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Ceramic pigment obtained by polymeric precursors

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Abstract

Fe_2O_3 has been used as ceramic pigment due to excellent colorimetric characteristics combined with thermal stability. The introduction of La^{+3} to Fe_2O_3 yields the precipitation of the perovskyte structure ($LaFeO_3$) with corresponding differences in the color of the resulting pigment. The compound was synthesized from polymeric precursors and characterized by thermal and colorimetric analyses, infrared and UV–visible spectroscopy, and X ray diffraction. The characteristic light brown color of Fe_2O_3 changed to orange with the addition of La^{+3}. As the calcination temperature increased from 900 °C to 1100 °C the pigment darkened as a result of the reduction of $Fe^{+3} \rightarrow Fe^{+2}$ with corresponding change of the colorimetric coordinates from L^* a^* b^* = 49.003, 10.541, 12.609 to L^* a^* b^* = 31.279, 6.096, 6.877.

Keywords: Lanthanum; Ceramic pigments; Polymeric precursors; $LaFeO_3$; Color centers and oxide

1. Introduction

Pigment manufacturers have increasingly removed heavy metals from their formulations. Potential substitutes include encapsulated products or even completely new materials thermally stable at the firing temperature and to the action of the melted glaze [1–3]. Pigments usually consist of a host lattice into which chromophorous ions are incorporated. These are normally transition metals responsible for stabilizing the colorimetric properties of the material [4]. The present study investigated the preparation of pigments from Fe_2O_3 using La^{+3} to form perovskyte from polymeric precursors. The synthesis route is an additional aspect to determine the final properties of the pigment. Usual synthesis routes applied to ceramic pigments include Pechini method [5], combustion synthesis [6], sol–gel processing [7] and powder processing [8,9]. The synthesis route affects the color of the compound, particle size distribution, and resistance to acids, alkalis or abrasives.

2. Materials and methods

$LaFeO_3$ [10–12] was synthesized according to the method proposed by Pechini [5]. $La(NO_3)\cdot 6H_2O$ was obtained from the reaction between La_2O_3 (Aldrich) and HNO_3 (Merck). The presence of the metallic precursor (La^{+3}) was established by complexometric titration using EDTA. Fe^{+3} citrate solution was prepared from $Fe(Cl_3)_{3(aq.)}$ at 60 °C under constant stirring. The molar ratio of this solution with respect to HNO_3 was 1:3. $La(NO_3)_{3\ (aq.)}$ and Fe^{+3} citrate solution were mixed and heated up to 90 °C at which point ethyleneglycol was added at a ratio of 60/40 (citric acid/ethyleneglycol). A transparent gel was then formed and subsequently heat-treated at 300 °C for 2 h (5 °C/min). The resulting puff was ground down to a fine powder using a Pulverisete 2000 planetary mill. The perovskyte structure resulted from the calcination of the powder

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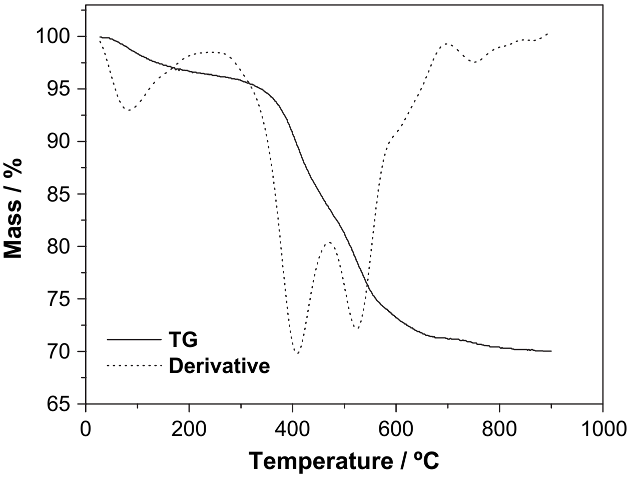


Fig. 1. Thermogravimetric curve of $LaFeO_3$ precursor resin calcinated at 300 °C.

