Effect of Calcination Temperature on the Stability of the Perovskite Materials – Study of Structural and Morphological Properties

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ABSTRACT
In this research, the solid-state method was utilized to synthesize LaFeO3 powders, with La2O3 and Fe2O3 being employed as precursor materials. The prepared samples were calcined at different temperatures 800°C, 900°C, 1000°C, 1100°C, 1200°C and 1300°C for 4h to study phase stability. The thermal effect on structural and morphological properties was reported. The X-ray diffraction results confirmed the pure phase in its orthorhombic configuration at 1200°C and 1300°C, which was confirmed by Rietveld’s analysis. Scanning electron microscopy coupled with Energy-dispersive X-ray spectroscopy was employed to analyze the surface morphology and compositional characteristics. In addition, the samples were analyzed by Fourier Transform Infrared Spectroscopy. The thermal behavior of the product was investigated through the utilization of thermogravimetric analysis.

Keywords: LaFeO3, perovskites, solid-state, X-ray diffraction, infrared spectroscopy, thermogravimetric analysis.

INTRODUCTION
The ABO3 perovskites are crystalline and stable materials. They exhibit the flexibility to fabricate novel materials with enhanced material properties, based on large-size rare earth or alkaline earth metal at A-site, while transition metal at B-site. Thus, the properties of these types of material will be improved by the substitution or doping of new elements at different sites (Saumitra et al. 2012; Toan et al. 2003). Perovskites are materials characterized by several properties (structural, dielectric, electrical, optical, magnetic, and photocatalytic, etc.) which have attracted the attention of many researchers over the last few years to use them in several applications: as a catalyst, sensor materials, cathode material in solid oxide fuel cells, sewage treatment, and gas-sensitive materials (Sun et al. 2011; Mahapatra et al. 2018). In practice, the rare-earth orthoferrites RFeO3 (R = rare earth element) have an orthorhombic symmetry with a Pbnm space group. Lanthanum ferrite oxide LaFeO3 (LFO) is the most studied one of these materials (Gao et al. 2019; Lee et al. 2021). Consequently, the Néel temperature (TN=740 K) of LFO is the highest in the ferrite system (Qing Lin et al. 2018). Due to its advantageous features, such as a unique crystal structure, distinctive electromagnetic behavior, high electron/ion conductivity, excellent catalytic activity, suitable thermal expansion coefficient, and chemical stability, this perovskite material finds extensive use in various industrial applications (Qing Lin et al. 2018). LFO has been prepared using various methods, including co-precipitation (Kumar et al. 2009; Nakayama 2001), sol-gel (Ismael and Wark 2019; Qing Lin et al. 2018), hydrothermal (Mesbah et al. 2020; Jairo et al. 2016; Wenjun Zheng et al. 2000), the polymerized complex method (Phokha et al. 2014), combustion method (Priti et al. 2010; Komova et al. 2016), and solid-state method (Qiang Li et al. 2021; Sazelee et al. 2019). Most researchers on this perovskite are interested in the catalytic, photocatalytic, dielectric, and magnetic properties; Kucharczyk et al. reported that the physicochemical properties of LFO perovskite
and its methane oxidation activity depend on the preparation conditions (temperature and calcination time) and they found that when the calcination temperature increases the BET-specific surface area of perovskite decreases (Kucharczyk et al. 2019). Saumitra et al. synthesized LFO by using the sol-gel method and they studied the photocatalytic water splitting reaction for hydrogen generation under visible light irradiation, showing noticeable hydrogen enhancement using ethanol as a sacrificial donor and Platine as co-catalyst (Saumitra et al. 2012). Lee et al. (2021) reported the colossal dielectric response, multi-ferroic properties, and gas-sensing characteristics of the rare earth orthoferrite LFO ceramics. All these works have not discussed the thermal effect of calcination on the properties structural and morphologic for LFO. For this reason, this article focused on the synthesized LaFeO$_3$ powders by using a solid-state method and calcined at different temperatures, i.e. 800°C, 900°C, 1000°C, 1100°C, 1200°C, and 1300°C for 4 h for the study of stability phase of LFO. The powders were subjected to characterization using X-ray diffraction (XRD), Fourier transform infrared (FTIR), scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDS), and thermogravimetric analysis (TGA). These techniques were employed to investigate the impact on the structural and morphological properties of the samples.

