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Article in *Materials Science Forum* · July 2017

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Structural and Magnetic Characterization of $\text{LaFe}_{1-x}\text{Al}_x\text{O}_3$ ($x = 0$ and 0.2) Orthoferrites Synthesized by Gelatin Method

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Keywords: orthoferrites, gelatin, magnetic properties.

Abstract: The rare-earth orthoferrites (LnFeO_3) are promising materials for various applications, such as chemical sensors, cathode for SOFC, catalysts, among others. In general, these oxides are synthesized at temperatures higher than 700 °C. In this work, nanocrystalline $\text{LaFe}_{1-x}\text{Al}_x\text{O}_3$ ($x=0$, $x=0.2$) powders were synthesized by a method that uses gelatin as organic precursor and heat treated at 400, 600 and 800 °C. The structural and magnetic characterization of powders was carried out by X-ray diffraction (XRD) and vibrating sample magnetometry (VSM). Morphological analysis was performed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The XRD patterns revealed the formation of orthoferrites single phase since 400°C. The powders exhibited weak ferromagnetic behavior at room temperature where the values of saturation magnetization, remanence and coercivity varied with the doping and heat treatment temperature.

Introduction

Perovskite-type oxides with the formula ABO_3 have been studied extensively due to their interesting properties favoring application in many fields, such as magnetic, electronic, optic, refractories, heterogeneous catalysis, etc [1-3]. Rare-earth orthoferrites (RFeO_3) constitute a family of distorted perovskite with an orthorhombic structure. Several studies concerned on the investigation of magnetic and electric properties of these materials have been published [4]. Among the various rare-earth orthoferrites, pure and substituted LaFeO_3 perovskites are of special interest for applications to SOFC [4], gas sensors [2,5], photocatalyst [6], ceramic pigment [3], etc. LaFeO_3 is known to be weak ferromagnetic, the origin of behavior may be results of the uncompensated canted spins from the surfaces and also due to internal canted spin [7].

Several synthesis process of have been applied to synthesize perovskite-type oxides, such as, solid state reaction, sol-gel, combustion, hydrothermal, and others [2-4, 6-8]. However, some these methods require expensive reactants, unfriendly environmental compounds, several steps synthesis, mixtures time prolonged, heating at high temperatures to produce desired phase, and so on. Recently, a method for obtaining single phase powders has been developed using commercial gelatin as organic precursor. This method provides an interesting alternative to other methods because it offers several attractive advantages such as: simplicity of experimental procedure and short time between the preparation of precursor polymeric and the availability of the final product [9, 10]. The procedure consists on the formation of colloidal dispersions between the gelatin and metal ions, which chelate cations through their amino and carbonyl groups [11]. In this present study, we report for the first time the preparation of $\text{LaFe}_{1-x}\text{Al}_x\text{O}$ perovskites by a gelatin method, in order to evaluate the viability of this synthesis route to obtain these powders. In addition, the effect of calcination temperature and introduction of Al^{3+} ion on the structural and magnetic properties of LaFeO_3 also were evaluated

Experimental

$\text{LaFe}_{1-x}\text{Al}_x\text{O}_3$ ($x=0.0, 0.2$) oxides were synthesized by gelatin method. Initially gelatin powder (GELITA) was added into a beaker with 150 ml of deionized water under constant stirring at a temperature of about 50°C for dissolution. Stoichiometric amounts of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%-SIGMA-ALDRICH), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99.9%-SIGMA-ALDRICH) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99.9%-SIGMA-ALDRICH) were added to the solution at 70°C for some minutes. The temperature was slowly increased up to 90°C and the solution was stirred on a hot plate until it became a resin. This resin was calcined at 400°C , grounded into powders and then submitted to calcined at 600 and 800°C for 4 h to produced perovskite phase. The powders obtained were characterized for several techniques.

