

# Synthesis and application of pigments based on lanthanide orthoferrites

Patrícia M. Pimentel<sup>1</sup>, Jairo L.S. Dutra<sup>1</sup>, Maria S.C. Câmara<sup>2</sup>, Gerbeson C.B. Dantas<sup>1</sup>, Osmar R. Bagnato<sup>3</sup>, Glauber S. Godoi<sup>4</sup>, Rosane M.P.B. Oliveira<sup>5,\*</sup>

<sup>1</sup>Federal Rural University of Semi-arid Region, Angicos, RN, 59515-000, Brazil

<sup>2</sup>Federal Rural University of Pernambuco, Serra Talhada, PE, 56900-000, Brazil

<sup>3</sup>Brazilian Synchrotron Light Laboratory, Campinas, SP, 13083-100, Brazil

<sup>4</sup>Department of Chemistry, Federal University of Sergipe, São Cristóvão, SE, 49100-000, Brazil

<sup>5</sup>Department of Materials Science and Engineering, Federal University of Sergipe, São Cristóvão, SE, 49100-000, Brazil

Received 9 October 2019; Received in revised form 12 April 2020; Accepted 24 April 2020

## Abstract

In this work, we synthesized oxides with perovskite  $LnFeO_3$  type structure (where Ln = La, Pr and Nd), aiming their use as ceramic pigments. The as-synthesized powders, prepared by gelatin method, were thermally treated at 600 and 800 °C to obtain the perovskite phase. The characterization was performed using X-ray diffraction technique, followed by Rietveld refinement, scanning and transmission electron microscopy, spectroscopy in the UV-Visible region and CIE Lab colorimetry. The calcined powders were also used for fabrication of ceramic pieces to evaluate the colour when 2 wt.% of the powders was added into a transparent glaze. The pigments presented shades ranging from pale brown for the powdered samples to yellowish when applied in the glazes.

Keywords: orthoferrites, perovskites, colour, pigments

## I. Introduction

Rare earth ferrites have attracted much attention in recent years due to their potential applications in various fields of technology, including catalysts [1], cathodes in solid oxide fuel cells [2], sensor materials [3], magnetic materials [4,5], semiconductor ceramics [6] and many others. Nowadays, the interest in the application of these ferrites as environmentally friendly pigments has increased, since lanthanides are used instead of toxic elements [7,8]. Lanthanide ferrites have been proposed as viable alternatives to traditional toxic pigments due to their low toxicity and perovskite structure which gives stability at high temperatures and chemical resistance [8,9].

Perovskite-type oxides  $(ABO_3)$  consist of large-sized cations at the A-site (alkali metal or lanthanide) with a 12-fold coordination and smaller cations (transition *d*-metal) at the B-site with a 6-fold coordination. The ideal perovskite structure has a cubic unit cell, however

distortions to orthorhombic, tetragonal and rhombohedral are possible. Rare-earth orthoferrites crystallize in a distorted perovskite structure with an orthorhombic unit cell. A unit cell of  $LnFeO_3$  has four formula units with  $Fe^{3+}$  ions surrounded by six oxygen ions in an octahedral coordination resulting in an orthorhombic structure with a *Pbnm* space group [10].

It is known that the characteristics of the materials are greatly affected by the synthesis route and processing conditions. For this reason, many methods have been used to prepare these oxides with control over the powder characteristics, such as purity, chemical homogeneity, morphology and average particle size. Proper control of these factors may improve known properties and promote new ones. Among the ferrite synthesis methods, we can cite conventional solid-state reaction [11–13], sol-gel [14], combustion reaction [15,16] and Pechini [17]. The gelatin method stands out as a promising alternative procedure for obtaining these oxides [18–20]. This method has some advantages, such as high homogeneity and obtaining nanometric particles, besides being a simple technique of low cost which

<sup>\*</sup>Corresponding author: tel: +55 79 3194 6344,

e-mail: rosaneboliveira@ufs.br

does not generate solid toxic residues. The gelatin synthesis is a variation of the Pechini method, wherein the polymeric precursors are replaced by gelatin. The dispersion obtained between the gelatin and metal ions is first heated at lower temperature to reduce volume and form a gel and then calcined at a predetermined temperature to form corresponding inorganic oxide. Thus, this study aims to evaluate the influence of calcination temperatures on the structural and colour properties of lanthanide ferrites obtained using the gelatin method. The ferrites applied into transparent glaze were also studied.