**EXPERIMENT**

**Samples preparation:**

The LaFeO$_3$ powders were elaborated by the solid-state reaction using lanthanum oxide La$_2$O$_3$ and iron oxide Fe$_2$O$_3$ with high purity (99.99%) starting materials. These precursors were mixed in a stoichiometric amount according to the following reaction:

$$\frac{1}{2} \text{La}_2\text{O}_3 + \frac{1}{2} \text{Fe}_2\text{O}_3 \rightarrow \text{LaFeO}_3$$

The precursor materials were initially mixed for 0.5 hours and subsequently homogenized by milling in the presence of acetone for a total of 4 hours. Following this step, the resulting powders were dried at a temperature of 100°C for a period of 24 hours. Finally, the dried powders were further mixed using an agate mortar for 30 minutes. The powder mixture was transferred into an alumina crucible and subjected to calcination in an air environment at various temperatures, namely 800°C, 900°C, 1000°C, 1100°C, 1200°C, and 1300°C. The calcination process was carried out in a Nabertherm furnace, under a static air atmosphere, with a heating rate of 3°C per minute. Following the calcination, all specimens were allowed to cool down to room temperature in ambient air. A visual representation of the different steps involved in the preparation method of LaFeO$_3$ is depicted in Figure 1.

**Characterization**

X-ray diffraction analysis: the LFO powders were characterized by X-ray diffraction measurement using a Panalytical X’Pert Pro X-ray diffractometer equipped with a Cu-Kα monochromatic source ($\lambda = 1.54056 \text{ Å}$). For scanning electron microscopy coupled to EDS, the morphology and microstructure were made by using a scanning microscope (Jeol it500 HR). The samples were analyzed using a Bruker vortex 70 FTIR spectrometer resting on ATR mode. The registering of FTIR spectra for a wavelength ranged from 400 to 4000 cm$^{-1}$. For the thermogravimetric analysis, recorded the mass loss between 25°C and 1250°C at a heating rate of 3°C/min using a simultaneous thermobalance (TG+DSC) with a LINSEIS high range type (LINSEIS STA PT 1600).

**RESULTS AND DISCUSSION**

**X-ray diffraction**

Figure 2 shows the XRD patterns of the synthesized LFO samples calcined at different temperatures for 4 hours. All diffractograms for these ceramics were acquired under the same operating conditions. For calcination temperatures lower than 1100°C, crystallization of the phase in its Orthorhombic (Pbnm space group) configuration was observed with the presence of various secondary phases associated with La$_2$O$_3$ and Fe$_2$O$_3$ (starting precursor). Beyond this temperature, the structure remains stable and the intensity of the secondary peaks decreased until its complete disappearance at the temperature of 1200°C. From the literature, it was found that the calcination temperature of LFO material is not fixed. According to previous works which
prepared this material with the same method as the one used in this paper (solid state method), this temperature varies between 1000 for 24 and 1500°C as shown in Table 1. All of these studies confirm the orthorhombic phase of LFO with different space groups. Considering this, it was decided to subject the compound to various calcination temperatures to examine both its behavior and phase stability.

Rietveld refinement

For more information on the structure and to confirm the results obtained in the X-ray diffraction, the Rietveld refinement was studied using the Fullprof software. The peak pattern was carried out using a pseudo-Voigt function. In detail, the background level was described by a polynomial function with 12 coefficients. The Rietveld refinement of the studied samples calcined at 1100°C, 1200°C and 1300°C was presented in Figure 3. In the visual representation, the experimental data is depicted by the red color, while the black line in red color represents the Rietveld refinement. Additionally, the blue line represents the difference between the experimental data and the Rietveld refinement. The obtained refinement results provide confirmation of the presence of three distinct phases: LaFeO$_3$ (orthorhombic phase with Pbnm space group), Fe$_2$O$_3$, and La$_2$O$_3$. In addition, this result confirms the pure phase at 1200°C (i.e. no peaks indicating the existence of secondary phases of La$_2$O$_3$ and Fe$_2$O$_3$). The Rietveld refinement was allowed to plot by the software VESTA the crystal structure of LFO calcined at 1200°C was presented in Figure 3, this structure shows that site A is La and site B is occupied by Fe, and (O$_1$, O$_2$) the different oxygen sites. La$^{3+}$

