



Synthesis and characterization of pigments of the $\text{LaAl}_{1-x}\text{Fe}_x\text{O}_3$ system – Application in ceramic and polymer



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ABSTRACT

Pigments from the $\text{LaAl}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0.00$ to 1.00) system were synthesized through the citrate method and thermally treated at 910°C for 4 h. The samples obtained were characterized through X-ray diffraction (XRD), Mössbauer spectroscopy (MS), field effect scanning electronic microscopy (FE-SEM), energy dispersive spectroscopy (EDS) and diffuse reflectance spectroscopy in the UV–Visible (DRS UV–Vis). The XRD analysis revealed the formation of perovskite as a single phase, crystallizing in the rhombohedral crystalline system with values $0.00 \leq x \leq 0.80$, and in the orthorhombic system with $x > 0.80$ value. Through the Mössbauer spectroscopy, it was possible to follow the phase transformation and determine at which iron concentrations the coexistence of the perovskite rhombohedral and orthorhombic phases occurred. The electronic microscopy enabled to identify that the pigments presented particles of ideal size to be applied as ceramic pigments. Regarding coloration, the increase in Fe^{3+} concentration in the $\text{LaAl}_{1-x}\text{Fe}_x\text{O}_3$ system provoked lattice distortions, altering the pigment band gap values and consequently their color. The pigments obtained presented coloration varying from white (LA), greenish-yellow (LAF1 to LAF5) and orange (LAF6 to LF). The pigments were applied to the enameling of ceramic pieces at 850°C , decorative burning temperature and presented good color and opacity. Thus, the system under study presented suitable properties to be used as pigment to ceramic and polymer, in addition to presenting low toxicity, a fundamental characteristic in the current scenery of environmental and human health concerns.

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1. Introduction

Traditional inorganic pigments widely employed in the ceramic industry are applied aiming at coloring decorative flooring, glazed tiles and ceramic supports [1,2]. Therefore, they must present intense color, opacity, insolubility to the application medium and also be thermally stable [3,4]. Regarding pigments for polymeric material, the main characteristics required are insolubility, high polymer dispersion (the ideal particle size varies from 0.2 to $1.0\ \mu\text{m}$), intense color, and high coloring ability [5–8]. They are used

when opacity is desired and higher stability regarding exposure to light and heating. In addition, inorganic pigments present higher stability when in contact with chemical products and lower migration effect, inorganic pigments are used in substitution to organic pigments [6,8,9]. However, in order for the inorganic pigments to be used to color polymers, they must show compatibility, so that the presence of superficial deformity or alteration in their mechanical properties can be prevented [6,10].

A problem associated to several inorganic pigments is the high toxicity associated to the presence of elements such as Cd, Pb, Cr, Mn and Co. Several countries have regulations that require the reduction or even ban the use of pigments containing Cd or Pb [4,11–13]. Therefore, studies aiming at obtaining compounds able to substitute toxic pigments have deserved special attention [14,15].

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Several studies reported in the literature present systems containing Fe^{3+} and rare-earth ions such as La^{3+} , Ce^{4+} , $\text{Pr}^{3+}/\text{Pr}^{4+}$ as intense color inorganic pigments, which are thermally stable and present low toxicity [14,16–18].

For the reasons presented above, the objectives of this study were to investigate the influence of the LaAlO_3 system in the color with the insertion of Fe^{3+} using the citrate method and evaluate the applicability of the $\text{LaAl}_{1-x}\text{Fe}_x\text{O}_3$ system to the enameling of ceramic pieces and polymer coloration.

2. Experimental procedures

2.1. Pigment synthesis

The $\text{LaAl}_{1-x}\text{Fe}_x\text{O}_3$ system was obtained through the citrate method, at different stoichiometric ratios ($x = 0.00$; 0.10; 0.20; 0.30; 0.40; 0.50; 0.60; 0.70; 0.80; 0.90 and 1.00) and the pigments obtained were labeled LA, LAF1, LAF2, LAF3, LAF4, LAF5, LAF6, LAF7, LAF8, LAF9 and LF, respectively.

The citric acid ($\text{C}_6\text{H}_8\text{O}_7$, VETEC, 99.5% grade) was initially solubilized in distilled water. Then, precursor salts, aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, VETEC, 98.0% grade), lanthanum nitrate hexahydrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, SIGMA-ALDRICH, 99.0% grade) were added in pre-determined concentrations. The solutions were constantly stirred and heated up to complete solubilization. Later on, the ethyleneglycol ($\text{C}_2\text{H}_6\text{O}_2$, DINÂMICA, 99.5% grade) was added slowly and the solution kept at 150°C until the polymeric resin was obtained. The resins obtained were submitted to thermal treatment at 400°C for 120 min for organic matter removal. The resulting powders were dispersed in agate mortar and submitted to thermal treatment at 500°C for 150 min to remove residual organic matter. Finally, the powders obtained after the second thermal treatment were thermally treated at 910°C for 240 min, with a 5°C min^{-1} heating rate so that the solid state reaction could occur and the relevant pigments be obtained.