#### **II. Experimental**

 $LnFeO_3$  (Ln = La, Pr and Nd) oxides were synthesized by gelatin method. Initially, gelatin powder (Gelita) was added to 150 ml of deionized water and kept under constant stirring at 50 °C until dissolution. According to the desired formulation, stoichiometric amounts of  $Fe(NO_3)_3 \cdot 9H_2O$  (99.9%) Sigma-Aldrich),  $La(NO_3)_3 \cdot 6H_2O$  (99.9% Sigma-Aldrich),  $Pr(NO_3)_3 \cdot 6H_2O$  (99.9% Sigma-Aldrich) and  $Nd(NO_3)_3 \cdot 6H_2O$  (99.9% Sigma-Aldrich) were added to the dispersion under stirring at 70 °C for a few minutes. Temperature was slowly increased to 90 °C until it became a resin. Ceramic powders were obtained by calcination of this resin at 400 °C. Then the precursors were calcined at 600 and 800 °C for 4 h to obtain perovskite phase. All synthesized lanthanide ferrites were used to prepare bulk samples by adding 2 wt.% of the calcined powder into transparent glaze. A local industry provided the glaze (80% feldspar and 20% borax) and the glazing temperature was 1100 °C.

X-ray diffraction patterns were obtained in the Miniflex diffractometer using a monochromatic CuK $\alpha$  radiation source ( $\lambda = 1.5406$  Å), with a 2 $\theta$  angular range between 10° and 80°, the scan speed of 2°/min and step of 0.02°. Crystalline phases present in the powders were identified using the International Center for Diffraction Data (ICDD) database. The Rietveld method using Maud software was applied to refine experimental diffraction data. The average crystallite sizes were also calculated according to the Debye-Scherrer equation [21].

SEM images were obtained by JEOL SEM LV scanning electron microscope. The samples were pre-coated with a thin gold layer to make them conductive before inserting them into SEM. HR-TEM images were obtained in a JEM 3010 URP electron transmission microscope with 300 kV accelerating voltage. Before analysis, small amounts of the samples were dispersed in ethanol by ultrasonic agitation. Diffuse reflectance spectra of the powdered samples were obtained by using a UV-Vis spectrophotometer (Shimadzu UV-2550) with integrating sphere. Barium sulphate was used as standard white and the spectra were scanned in the 200–900 nm range. The band gap energy  $(E_g)$  was obtained by plotting  $[F(R) \times h \cdot v]^2$  against  $h \cdot v$  according to the following equation:

$$[F(R) \times h \cdot v]^2 = A \left( h \cdot v - E_g \right) \tag{1}$$

where F(R) is Kubelka-Munk function [22,23], *R* is the reflectance of the samples, *A* is a proportionality constant and  $h \cdot v$  is photon energy.

The CIE -  $L^*a^*b^*$  colour parameters were measured by a Gretac Macbeth Color-eye 2180 spectrophotometer in the 300–800 nm range, using the D65 illumination. In this method,  $L^*$  is the lightness axis which ranges from 0 (black) to 100 (white);  $a^*$  and  $b^*$  represent red(+) – green(-) and yellow(+) – blue(-) hue intensities, respectively. The  $C^*$  (chroma) parameter represents the colour saturation, and it can be calculated by using the following formula [23]:

$$C^* = \left(a^{*2} + b^{*2}\right)^{1/2} \tag{2}$$

#### III. Results and discussion

Figure 1 shows X-ray patterns of the lanthanide ferrites calcined at 600 and 800 °C. All samples were single phase and presented reflections assigned to orthorhombic perovskite (space group Pbnm). According to the Rietveld analysis, the diffraction data are in good agreement with ICSD cards for LaFeO<sub>3</sub> (53536),  $PrFeO_3$  (27275) and NdFeO\_3 (63645). The distortion of the cubic perovskite occurs mainly in the position of the lanthanide ions, once the Fe<sup>3+</sup> ions are surrounded by six oxygen ions that constitute the octahedral coordination [24]. The lattice parameters and average crystallite size obtained by the Maud software are given in Table 1. The GOF (goodness of fit) values were smaller than 2, which is an indicative of the satisfactory refinement accuracy. The average crystallite sizes ranged from 49– 58 nm and 80-83 nm for the powders calcined at 600 and 800 °C, respectively.