Table 1. Comparison of the thermal treatment, crystal system/space group, of the LFO powder synthesis by solid-state method with previous works

<table>
<thead>
<tr>
<th>No.</th>
<th>Crystal system/space group</th>
<th>Thermal treatment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Orthorhombic/Pbnm</td>
<td>Calcined at 1400 °C/4h</td>
<td>[21]</td>
</tr>
<tr>
<td>2</td>
<td>Orthorhombic/Pbnm</td>
<td>Preheated at 1000 °C/2h, Calcined at 1200 °C/4h</td>
<td>[5]</td>
</tr>
<tr>
<td>3</td>
<td>Orthorhombic/Pnma</td>
<td>1500 °C/6h</td>
<td>[22]</td>
</tr>
<tr>
<td>4</td>
<td>Orthorhombic/Pnma</td>
<td>La$_2$O$_3$ calcined at 900 °C/12h, LaFeO$_3$ calcined at 1000 °C/24h</td>
<td>[23]</td>
</tr>
<tr>
<td>5</td>
<td>Orthorhombic/Pbnm</td>
<td>1200 °C/4h</td>
<td>This work</td>
</tr>
</tbody>
</table>
is attached to eight O²⁻ atoms in eight-coordinate geometry and Fe³⁺ is related to six O²⁻ atoms to form FeO₆ octahedra with divided corners.

Table 2 displays the lattice parameters (a, b, c), unit cell volume (V), and Rietveld refinement Σ² values for the LFO material calcined at different temperatures (1100°C, 1200°C, and 1300°C). From this table, it can be seen that with increasing temperature, the value of the quality of fit Σ² decrease which indicates good crystallinity of the phase with a small change in lattice parameters which that confirmed the stability of the phase. The average grain size of this sample was calculated by the Debye-Scherrer equation (Ismael and Wark 2019; Qing Lin et al. 2018):

\[ D = \frac{K\lambda}{\beta \cos\theta} \]  

At a calcination temperature of 1200°C, the average grain size (D) of the LFO material was determined to be 95.63 nm. The calculation of D involves the parameters: K (crystallite shape factor), λ (copper wavelength, λ = 0.15405 nm), θ (Bragg diffraction angle), and β (full width at half maximum FWHM) obtained from the Rietveld refinement in the output file.

**Infrared spectroscopy**

Figure 4 shows the infrared spectrum of calcined LFO powders at different temperatures in the region 400–4000 cm⁻¹. The spectra exhibit two main bands, with the first band observed at 533 cm⁻¹ attributed to the Fe-O stretching vibration. The second band, centered around 474 cm⁻¹, is likely associated with the O-Fe-O deformation vibration (Priti V et al. 2010). In addition, the presence of some bands can be observed for

Table 2. Lattice parameters (a, b, c), Unit cell V, and Σ² at 1100°C, 1200°C and 1300°C for 4 hours

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Lattice constant</th>
<th>V(Å³)</th>
<th>Σ²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a (Å)</td>
<td>b (Å)</td>
<td>c (Å)</td>
</tr>
<tr>
<td>1100</td>
<td>5.5498</td>
<td>5.5614</td>
<td>7.8474</td>
</tr>
<tr>
<td>1200</td>
<td>5.5503</td>
<td>5.5622</td>
<td>7.8483</td>
</tr>
<tr>
<td>1300</td>
<td>5.5496</td>
<td>5.5612</td>
<td>7.8488</td>
</tr>
</tbody>
</table>
temperature lower than 1000°C, one at 3610 cm$^{-1}$ which is related to the vibration of the OH group according to the work reported in the literature (Lin et al. 2018; Li et al. 2007; Bhat et al. 2013; Khalil et al. 2022). The presence of two bands in the range of 1380 to 1490 cm$^{-1}$ can be attributed to the asymmetric stretching vibration of metal carbonates, specifically corresponding to the C-H and C-C bonds (Lin et al. 2018; Khalil et al. 2022; Feng et al. 2011; Tang et al. 2013), respectively. For the other temperatures and above two bands related to the LFO material (Fe-O, O-Fe-O) the disappearance of the OH, C-H, and C-C bands and the appearance of two new bands in the range between 1990 and 2110 cm$^{-1}$ were noted. These two bands are corresponding to the specific C=O double bond vibration of carbon dioxide CO$_2$ according to Vijayaraghavan et al. (2017). On the other hand, with the increase in calcination temperature, the intensity of the bands related to carbon bonds and OH bonds gradually decreases, which is probably related to small amounts of acetone residues. These bonds are not detected by XRD and are observed in Infrared analysis and formed mainly at the surface due to exposure to ambient air (Feng et al. 2011). Also, there is the appearance of CO$_2$ which can be related to their release on the surface of the powders.

