaFeO_3 conductivity with Sr-substitution.^{1,4} The Sr^{2+} cation is a known dopant, that causes the emerging oxygen vacancy, Fe element oxidation, and increased O^{2-} anion mobility, resulting in the increase in electrical and thermal conductivities of LaFeO_3 .⁴ Suresh *et al.*¹ reported that $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0.0$ – 0.4), synthesized by the solution combustion method, exhibited low resistivity values near its Neel temperature and the surface area increased as the Sr concentration increased, resulting in semiconductor behavior. As reported by Cui *et al.*,⁴ $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ synthesized by the screening method had a transition structural phase from orthorhombic ($x < 0.4$) to rhombohedral ($x > 0.4$) because the Fe oxidation number changed from Fe^{3+} to Fe^{4+} and Fe^{5+} , resulting in a decreasing in volume for the unit cell (smaller ionic radius); the highest conductivity was found at $x = 0.4$.

However, the electrical properties of Sr-doped LaFeO_3 , i.e., the electrical conductivity and dielectric properties, have not been widely studied using the impedance spectroscopy (IS) method. In this study, we performed IS measurements for the electrical properties of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0.1, 0.2, 0.3$, and 0.4). The physical structures were investigated by X-ray diffraction (XRD) and transmission electron microscopy (TEM).

2. Experimental Details

Nanocrystalline $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0.1, 0.2, 0.3$, and 0.4) powders were prepared by the sol-gel method using lanthanum oxide (La_2O_3 (Merck)), strontium nitrate ($\text{Sr}(\text{NO}_3)_2$ (Merck)), ferrite nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck)), and citrate acid monohydrate (Merck) as a precursor. All chemicals were of analytical grade. All of the precursors were mixed in water at room temperature. The resulting suspensions were continuously stirred and heated at 120°C on a hot plate until a highly viscous gel phase was formed. The gel was then dried at 200°C and the obtained powder was carefully crushed to a fine powder. The samples were placed in a furnace and heated at 900°C under high pressure. To form the bulk phase, the powders were pressed into pellets (10 mm diameter and 1.5 mm thick) using a uniaxial pressure system and sintered at 1300°C .

The crystal structure was characterized using XRD with $\text{Cu K}\alpha$ radiation, θ , ($25^\circ \leq 2\theta \leq 75^\circ$) with a scanning rate of

0.02°/s. Structural parameter refinement was carried out with the Fullprof 2 k software. The morphology of all samples was characterized using TEM with selected area electron diffraction (SAED) patterns. The electrical parameters were obtained by IS in the frequency range from 1 kHz to 1 MHz at different temperatures (300–373 K) using an LCR-Meter (LCR-Meter Merck. FLUKE-PM6306).

3. Results and Discussion

3.1. Structural properties

Figure 1 presents the XRD spectrum of the obtained $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ samples. All samples show an orthorhombic

Fig. 1. (a). XRD patterns of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0.1, 0.2, 0.3$, and 0.4) samples sintered at 1300°C for 1 h and (b) the most intense diffraction peak and the corresponding crystal plane.

perovskite crystal structure with the $pbnm$ space group without a second phase. The absence of secondary phases after sintering indicated that La^{3+} ion sites substituted with Sr^{2+} ions did not achieve the solubility limit. The substitution with Sr^{2+} in to La^{3+} -site caused the peaks to shift toward higher Bragg angles, as shown in Fig. 1(b), indicating that the interplanar crystal spacing decreased without changing the crystal structure.⁴ Structural parameter refinements of the synthesized $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ are summarized in Table 1. The lattice parameters and crystallite sizes decreased with increasing Sr-substitution. As the ionic radius is 118 pm for Sr^{2+} and 103.2 pm for La^{3+} ,⁶ the increase in the lattice parameters and unit cell was anticipated. Simultaneously, a portion of the Fe^{3+} ions in the B-site might be oxidized to Fe^{4+} and Fe^{5+} (smaller ionic radii) and allowed the lattice parameters and the unit cell to contract. Overall, the effect of Fe-valence change in the lattice was more dominant than the effect of Sr^{2+} substitution, causing the lattice parameters and the unit cell to decrease.⁴

The crystal structure stability can be calculated using the Goldschmidt tolerance factor (t)⁵ (Table 1). The t -values increased with an increase in Sr-substitution, suggesting an increase in crystal structure stability. As the t -value approaches 1, the crystal structure distortion decreases and the structure approaches a cubic form.

Figure 2 presents the TEM bright field images for all samples. The TEM images show the presence of uniform and homogeneous particles less than 200 nm in size. Figure 3 shows the SAED patterns of the $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ nanoparticles. The spotty ring patterns suggest a polycrystalline nature. The SAED patterns for all samples agreed well with the XRD results.