X-ray diffraction patterns were recorded on a Miniflex diffractometer with monochromatic radiation of CuK ($\lambda=1.5406 \text{ \AA}$). A 2θ angular range was used between 10 and 80° with a scan rate of 2° min^{-1} and step of 0.02° . Crystalline phases were identified using the International Center for Diffraction Data (ICDD) database. The Rietveld method was used to refine the XRD data using the MAUD program. Magnetic measurements were performed at 300 K in a Thermoflex 2500 Lakeshore vibrating magnetometer using a maximum applied field of 15Koe . SEM Images were examined in a JEOL SEM LV microscope. TEM images were obtained with a JEM 3010 URP electron microscope.

Results and Discussion

X-ray diffraction patterns of LaFeO_3 and $\text{LaFe}_{0.8}\text{Al}_{0.2}\text{O}_3$ calcined at $400, 600$ and 800°C are illustrated in Fig 1a and 1b, respectively. As shown in these figures, all samples present diffraction lines assigned to perovskite with orthorhombic structure and Pbnm space group (153536-ICSD). The distortion from the cubic perovskite occurs mainly in the position of the lanthanide ions, whereas the Fe^{3+} ions are surrounded by six oxygen ions forming the octahedral coordination [12]. The quantitative analysis of phases and crystallite size obtained by MAUD program is given in Table 1. No traces of secondary phases were identified in the XRD patterns. The formation of single phase in all the powders calcined at different temperature has been confirmed by Rietveld analysis. The addition of Al^{3+} ion did not change the structure of LaFeO_3 phase, however, it shifts the reflections in toward the higher diffraction angles in comparison with those of the pure perovskite (LaFeO_3 $2\theta = 32.21$; $\text{LaFe}_{0.8}\text{Al}_{0.2}\text{O}_3$ $2\theta = 32.52$). The substitution of La^{3+} for Al^{3+} ions caused a reducing of lattice parameters and crystallite size of unsubstituted perovskite ($x=0.0$). The crystallites sizes are in range of $43\text{-}55 \text{ nm}$ and $50\text{-}80 \text{ nm}$ for LaFeO_3 and $\text{LaFe}_{0.8}\text{Al}_{0.2}\text{O}_3$, respectively.

