Structural, optical, and room temperature dielectric properties of $\text{La}_{1-x}\text{A}_x\text{FeO}_3$ ($\text{A} = \text{Mg, Sr, and Ba}$) perovskite nanomaterials

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Abstract. This paper investigated the variation of structure, optical and electrical properties of LMFO, LSFO, and LBFO. All samples were synthesized by sol gel method. For this present research study, the structure of the material was investigated by X-Ray Diffraction (XRD). Nevertheless, the electrical properties of this materials were investigated by using RLC Meter. The optical band gap energy was obtained by using UV-Vis Spectroscopy. The optical gap energy evaluated by Kubelka Munk method are 1.58 eV, 1.32 eV and 1.38 eV for LMFO, LSFO and LBFO respectively. Therefore, this small gap energy impacted sensitivity of the material towards its optical properties. To sum up, this what makes all samples are the suitable candidates for alcohol gas sensor.

1. Introduction
Lanthanum orthoferrite is one of eminent perovskite materials, which has been studied extensively for substantial purposes, due to the surface oxygen species activation and rife of oxygen vacancies [1]. It has marvelous reactivity in oxidation activities and thermal stability than other ABO$_3$ perovskite. The fe-ion lattice distortion causes oxygen vacancies inside the crystal to appear in conformity with surface oxygen exchange [2,3]. Therefore this material have excellent oxygen reaction catalytic and oxygen separators membran behavior, which plays main role as gas sensors [3,4] and potential cathode for SOFC in syngas production [5,6].

Moreover, the performance on catalytic activity improved sufficiently by doping on A or B site with various metals. Presence of dopants deformed the structural, optical and dielectric properties of crystal, mainly at A’ sites. A sites of perovskite is the largest ionic radii among another ion in ABO$_3$ perovskite. Therefore, adding dopants into A-site fabricate defect in crystal structure, especially earth alkaline and 3d metal such as magnesium (LMFO), strontium (LSFO), and barium (LBFO). Previous works impressed all the series of LMFO, LSFO, and LBFO in which chiefly generated most labile oxygen species, without implicate the structural changes [1,3,5,7].

However, in this work, $\text{La}_{1-x}\text{A}_x\text{FeO}_3$ ($\text{A} = \text{Mg, Sr, and Ba}$), which labelled as LMFO, LSFO, and LBFO respectively, were chosen to investigate the structure, optic and dielectric property. The characterization series encompassed X-Ray Diffraction (XRD), UV-Vis Spectroscopy, and dielectric behavior at room temperature.
2. Experimental method

2.1. Preparation
At the first step, the La$_{1-x}$A$_x$FeO$_3$ (A = Mg, Sr, and Ba) with x = 0.2 perovskite were prepared by sol-gel method. The gel was pre-calcined (drying) in a furnace at 473K for 5 h. The precursor was then calcined at temperatures 1173K for 6 h to form a perovskite phase of compound. At the last of this preparation step, the powder as calcined sample was pressed at a pressure 5kN, then continue to be sintered for 3 h at a temperature 1573K.

2.2. Structure characterization
The crystalline structure of powder sample were characterized by an X-ray diffraction (XRD). XRD patterns were examined by using XRD type PANalytical-X Pert PRO with source radiation Cu Kα ($\lambda=1,5418$ Å) in the 2$\theta$ range of 20 – 80°. The composition of sample equipped with X-ray fluorescence (XRF).

2.3. Optical energy gap characterization
The band gap energy was measured by UV-VIS (Agilent Cary 100/300) to estimate the value.

2.4. Dielectric characterization
The electrical properties of bulk samples were characterized by RLC-Meter FLUKE-PM6306 type as a function of wide range frequency 100Hz–1MHz with selected temperature range around 348-548K. Next, the impedance data was represented by Nyquist plot and Bode plot. Then, the parallel plate method were using to calculate dielectric behavior.

3. Results and discussion

3.1. Structure
Structure characterization consist of XRD pattern.

3.1.1. XRD pattern. This XRD patterns for LMFO, LSFO, and LBFO was reported in figure 1. Every pattern identified as orthorhombic perovskite, corresponds with the standard peak of perovskite type oxide structure is characterized by othorhombic system (JCPDF No. 47-1049) [3]. The extra peaks for LBFO sample indicate the distortion of crystal structure due to the second phase, which agree with previous report [5,8], without negate the orthorhombic structure. However, the perovskite phase and Pnma space group were dominated in in all XRD patterns [9,10]. The observed peaks pattern for LMFO,LSFO, and LBFO agree with the expectation from another research [5,7,9]. In the XRD pattern, the LMFO has the sharp-pointed peaks intensity, and is linear with the highest crystallinity of the samples. LBFO sample, which has wider peaks, is being the most reducible crystal, and again agrees with previous report [9].
Figure 1. XRD pattern of LBFO, LSFO, and LMFO.