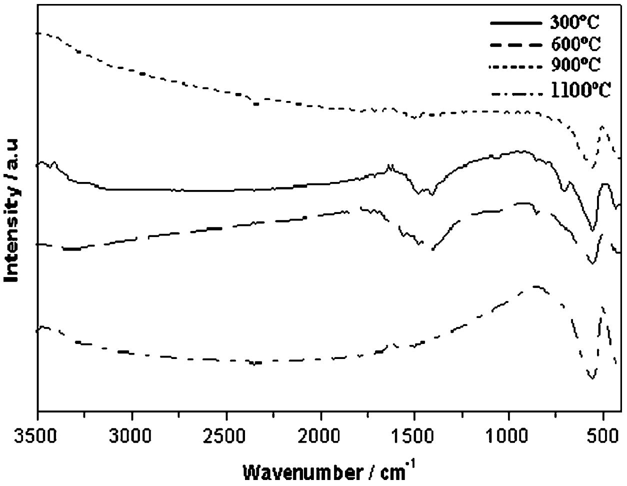


Fig. 3. Infrared spectroscopy of $LaFeO_3$ calcinated at 300, 600, 900 and 1100 °C.

at different temperatures. These were established from thermogravimetric analyses carried out in air using a Perkin Elmer setup. The heating rate was 10 °C/min.

The eventual presence of organic material after calcination was determined by infrared spectroscopy in a Perkin Elmer FTIR-16 PC system. The samples consisted of 1 wt.% powder pressed under 4 tons for 5 min in KBr pellets previously dried at 100 °C for 4 h. The crystallographic structure of the calcinated powders was determined by X ray diffraction. A Shimadzu XRD-6000 diffractometer was used to scan the angular range $5° \leq 2\theta \leq 100°$ with Cu Kα radiation. Specific surface area and porosity were evaluated by BET from 0.3 g samples using a Quantachrome NOVA 2000 adsorption equipment. Ultra pure N_2 (White Martins, Brazil) was used as adsorbate. The average particle size of the calcinated powders was obtained using a CILAS laser analyzer. In order to prevent the formation of agglomerates, the powder was maintained in ultrasonic bath for 90 s prior to feeding the solution into the analyzing cell. The diffuse reflectance of the powders was measured in the 300–800 nm range using a Gretac Macbeth 2180–2180 UV spectrophotometer (D-65 light). Finally the color of the pigment was established from the $L^*a^*b^*$ colorimetric coordinates following CIE (Commission Internationale ÍEclairage) standards according to

$$\Delta E^2 = L^2 + a^2 + b^2 \tag{1}$$

where L^* varies from black (0) to white (100), a^* from green (−) to red (+), and b^* from blue (−) to yellow (+). The microstructure of the powders was revealed observing Au-coated samples under a Philips ESEM-XL30 scanning electron microscope set at high-vacuum mode.

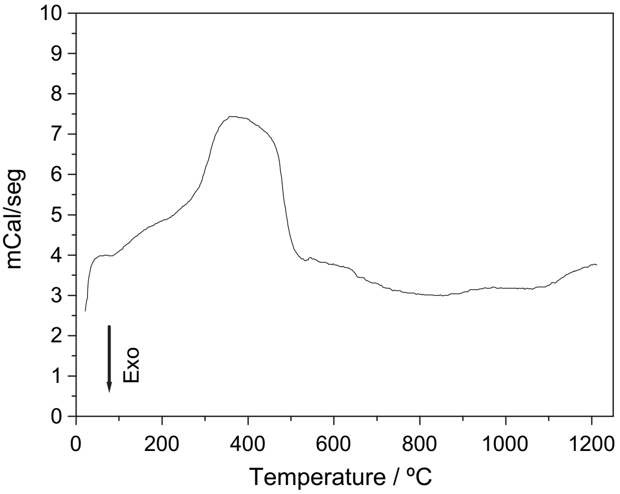


Fig. 2. DTA of $LaFeO_3$ precursor resin calcinated at 300 °C.