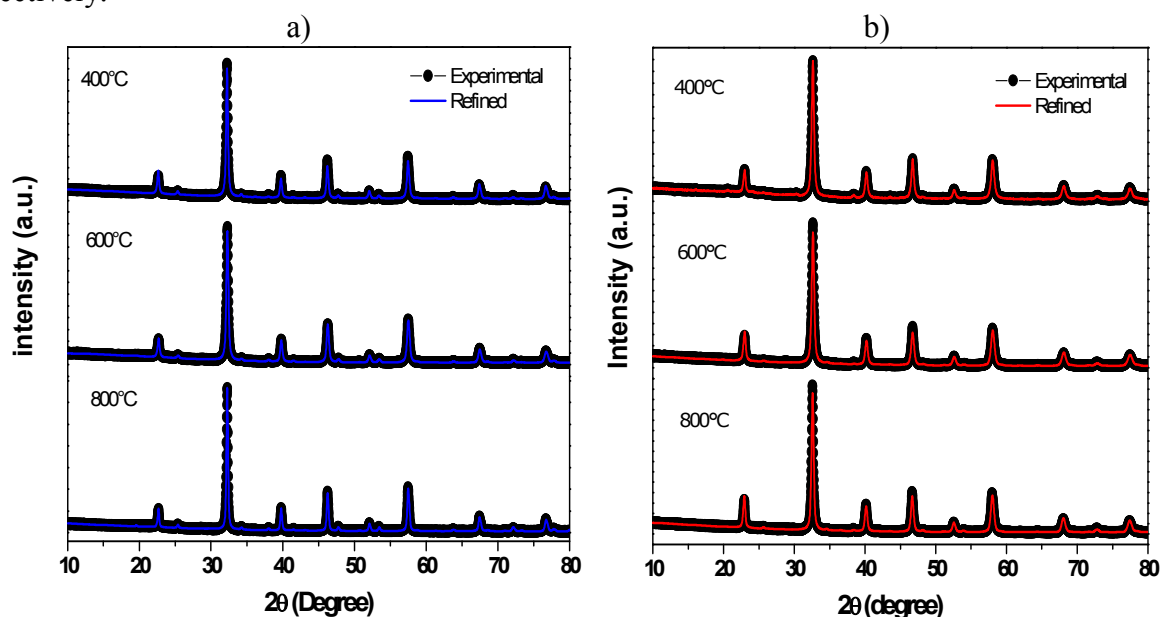
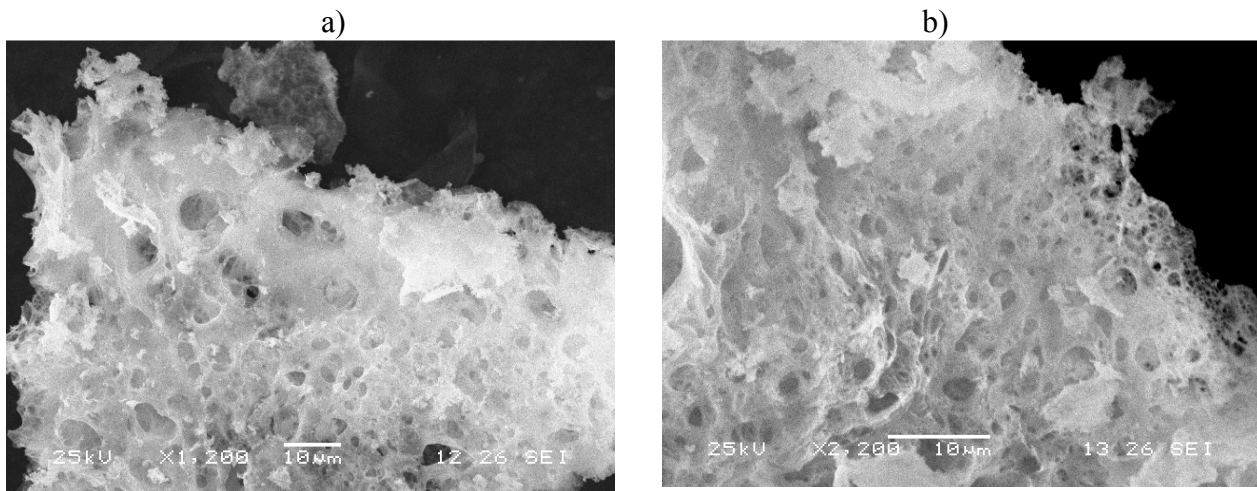
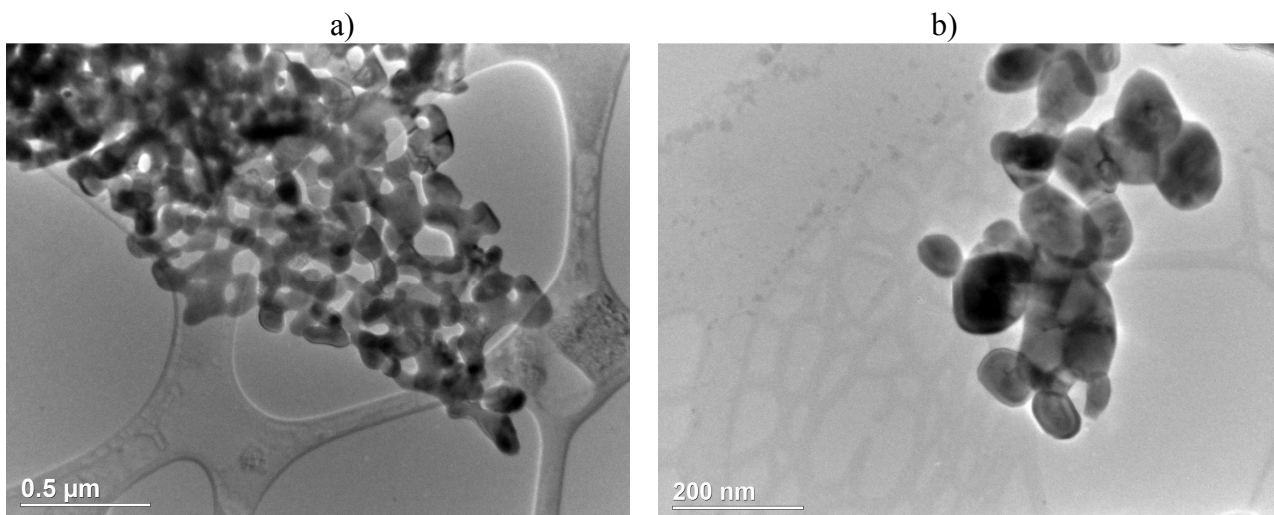