3.2. Electrical properties

Figure 4 shows the Nyquist plots of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x =$ (a) 0.1, (b) 0.2, (c) 0.3, and (d) 0.4) at 300–373 K. An increase in temperature caused the semicircle diameter to decrease, indicating the impedance values decreased. The impedance values also decreased as the Sr-substitution increased.

The Nyquist plots were fitted by using Zsimpwin 7.0 software to interpret the best equivalent circuit model and electrical parameters in order to understand the conduction mechanism. The best equivalent circuit fit was made by two parallel combinations of resistance and constant phase element ($(R_1\text{CPE}_1)(R_2\text{CPE}_2)$). The high frequency semicircle is the grain contribution and the grain boundary contribution comes from the low frequency semicircle.^{7,17} The grain conductivity and grain boundary contribution can be calculated¹⁰ with the following equations:

$$\sigma_g = \frac{t}{R_g A}, \quad (1)$$

$$\sigma_{gb} = \frac{t}{R_{gb} A}, \quad (2)$$

Table 1. The refined structural parameters of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0.1, 0.2, 0.3$, and 0.4) samples sintered at 1300°C for 1 h.

Samples	$\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$			
	$x = 0.1$	$x = 0.2$	$x = 0.3$	$x = 0.4$
Lattice parameters				
a (Å)	5.563	5.553	5.536	5.532
b (Å)	5.538	5.511	5.508	5.483
c (Å)	7.833	7.847	7.835	7.798
Volume unit cell (Å ³)	241.3	240.1	238.9	236.5
Crystallite size (nm)	35	27	24	20
Atomic position				
La				
x	0.9923	0.9923	0.9923	0.9923
y	0.0229	0.0229	0.0229	0.0229
z	0.2500	0.2500	0.2500	0.2500
Sr				
x	0.9923	0.9923	0.9923	0.9923
y	0.0229	0.0229	0.0229	0.0229
z	0.2500	0.2500	0.2500	0.2500
Fe				
x	0.0000	0.0000	0.0000	0.0000
y	0.5000	0.5000	0.5000	0.5000
z	0.0000	0.0000	0.0000	0.0000
O_1				
x	0.0748	0.0748	0.0748	0.0748
y	0.4935	0.4935	0.4935	0.4935
z	0.2500	0.2500	0.2500	0.2500
O_2				
x	0.7191	0.7191	0.7191	0.7191
y	0.2856	0.2856	0.2856	0.2856
z	0.0388	0.0388	0.0388	0.0388
Occupancy				
La	0.45	0.40	0.35	0.30
Sr	0.05	0.10	0.15	0.20
Fe	0.50	0.50	0.50	0.50
O_1	0.50	0.50	0.50	0.50
O_2	1.00	1.00	1.00	1.00
Tolerance factor, t	0.861	0.867	0.872	0.878

where σ_g and σ_{gb} are conductivity contributed by grain and grain boundary, t is thickness of the samples, A is surface area of the samples, and R_g and R_{gb} are resistivity contributed by grain and grain boundary.

Table 2 shows the grain and grain boundary conductivity obtained from the equivalent electrical circuit model of the $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ samples. According to the Nyquist plot in Fig. 4, the low frequency semicircles were higher than the high frequency semicircles, which indicated that σ_g was higher than σ_{gb} . It indicates that the low charge carrier trapped in the grain boundaries⁹ results in the lower contribution of the grain boundaries on electrical conductivity in comparison with the contribution of grain. However, the charge carrier contribution should increase for as the crystallite size

(Table 1) decreases because the number of grain boundary contacts increases.

The energy needed by a charge carrier to hop between the lattice is termed the activation energy (E_a). Using the Arrhenius relation,⁸ E_a values were estimated for the grain and grain boundary as follows:

$$\sigma = \sigma_0 e^{-\frac{E_a}{k_B T}}. \quad (3)$$

From the slope of the fitted straight line of $\log \sigma$ versus $\frac{1}{T}$, all of the activation energies were obtained. $E_a \geq 1$ eV was attributed to the ionic conduction at a high temperature. $E_a < 1$ eV was attributed to small polaron hopping.¹⁴ Table 3 shows the grain activation energy (E_g) and grain boundary activation energy (E_{gb}). These values indicate that the polaron-hopping mechanism may be a key factor in the grain and grain boundary conduction mechanisms. Electron conduction is known to be affected by the migration barriers and charge carrier concentration, in this case, polarons.¹⁵ A low migration barrier and high carrier concentration are required for electron conduction enhancements. The substitution of Sr to La-sites creates impurities and gives rise to small polarons that act as charge carriers, resulting in a rise in the conductivity values for both grain and grain boundary.