3. Results

The thermogravimetric plot of the $LaFeO_3$ precursor resin (Fig. 1) revealed that the onset of metallic citrate decomposition took place at 150 °C. Full decomposition and formation of an oxide occurred at 600 °C. DTA analyses (Fig. 2) confirmed the burn out of the organic material as depicted by the endothermic event that took place between 150 and 600 °C. Calcination was then carried out at 600 °C, 900 °C or 1100 °C to promote the formation of the perovskyte phase. The calcination at 1100 °C also aimed at evaluating the thermal stability of the compound at typical ceramic firing temperatures.

Table 1
BET surface area of powders calcinated at 900 °C or 1100 °C

Sample	S_{BET} ($m^2 g^{-1}$)	Average diameter (μm)
$LaFeO_3$—900 °C	5.10	3.10
$LaFeO_3$—1100 °C	3.20	4.25

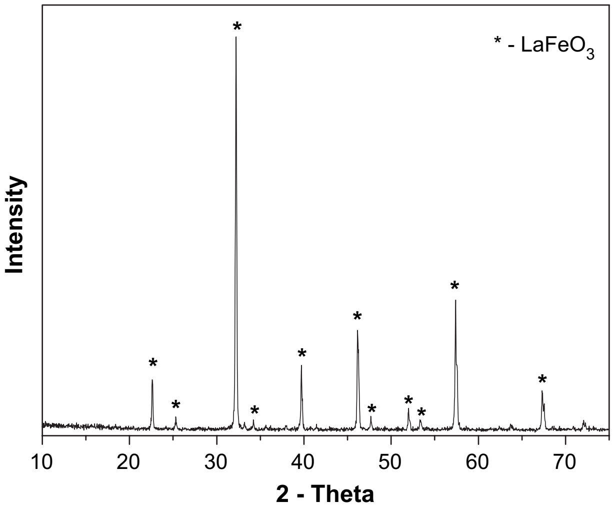


Fig. 4. X-ray diffraction pattern of $LaFeO_3$ calcinated at 900 °C.

Infrared analyses (Fig. 3) indicated that increasing the calcination temperature stretched the bands characteristic of the metallic citrate (1500 cm^{-1}). The formation of the oxide at 900 °C could be verified by the presence of the corresponding vibrational band at 500 cm^{-1}. Table 1 indicated that increasing the calcination temperature decreased the specific area of the powder possibly due to powder aggregation. The relatively low values encountered are typical of Pechini synthesis and can be attributed to the M:AC (M = Metal; AC = citric acid) molar ratio used in the synthesis, and consequently, to the chain polymer size used in the catalyst preparation. The formation of single phase $LaFeO_3$ perovskyte at 900 °C could be established by X ray diffraction (Fig. 4). The experimental pattern matched that of JCPDS file # 37-1493. The results from UV–vis spectroscopy (Fig. 5) revealed that the powder was predominantly orange, as it emitted in the 600–700 nm range, typical of compounds containing Fe. This was further confirmed by colorimetric analyses (Table 2), which showed the predominance of red in all samples (positive values of a^*). Increasing the calcination temperature to 1100 °C decreased the value of a^*, indicating that the pigment darkened. Along with changes in particle morphology as a function of