Fig. 1. DRX patterns of a) LaFeO_3 and b) $\text{LaFe}_{0.8}\text{Al}_{0.2}\text{O}_3$ calcined at different temperatures.

Table 1. Lattice parameters and average crystallite size of the $\text{LaFe}_{1-x}\text{Al}_x\text{O}_3$ powders.

| Temperature °C | Samples | Lattice Parameters (Å) | | | Unit cell volume (Å ³) | Crystallite size (nm) |
|-------------------|--|------------------------|-------|-------|---------------------------------------|--------------------------|
| | | a | b | c | | |
| 400 | LaFeO_3 | 5.565 | 7.856 | 5.553 | 242.770 | 50 |
| | $\text{LaFe}_{0.8}\text{Al}_{0.2}\text{O}_3$ | 5.524 | 7.807 | 5.521 | 238.098 | 43 |
| 600 | LaFeO_3 | 5.563 | 7.862 | 5.558 | 243.086 | 58 |
| | $\text{LaFe}_{0.8}\text{Al}_{0.2}\text{O}_3$ | 5.524 | 7.812 | 5.522 | 238.294 | 43 |
| 800 | LaFeO_3 | 5.564 | 7.855 | 5.555 | 242.782 | 80 |
| | $\text{LaFe}_{0.8}\text{Al}_{0.2}\text{O}_3$ | 5.524 | 7.810 | 5.523 | 238.276 | 55 |

The morphological analysis of oxides was performed by scanning electron microscopy (SEM). Transmission electron microscopy (TEM) was used aiming to measure more precisely the particles sizes of these oxides. Figures 2 and 3 displayed SEM and TEM images, respectively. SEM images show that the powders are sponge-like and porous agglomerates. This porous surface was, probably caused by the evolution of high gas content during the synthesis and calcination procedure. Spherical particles (< 200 nm) can be seen in TEM images. These particles are larger than the crystallite size obtained in the DRX patterns, primarily due to the presence of agglomerates in the powders. These agglomerates consist of small particles held together by interfacial forces which are responsible for the spherical shape of larger particles.

Fig. 2. SEM images of LaFeO_3 calcinated at a) 600 °C and b) 800 °C.Fig. 3. TEM images of LaFeO_3 calcinated at a) 600 °C and b) 800 °C.

The magnetization curves measured at room temperature of the LaFeO_3 and $\text{LaFe}_{0.8}\text{Al}_{0.2}\text{O}_3$ perovskites are shown in Fig 4. All samples exhibited a typical weak ferromagnetic behavior and it was not observed tendency to saturation when applied a magnetic field up to 15 KOe. In Table 2 are displayed the values of saturation magnetization (M_s), remanent magnetization (M_r) and coercive field (H_c). The results demonstrated that the replacement of Fe^{3+} by Al^{3+} ions and the increase of heat treatment temperature cause a slight reduction in M_s , M_r and H_c , favoring the antiferromagnetic ordering of such systems. LaFeO_3 is a very well-known antiferromagnetic material with weak ferromagnetism [13]. The weak ferromagnetism arises from a small canting between the adjacent Fe ions. Thus, it is expected that this canting is greater between the adjacent surface ions because they have lower coordination number. As a consequence, the weak ferromagnetism decreases with the increase of crystallite size, which explains the maximum magnetization values observed for the samples LaFeO_3 and $\text{LaFe}_{0.8}\text{Al}_{0.2}\text{O}_3$ treated at 400°C . When Fe^{3+} ions are replaced by Al^{3+} ions, the main effect is the decrease of unit cell volume because the ionic radius of Al^{3+} (0.54 \AA) is much smaller compared to that of Fe^{3+} (0.65 \AA), which leads to a shortening of the Fe-O-Fe bonds, contributing to the antiferromagnetic ordering is dominant [14].