2.2. Pigment characterization

The phases present in the pigments were evaluated through X-ray diffraction (XRD; Diffractometer SHIMADZU XRD-6000; CuK_α ($\lambda = 1.5406 \text{ \AA}$); 40 kV; 30 mA; 2° min^{-1} and 2θ from 10 to 120°). With the data obtained through the X-ray diffraction, the adjustment of relevant peaks was carried out using the software XFIT [19]. Lattice parameters were obtained by employing the software UnitCellWin [20].

The Mössbauer spectra were obtained employing a standard spectrometer at room temperature and with a ^{57}Co radioactive source dissolved in Rh matrix. The measurements were obtained in the transmission geometry without external field application.

Morphological properties and the composition were evaluated through the scanning electronic microscopy (FE-SEM; TESCAN MIRA3 LM). The software Mira TC was employed to determine particle average size.

The pigment colors were evaluated using the diffuse reflectance spectroscopy in the Ultra-violet and visible regions (DRS UV–Vis; VARIAN Cary 50, accessory “Barrelino”; 360–800 nm; CIE $L^*a^*b^*$; standard white Barium Sulphate (BaSO_4), CIE D65 illuminator and standard observer 10°). The optical absorption coefficient values, A , were obtained from the reflectance plots, according to Equation (1) [21].

$$A = \left(\ln \left(\frac{R_{\max} - R_{\min}}{R - R_{\min}} \right) \right)^2 \quad (1)$$

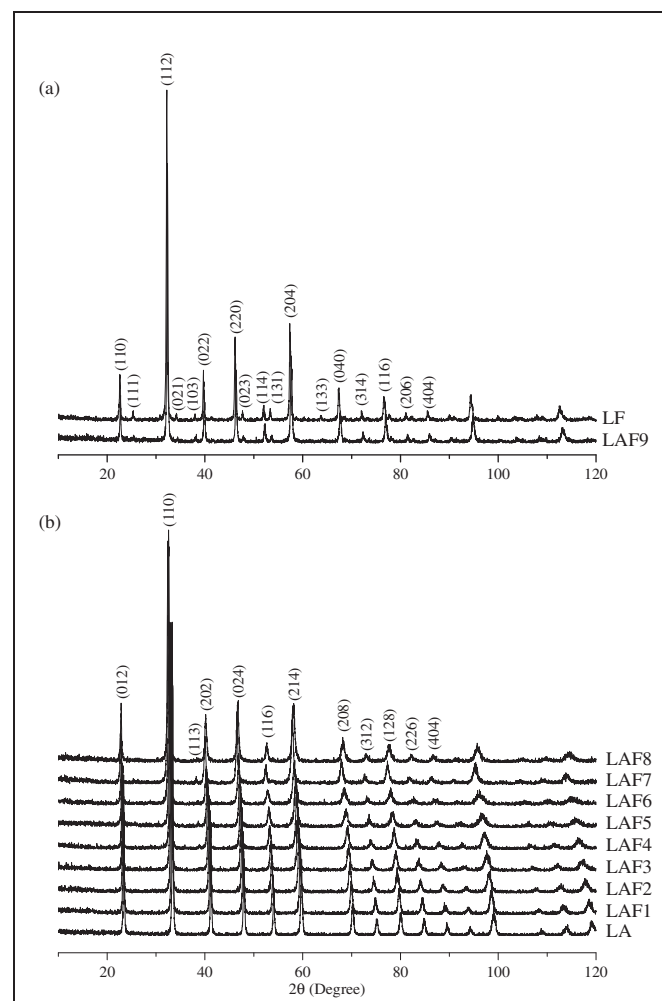


Fig. 1. X-ray diffractograms of pigments of $\text{LaAl}_{1-x}\text{Fe}_x\text{O}_3$ system: (a) orthorhombic structure and (b) rhombohedral structure.

Table 1

Lattice parameters and unit cell volume of $\text{LaAl}_{1-x}\text{Fe}_x\text{O}_3$ system.

Pigments	Crystalline structure	a (nm)	b (nm)	c (nm)	V (nm^3)
LA	Rhombohedral ^a	0.5360	0.5360	1.3115	0.3263
LAF1	Rhombohedral	0.5363	0.5363	1.3124	0.3269
LAF2	Rhombohedral	0.5405	0.5405	1.3214	0.3343
LAF3	Rhombohedral	0.5420	0.5420	1.3268	0.3375
LAF4	Rhombohedral	0.5445	0.5445	1.3313	0.3419
LAF5	Rhombohedral	0.5462	0.5462	1.3349	0.3449
LAF6	Rhombohedral	0.5493	0.5493	1.3384	0.3497
LAF7	Rhombohedral	0.5515	0.5515	1.3507	0.3559
LAF8	Rhombohedral	0.5496	0.5496	1.3477	0.3526
LAF9	Orthorhombic ^b	0.5531	0.7832	0.5535	0.2397
LF	Orthorhombic	0.5556	0.7858	0.5552	0.2424

^a $a = b \neq c$; $\alpha = \beta = 90^\circ$; $\gamma = 120^\circ$.

^b $a \neq b \neq c$; $\alpha = \beta = \gamma = 90^\circ$.

where: R = reflectance, $R_{\max}$ = maximum reflectance; $R_{\min}$ = minimum reflectance.

The pigment band gaps (E_g) were determined from the extrapolation of the optical absorption coefficient linear adjustment (A) as a function of the photon energy (eV).

2.3. Pigment application in ceramics

Some enamel was prepared using 92% in mass frit (major

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