As can be seen from Table 1, the increase in the calcination temperature did not produce significant changes in the lattice parameters of orthoferrites, causing only a small decrease in these parameters. It is also observed that there is a small variation of the lattice parameters with different lanthanide ions substituted in perovskite structure. As the lanthanide ionic radius decreases (from La<sup>3+</sup> to Nd<sup>3+</sup>), the values of *a* and *b* parameters decrease and a discrete splitting of major reflection (32.5°) is observed in the XRD patterns due to higher distortion in the structure.

The morphology of the powders was investigated by SEM (Fig. 2) and TEM (Fig. 3). The pores observed in these images are attributed to the release of gases during the gelatin decomposition process. In both Figs. 2 and 3, it is observed that the powder is composed of many agglomerated particles which probably consist of several small particles held together by interfacial forces which lead to the formation of larger particles. The grain boundaries are not clearly distinguishable in TEM image (Fig. 3a) due to the particles agglomeration and presented average size smaller than 200 nm. The high-



Figure 1. XRD patterns of LaFeO<sub>3</sub>, PrFeO<sub>3</sub> and NdFeO<sub>3</sub> calcined at different temperatures

Table 1. Lattice parameters and crystallite sizes of LaFeO<sub>3</sub>, PrFeO<sub>3</sub> and NdFeO<sub>3</sub> calcined at different temperatures

Sample	Temperature	Lattice parameters			Unit cell volume	Crystallite size	COF	
	[°C]	a [Å]	b [Å]	c [Å]	[Å <sup>3</sup> ]	[nm]	GOF	
LaFeO <sub>3</sub>	600	5.564	5.556	7.855	242.826	58	1.19	
	800	5.563	5.555	7.852	242.646	80	1.17	
PrFeO <sub>3</sub>	600	5.489	5.579	7.795	238.707	52	1.21	
	800	5.486	5.577	7.792	238.400	81	1.22	
NdFeO <sub>3</sub>	600	5.457	5.586	7.769	236.820	49	1.18	
	800	5.454	5.584	7.765	236.484	83	1.24	



Figure 2. SEM image of LaFeO<sub>3</sub> calcined at 800 °C

resolution TEM image (Fig. 3b) confirms that a region of a single grain consists of nearly equally spaced lattice rows which can be seen as the (111) crystal plane with d = 3.514 Å. The regular crystal lattice distance is also seen, which expresses the high crystallinity of perovskites.

The diffuse reflectance spectra of the perovskites are illustrated in Fig. 4. The broad absorption bands between 450–700 nm can be attributed to the  ${}^{6}A_{1g} \rightarrow {}^{4}T_{2g}$ transitions of Fe<sup>3+</sup> ion in an octahedral site [25,26]. In the NdFeO<sub>3</sub> perovskite spectra thin bands attributed to the *f-f* transitions in Nd<sup>3+</sup> ion were observed, since this ion possesses several absorption bands in the visible light total range. Liu *et al.* synthesized the LaFeO<sub>3</sub> particles doped with Al<sup>3+</sup> by the sol-gel method, and obtained similar results, attributing that the LaFeO<sub>3</sub> spectrum originates from the O<sub>2p</sub>–Fe<sub>3d</sub> transition charge transfer [15].