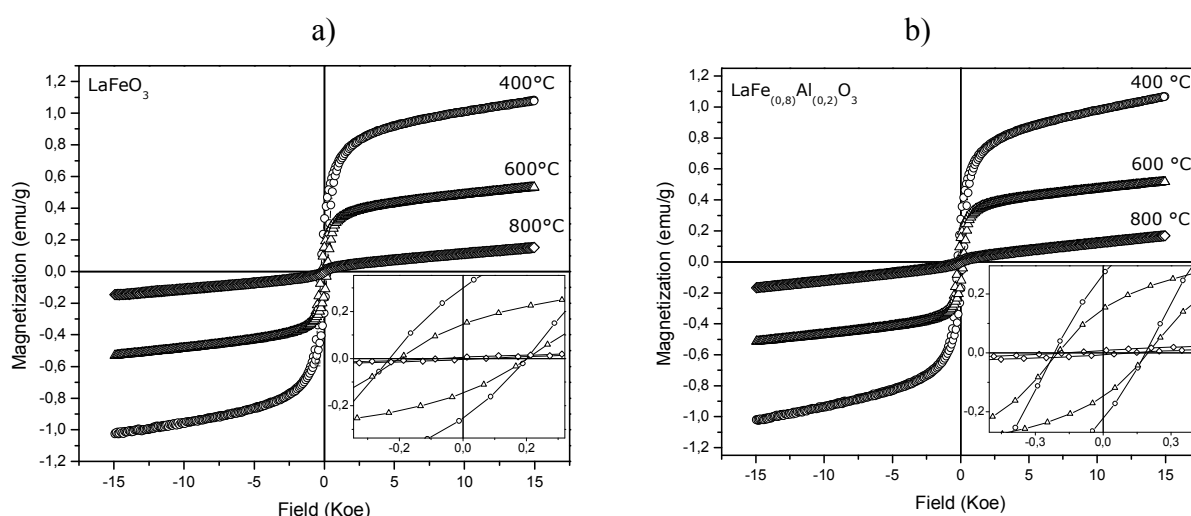


Fig. 4. Room temperature magnetization curves of the a) LaFeO_3 and b) $\text{LaFe}_{0.8}\text{Al}_{0.2}\text{O}_3$ calcined at different temperatures.

Table 2. Magnetic parameters of the $\text{LaFe}_{1-x}\text{Al}_x\text{O}_3$ powders.

| Temperature ($^\circ\text{C}$) | Samples | M_s | M_r | H_c |
|----------------------------------|--|---------|---------|-------|
| | | (emu/g) | (emu/g) | (Oe) |
| 400 | LaFeO_3 | 1.08 | 0.28 | 220 |
| | $\text{LaFe}_{0.8}\text{Al}_{0.2}\text{O}_3$ | 1.06 | 0.25 | 200 |
| 600 | LaFeO_3 | 0.53 | 0.15 | 203 |
| | $\text{LaFe}_{0.8}\text{Al}_{0.2}\text{O}_3$ | 0.52 | 0.15 | 201 |
| 800 | LaFeO_3 | 0.15 | 0.01 | 69 |
| | $\text{LaFe}_{0.8}\text{Al}_{0.2}\text{O}_3$ | 0.17 | 0.01 | 140 |

Conclusion

In this communication, we demonstrate that orthoferrites can be obtained at a temperature as low as 400°C by a cheap and simple method that uses gelatin as organic precursor. Powders produced by using this method were well crystalline, single phase and porous. The M-H hysteresis revealed that all orthoferrites synthesized exhibited better weak ferromagnetic behavior at room temperature.

Acknowledgments

The authors are grateful to CNPq for the financial support, GELITA for supplying the gelatin, and LNLS (National Synchrotron Light Laboratory) for SEM and TEM images.

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