Figure 5 shows the bode plots of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0.1, 0.2, 0.3$, and 0.4) at 300–373 K. The bode plots gradually increase to a maximum value and then decreases, which indicates the existence of a relaxation phenomenon.⁸ The maximum peak shift to higher frequencies with increasing temperature indicating a decrease in relaxation time and suggests the existence of thermal processes in this material. This can be derived from the existence of immobile species at lower temperature and defects at higher temperature.¹⁰ Detailed analysis reveals that the relaxation time follows the Arrhenius law as follows:

$$\tau = \tau_0 e^{-\frac{E_a}{k_B T}}. \quad (4)$$

From the slope of the fitted $\log \tau$ versus $\frac{1}{T}$ straight line, the activation energy due to the electrical relaxation were obtained for $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0.1, 0.2, 0.3$, and 0.4). The E_a for electrical relaxation is shown in Table 4. The E_a decreased as the Sr-content increased; the smallest electrical relaxation E_a was obtained at $x = 0.4$. A low electrical relaxation E_a allows the charge carrier to overcome a potential barrier in a relaxation process with as low energy as possible.

Figure 6 shows the dielectric constant (ϵ') and loss dielectric ($\tan \delta$) of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0.1, 0.2, 0.3$, and 0.4) at 300–373 K. A similar dielectric constant behavior was obtained from other study compositions.¹² The dielectric constant decreases as the frequency increases. Moreover, it decreases at lower frequencies and is unaffected at higher frequencies. This may result from the overall microstructure being unaffected at these temperatures^{11,12} and that the space charge polarization contribution is dominant for a polar

Fig. 2. TEM images of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ nanoparticles ($x = 0.1, 0.2, 0.3$, and 0.4).

Fig. 3. SAED of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ nanoparticles ($x = 0.1, 0.2, 0.3$, and 0.4).

Fig. 4. Nyquist plots of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0.1, 0.2, 0.3$, and 0.4) at 300–373 K. The lines are the best fit using Zsimpwin 7.0 software.

Table 2. The conductivity obtained from the electrical equivalent circuit parameters for $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ samples.

T (K)	$x = 0.1$		$x = 0.2$		$x = 0.3$		$x = 0.4$	
	σ_g (S m^{-1})	σ_{gb} (S m^{-1})	σ_g (S m^{-1})	σ_{gb} (S m^{-1})	σ_g (S m^{-1})	σ_{gb} (S m^{-1})	σ_g (S m^{-1})	σ_{gb} (S m^{-1})
330	0.094	0.017	2.25	0.452	2.34	0.553	3.65	1.45
340	0.105	0.029	2.58	0.542	2.61	0.679	4.12	1.61
350	0.126	0.048	2.90	0.611	2.89	0.738	4.25	1.78
360	0.351	0.059	3.13	0.773	3.03	0.861	4.52	2.08
370	0.654	0.078	3.39	1.042	3.31	1.114	5.08	2.58

Table 3. Activation energies of grain and grain boundary for $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0.1, 0.2, 0.3$ and 0.4).

Samples	Activation energy, E_a (meV)	
	E_g (grain)	(E_{gb}) grain boundary
$x = 0.1$	197	177
$x = 0.2$	46.9	92.5
$x = 0.3$	40.6	74.9
$x = 0.4$	34.7	64.9

material in this low frequency range.¹² The space charge polarization can be caused by mobile charge carriers during the relaxation process. The ϵ' increases with increasing temperature and this can be explained using the fact that electric dipoles are unable to orient themselves with frequency. Increasing temperature facilitates dipole orientation and the orientational polarization value increases, which leads to an increase in ϵ' .¹² The dielectric loss is temperature-dependent and shows the relaxation peak for each sample.

Fig. 5. Bode plot (imaginary part of impedance with frequency) of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0.1, 0.2, 0.3$, and 0.4).

The peak amplitude shifted to a higher frequency, consistent with Fig. 5. Moreover, for $x > 0.1$, the peaks did not change significantly (Fig. 5 and Table 4). The decrease in peak shifting suggests that E_a also decreased. In addition, the dielectric constant increased and dielectric loss decreased as Sr-content increased. However, it is difficult to find a material that has a high dielectric constant without a corresponding decrease in dielectric loss.