**Energy-dispersive X-ray spectroscopy analysis**

Figure 6 shows the energy-dispersive X-ray spectroscopy LFO material calcined at 1100°C, 1200°C, and 1300°C. SEM is a valuable technique employed to investigate the purity and chemical composition of the synthesized particles, providing qualitative insights into the sample composition. Analysis of Figure 6 and Table 3 reveals the presence of all essential elements of LaFeO$_3$, including lanthanum (La), iron (Fe), oxygen (O), and carbon (C). The detection of carbon, associated with the coating material on the sample, further confirms the findings obtained from the Infrared-spectrum analysis (Fig. 4).

**Scanning electron microscopy analysis**

Scanning electron microscopy is an imaging technique that utilizes electrons instead of light to generate high-resolution images. It enables the examination of the microscopic surface structure of materials by scanning their surfaces (Humera Sabeeh et al. 2018). This analysis has been performed to probe the morphology and grain size. Figure 5 presents the SEM images and the results of the grain size analysis of LFO powders calcined at 1100°C, 1200°C and 1300°C for 4 h. It was observed that the majority of the particles are homogeneously distributed and the grain size is not uniform and has a semi-spherical morphology. From these SEM images, the average particle size was calculated by fitting the particle size distribution histogram using ImageJ software. It was found that the average particle size is 820 nm, 1077 nm, and 1312 nm for 1100°C, 1200°C, and 1300°C respectively, which means that the particle size increases by increasing the calcination temperature. Therefore, it can be concluded that the calcination temperature significantly modifies the surface morphology.

**Thermogravimetric analysis**

To confirm the calcination temperature appropriate for the formation of a crystalline phase. The synthesized sample was characterized by thermogravimetric analysis. Figure 7 indicates the thermal analysis of the LFO particles. The result was registered in a temperature range of 25°C up to 1200°C with a heating rate of 3 degrees/min. It was found that a total mass loss of 10% in this temperature range is divided into three step; two steps of weight loss and one step of mass gain; the first is a loss of 4.61% occurs around 312°C up to 359.83°C which it was attributed to the evaporation of volatile organic substances. The second step is a gain of mass of 2.92% at 350°C to 460°C that is probably related to the fixation of a gas. The final step is a loss of 7.46% around 712.66°C up to 850°C; this may be due to the degassing of adsorbed elements. Furthermore, above 850°C, there is no loss of mass indicating the absence of organic matter, and residual
Fig. 5. SEM of the surface of LFO samples calcined at 1100°C, 1200°C, and 1300°C associated particle size distributions

Fig. 6. Results of EDS analysis of LFO powders calcined at 1100°C, 1200°C and 1300°C for 4h
reagents, which suggests the formation of the stable phase of LFO. The observations align with the findings from the X-ray diffraction patterns of LFO samples calcined at various temperatures, affirming the transition of the amorphous phase to the crystalline phase starting from 800°C.

CONCLUSIONS

In conclusion, the synthesis of LFO using the solid-state method was successfully achieved. The impact of varying calcination temperatures on the structural, microstructural, and morphological properties has been thoroughly discussed. The X-ray diffraction results, analyzed using the Rietveld refinement method, indicate that at temperatures starting from 1200°C, the LFO structure is pure, with no secondary phases present. This finding demonstrates the stability of the LFO phase at higher temperatures. Infrared analysis indicates the coexistence of the two principal bands Fe-O and Fe-O-Fe for all calcination temperatures. SEM images present a homogeneous semi-spherical structure and the average particle size rises with increasing calcination temperature. EDS results demonstrate the presence of elements composed of LFO (La, Fe, and O). The ATG analysis shows the calcination temperature adequate for LFO to be pure. On the basis of the extensive analyses conducted, it can be concluded that the optimal calcination temperature for achieving LaFeO$_3$ is 1200°C. Furthermore, the phase stability of LaFeO$_3$ is observed up to 1300°C.

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