The elemental constituents of these perovskite samples were also confirmed with XRF as demonstrated in Table 1.

| Structure | Component | Percentage (%) | Chemical Formulation |
|-----------|-----------|----------------|----------------------|
| LBFO      | Lanthanum | 50.012         | \(La_{0.8}Ba_{0.2}FeO_3\) |
|           | Barium    | 10.547         |                      |
|           | Ferrum    | 24.815         |                      |
| LSFO      | Lanthanum | 63.101         | \(La_{0.8}Sr_{0.2}FeO_3\) |
|           | Strontium | 4.2400         |                      |
|           | Ferrum    | 26.374         |                      |
| LMFO      | Lanthanum | 54.191         | \(La_{0.8}Mg_{0.2}FeO_3\) |
|           | Magnesium | 6.4360         |                      |
|           | Ferrum    | 25.204         |                      |

3.1.2. Lattice parameter. The values of lattice parameter, volume, and crystallite size for (LMFO, LBFO and LSFO) are reported in Table 2. Both of lattice parameters (a, b,c) along with the unit cell volumes of all samples show the same values with \(LaFeO_3\) lattice parameter from the previous report [11-13]. The orthorhombic structure is also agree with what was reported in the previous report [14]. The crystal volume of LMFO again agrees with previous report as was reported by Qing lin et. al, but this particular volume has bigger crystallite size [10].


| Structure | LBFO | LSFO | LMFO |
|-----------|------|------|------|
| $u = b = \gamma$ | Orthorombic | Orthorombic | Orthorombic |
| $a$ (Å)   | 90°  | 90°  | 90°  |
| $b$ (Å)   | 5,580 | 5,556 | 5,561 |
| $c$ (Å)   | 7,856 | 7,845 | 7,825 |
| Volume (Å³) | 243,8 | 241,7 | 242,6 |
| Crystallite Size (nm) | 36,48 | 76,45 | 96,37 |
| GOF       | 1,151 | 1,111 | 1,143 |

The average crystallite size of LBFO, LMFO, and LMFO were estimated by using Debye Scherer equation from the refined data. The crystallite sizes are comparable with the perovskite prepared by some other methods including co-precipitation, and sol gel [8,9]. Crystallite size will affect the physical properties of materials, including oxidation reaction. LBFO exhibits relatively low crystallinity with smaller crystallite size than LSFO and LMFO. Moreover, the smaller than LaFeO$_3$ crystall was synthesized by co-precipitation method that was reported previously. Resulting the crystallite size of LSFO that agrees with LaFeO$_3$ by co-precipitation synthesized method [9]. LMFO has larger crystallite size due to its smaller ionic radii of Mg$^{2+}$ (0.072) [9] and octahedral distortion of teller effect, thus, results more oxygen defects [15,16].

3.2. Optical properties
La$^{3+}$ in the 4f$^0$ state is spectroscopically silent. It should present only the weakest bands in the UV spectral region. From theoretical expectations, it may be concluded that the optical spectra of our samples should be diagnosed only for the Fe$^{3+}$ species. The optical bands, shown in Figure 2, occur for those which expected for d–d and ligand to metal charge transfer transitions of Fe$^{3+}$ in octahedral coordination [17].

![Figure 2. UV-Vis spectra of LBFO, LSFO, and LMFO samples.](image-url)
The optical gap energies that were evaluated by Kubelka Munk method are 1.58 eV, 1.32 eV and 1.38 eV for LMFO, LSFO and LBFO respectively. LSFO has smaller energy gap, agrees with SrNb$_{0.1}$Fe$_{0.9}$O$_3$$_8$[18]. Mg$^{2+}$ cation reduce atomic bonding between Fe/Mg-O in crystal, it reduces the charge carrier mobility and decreases the gap energy. Ion Fe$^{4+}$ is presented in LMFO, LSFO, and LBFO, that its content being compensated by cation defectivity. This cation defectivity raised the oxygen vacancy, which boosted the oxygen mobile due to lower activation energy and hasted the the reaction between water and carbon in alcohol compounds [3,5].

3.3. Dielectric Properties
Figure 3 evaluated the permittivity spectra of LBFO, LSFO, and LMFO at room temperature. The permittivity decreased as frequency increased and assimilated become one spectra at higher frequency. The vigorous permittivity at lower frequency showed the exixtance of space charge polarization [15,19]. LMFO showed the lowest permittivity compared with LSFO and LBFO, showed the lowest polarization at room temperature, it pointed LMFO was easier to polarized than LSFO and LBFO.

![Figure 3. Permittivity spectra of LBFO, LSFO, and LMFO samples at room temperature.](image)

4. Conclusions
In this work, a series of Lanthanum orthoferrite (LMFO, LSFO and LBFO) synthesized by sol gel method. XRD and XRF data proved the phase formation of orthorhombic perovskite with crystallite size of LBFO, LSFO and LMFO were 36.48, 76.45, and 96.37 nm respectively. The optical energy gap follows by sequence of LMFO>LBFO>LSFO.

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