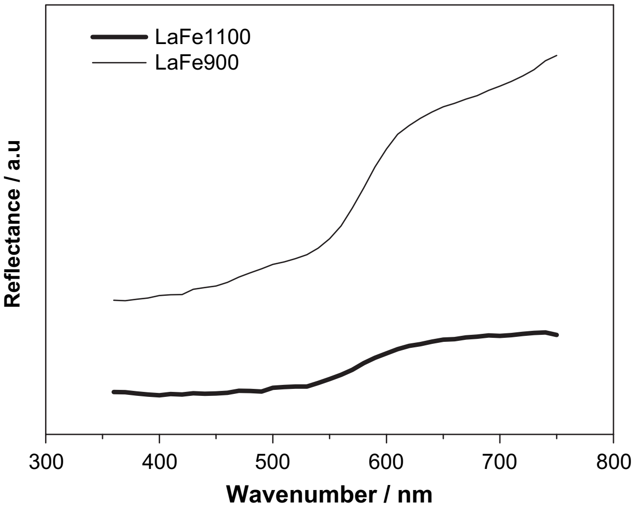
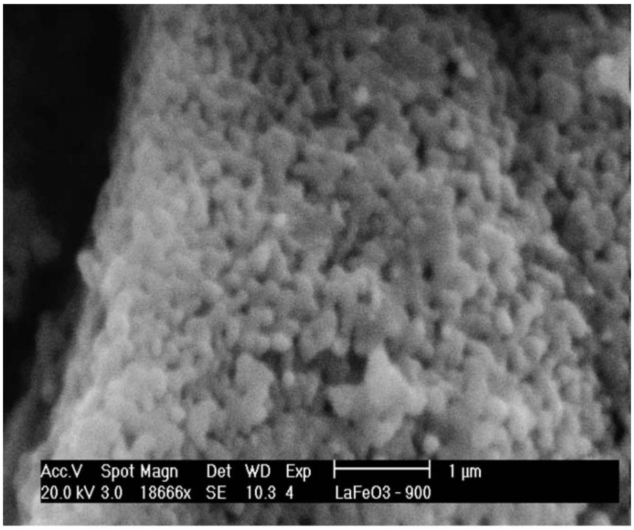


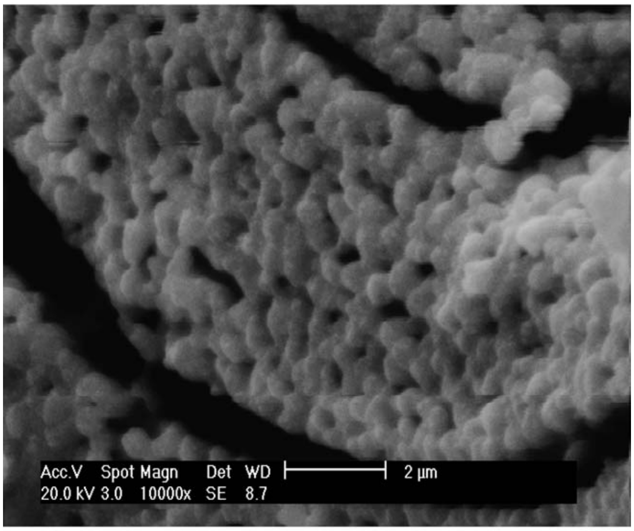
Fig. 5. UV–visible pattern of $LaFeO_3$ calcinated at 900 and 1100 °C.

Table 2
Colorimetric coordinates of calcined powders

Sample	Powder pigments			
	ΔE	L^*	a^*	b^*
$LaFeO_3$—900 °C	46.036	49.003	10.541	12.609
$LaFeO_3$—1100 °C	32.600	31.279	6.096	6.877



(a)



(b)

Fig. 6. SEM images of powders calcinated at (a) 900 °C and (b) 1100 °C for 4 h.

calcining temperature, heat-treating at 900 and 1100 °C (Fig. 6) resulted in substantial agglomeration of the powder.

4. Conclusions

Adding La^{+3} to Fe_2O_3 changed the color of the pigment due to the formation of $LaFeO_3$ with perovskyte structure at 900 °C. The hue of the resulting color (orange) can be adjusted by adjusting the calcination temperature. The pigment darkened by increasing the calcination temperature from 900 to 1100 °C possibly due to the reduction of Fe^{+3} to Fe^{+2}.

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