The frequency dependence total conductivity at different temperatures is shown in Fig. 7. The dispersion region was

observed at higher frequencies, corresponding to AC conductivity, whereas the plateau region corresponded to DC conductivity. According to the Jonscher theorem, the frequency dependence of total conductivity is caused by the relaxation phenomena in the system. The Jonscher equation was used to explain the behavior of AC conductivity as follows¹³:

$$\sigma(\omega) = \sigma_{dc} + B\omega^s, \quad (5)$$

where $\sigma(\omega)$ is total conductivity, σ_{dc} is DC conductivity, and s is the frequency exponent. The conductivity parameters are shown in Table 5. The value of s was found to be < 1 for $x = 0.1$ and > 1 for $x > 0.1$. σ_{dc} enhancement was found as Sr-substitution and temperature increased. The value of $s < 1$ suggests charge carrier movement in a translational motion. Correspondingly, $s > 1$ suggests that motion involves the localized charge carrier without leaving the local environment.¹³ The σ_{dc} component increased with increasing temperature, indicating that the conduction process was thermally activated. σ_{dc} also increased with increasing

Table 4. The fitted E_a of the relaxation process for $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0.1, 0.2, 0.3$, and 0.4).

Samples	Activation energy, E_a (meV)
$x = 0.1$	180
$x = 0.2$	60.2
$x = 0.3$	48.2
$x = 0.4$	6.39

Fig. 6. Dielectric constant (ϵ') and loss dielectric ($\tan \delta$) of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0.1, 0.2, 0.3$, and 0.4) at 300–373 K.

Fig. 6. (Continued)

Fig. 7. The frequency dependence of conductivity for $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0.1, 0.2, 0.3,$ and 0.4) at 300–373 K.

Table 5. Jöhscher’s power-law fitting results for AC conductivity. $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0.1, 0.2, 0.3,$ and 0.4) at 300–373 K.

T (K)	330	340	350	360	370
$x = 0.1$					
σ_{DC} (S m^{-1})	0.009	0.012	0.015	0.025	0.047
B ($\times 10^{-6}$)	9.879	372.5	1680	2260	1550
s	0.725	0.465	0.368	0.363	0.405
$x = 0.2$					
σ_{DC} (S m^{-1})	0.395	0.471	0.583	0.701	0.877
B ($\times 10^{-7}$)	2.730	0.528	0.052	0.013	0.004
s	1.129	1.246	1.416	1.509	1.586
$x = 0.3$					
σ_{DC} (S m^{-1})	0.462	0.555	0.669	0.835	0.962
B ($\times 10^{-10}$)	5.459	1.862	0.609	0.241	0.121
s	1.582	1.652	1.722	1.773	1.812
$x = 0.4$					
σ_{DC} (S m^{-1})	1.395	1.511	1.669	1.964	2.271
B ($\times 10^{-10}$)	251.8	181.1	221.9	30.77	12.30
s	1.334	1.349	1.326	1.464	1.519

Fig. 8. The frequency dependence of $\ln \sigma_{\text{dc}}$ for $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0.1, 0.2, 0.3,$ and 0.4) at 300–373 K.

Sr-substitution. σ_{dc} can be caused by the number of charge carrier compensation increases because Sr-substitution causes the presence of Fe^{4+} and Fe^{5+} for electric charge compensation.

Based on the values obtained for σ_{dc} at all temperatures (T), the conduction activation energy can be calculated using the Arrhenius relation.^{8,17} Figure 8 shows the linear relation between $1000/T$ and $\ln \sigma_{dc}$. The conduction activation energy decreased with increasing Sr-substitution. Since the linear relation and activation energy for conduction were low, the electrical conduction process can be considered to occur through a small polaron-hopping transport mechanism where the charge carrier becomes localized as a small polaron near a (La, Sr) impurity.^{15,16}

4. Conclusion

In this work, $La_{1-x}Sr_xFeO_3$ with $x = 0.1, 0.2, 0.3$, and 0.4 were successfully synthesized using the sol-gel and sintering methods. All samples showed a single phase orthorhombic structure (*pbnm* space group). The decrease in lattice parameters and cell volume with increasing Sr-substitution may be caused by the concurrent creation of Fe^{4+} and Fe^{5+} (smaller ionic radii) as electric charge compensation. The impedance spectra of the complexes can be described by two parallel combinations of resistance and constant phase elements (grain and grain boundary contributions). The activation energies from conduction and relaxation processes were calculated and these activation energies confirmed the presence of small polarons that act as charge carriers. Sr substitution decreases the activation energy as barrier that blocks the movements of space charges in lattice and increases the conductivity and dielectric constant of the materials.

Acknowledgment

The authors would like to thank Ministry of Technology Research and Higher Education of Republic of Indonesia under KLN Grant No. 537/UN2.R3.1/HKP05.00/2018.

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