Figure 3. TEM (a) and HR-TEM (b) images of LaFeO<sub>3</sub> calcined at 800  $^\circ\mathrm{C}$ 



Figure 4. Diffuse reflectance spectra of LaFeO<sub>3</sub>, PrFeO<sub>3</sub> and NdFeO<sub>3</sub> powders calcined at different temperatures

Temperature	perature Sample		Powdered pigments				λ	Colour
[°C]	Sample	$L^*$	$a^*$	$b^*$	$C^*$	[eV]	[nm]	Coloui
	LaFeO <sub>3</sub>	59.22	7.03	24.79	25.77	2.021	613.0	
600	PrFeO <sub>3</sub>	58.81	6.73	19.75	20.87	1.970	630.0	
	NdFeO <sub>3</sub>	57.81	7.50	20.10	21.46	1.998	621.0	
	LaFeO <sub>3</sub>	58.63	6.21	26.39	27.11	2.024	614.0	
800	PrFeO <sub>3</sub>	60.17	6.87	22.68	23.70	1.936	641.0	
	NdFeO <sub>3</sub>	59.15	5.67	22.08	22.80	1.996	621.6	



Table 3. Colorimetric parameters of glazes with 2 wt.% of pigments



Figure 5. Chromaticity diagrams of the LaFeO<sub>3</sub>, PrFeO<sub>3</sub> and NdFeO<sub>3</sub> samples: a) pigments calcined at 600 °C, b) pigments calcined at 800 °C, c) glazes with 2 wt.% of pigment calcined at 600 °C and d) glazes with 2 wt.% of pigment calcined at 800 °C

In all spectra, the percentage reflectance is lower in the powders synthesized at 600 °C. This low reflectance might be because the powders calcined at lower temperature have smaller particle size with larger surface area, resulting in broader scattering of light [27]. The colour coordinate values of the powdered samples and glazes with 2 wt.% of the pigments are given in Tables 2 and 3. The chromaticity coordinate values were inserted in chromaticity diagrams, which are illustrated in Fig. 5. Several standard illuminants are used to measure the colour of materials, but in this work we used CIE standard illuminant D65, which is the most common representative of solar-light illuminant. By replacing  $La^{3+}$ ion for Nd<sup>3+</sup> and Pr<sup>3+</sup>, a small decrease of the yellow hue and hence chroma values were noted. The larger  $C^*$  values at higher calcination temperature were observed indicating a higher saturation with the increase of temperature. The  $b^*$  values also increased with temperature indicating a small increase in the yellow component in the final colour. The shift to smaller  $a^*$  values and higher  $b^*$  values of the glaze tiles in comparison with values obtained for the powdered pigments caused a subtle yellowish colouration of the tiles. The colour of these tiles in comparison to the powder changed from pale brown to yellow. The variation in the colour coordinates of the glaze tiles with replaced lanthanide ion in the perovskite structure was more significant in the NdFeO<sub>3</sub> perovskite.

Having in mind that the colour of absorbed light includes the band gap energy  $(E_g)$  and all colours of shorter wavelength, the wavelength of absorbed light was determined using  $E_g$  values ( $\lambda < 1240.8/E_g$ ) [28]. The band gap energy  $(E_g)$  was determined according to Eq. 1. Based on slight changes of width and energy of band gap, Table 2, it is observed that all pigments absorb light when  $\lambda < 613$  nm, resulting in colours of light reflected with pale brown hues. The highest band gap energy values were obtained for the LaFeO<sub>3</sub> samples.

### **IV. Conclusions**

The main goal of this work was to study the influence of calcination temperature (600 and 800 °C) and lanthan ide ions ( $Ln = La^{3+}$ ,  $Pr^{3+}$  and  $Nd^{3+}$ ) on colour and structural properties of LnFeO<sub>3</sub> type perovskites. The synthesized powders were single phase with orthorhombic perovskite structure. Therefore, the optimal calcination temperature is lower (600 °C), since it means spending less energy and times to obtain the powder. In addition, no significant changes were observed in the calcined powders at different temperatures. The colours can be described by different pale brown and yellowish colour hues for the powdered sample and transparent glazes containing 2 wt.% of the pigments, respectively. The prepared perovskites were suitable to convert commercial glazes in colour product, and they can be an alternative material for use as non-toxic pigments.

Acknowledgements: The authors would like to thank the CNPq, CNPEM and VITTRA.

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