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Synthesis of $LnCrO_3$ perovskites and their color properties

Síntese de perovskitas $LnCrO_3$ E suas propriedades de cor

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ABSTRACT

The aim of this current study was to prepare $LnCrO_3$ (Ln= La, Pr, Nd) in order to investigate the influence of lanthanides ions on the structural and color properties of the chromites. The powders were synthesized by the microwave-assisted auto-combustion method using urea as a fuel. After calcination at 800 and 1000 °C, characterizations were performed by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), UV–vis spectroscopy and colorimetric analysis using CIE-Lab system. All the samples are considered single phase and nanocrystalline. There were not significant changes in the colorimetric parameters doped with lanthanides ions. The chromites presented colors with greenish gray tones which became darker in the calcined powders at higher temperatures. No change in the pigment color was observed when incorporated into transparent glaze.

Keywords: Perovskite, microwave assisted synthesis, color properties, chromite.

RESUMO

O objetivo deste estudo foi preparar $LnCrO_3$ (Ln = La, Pr, Nd) para investigar a influência de íons lantanídeos nas propriedades estruturais e de cor dos cromitos. Os pós foram sintetizados pelo método de auto-combustão assistida por microondas, usando a uréia como combustível. Após a calcinação a 800 e 1000 ° C, as caracterizações foram realizadas por difração de raios X, microscopia eletrônica de varredura, microscopia eletrônica de transmissão, espectroscopia UV-vis e análise colorimétrica usando o sistema CIE-Lab. Todas as amostras são monofásicas e nanocristalinas. Não houve alterações significativas nos parâmetros colorimétricos dopados com íons lantanídeos. As cromitas apresentaram cores com tons de cinza que se tornaram mais escuros nos pós calcinados a temperaturas mais altas. Nenhuma mudança na cor do pigmento foi observada quando incorporada ao esmalte transparente.

Palavras-chave: Perovskita, síntese assistida por microondas, propriedades de cor, cromita.

1. INTRODUCTION

The perovskite type oxides ABO_3 presents a structure with larger cations with ionic radius (alkali metal or lanthanide) and occupy the site A cations with smaller radius (transition metal d) and occupies the site B, as well [1]. The ideal structure has cubic symmetry, but distortions to tetragonal, orthorhombic and rhombohedral may occur, determined by the atomic radius and the crystallization temperature [2].

Lanthanide chromite with perovskite structure, exhibits high mechanical and chemical stability, high electric conductivity for use in SOFC, oxygen sensors, ionic conductors and catalytic activity for the oxidation reaction [3-9]. However, their optical properties have not yet been studied. These materials due to their

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high temperature and chemical stability could be used as a ceramic pigment. In addition, the possibility of introducing different chromophores ions into a perovskite structure could produce interesting colors. According to the crystalline field theory, the color in the lanthanide ions and in the transition metals d are due to the transition bands f-f and d-d, respectively. Few studies report the synthesis of ceramic pigments containing these two types of chromophores in the same structure.

A good pigment should be able to present interesting properties, such as high temperature resistance, chemical stability, resistance to chemical attack, high surface area and color homogeneity. In this context, several authors have studied pigments containing lanthanides in their composition [10-13].

The method of synthesis causes substantial influence on the properties of the pigments obtained [9]. Several routes of synthesis have been used to obtain lanthanum chromite, such as coprecipitation, sol-gel, and combustion and among others [14-18]. These alternatives methods have been used replacing the solid state reaction method, which generally uses several processing steps and high temperatures, in addition to synthesizing pigments with heterogeneous properties, resulting in low added value to the pigment.

The aim of this current study was to synthesize lanthanum chromite through the microwave assisted self-combustion method for use as a ceramic pigment, analyzing the influence of the f and d transition ions on color properties, the microstructure and the interaction of the pigment with the transparent glaze.

2. MATERIALS AND METHODS

2.1 Materials

The synthesis of the powders was carried out by the microwave assisted combustion method. mixture of reagents used to obtain the samples [2]. The materials used were urea ($CO(NH_2)_2$ as fuel and the metallic nitrates: $(LaNO_3)_3.6H_2O$ $(Cr(NO_3)_3.9H_2O$, $Pr(NO_3)_3.6H_2O$, $Nd(NO_3)_3.6H_2O$ as sources of cations.

2.2 Methods

The amount of each reactant mass was calculated from their respective molecular weight. The ratio of the reactants favors the ratio oxidant / fuel = 5/6, according to the chemical propellant. The mixture consists of the following proportions: one mole of metal nitrate (lanthanum, praseodymium and neodymium) to one mole of chromium nitrate, to five moles of urea. The synthesis reaction starts from the dissolution of urea with deionized water in a beaker with constant stirring at 70 °C. Afterwards the urea was completely dissolved, furthermore, chromium nitrate added was dissolved in deionized water at a temperature of about 80 °C. The solution was kept under stirring for about 30 minutes. After that, the metal nitrate was added (lanthanum, praseodymium, or neodymium) dissolved also in deionized water at a temperature of about 90 °C. The proposed idea was to reduce the amount of water with heating to enter into a microwave oven, with autoignition occurring between 5 and 7 minutes. The resulting powders then were calcined at 800 and 1000 ºC for 4 hours in air to obtain products possessing a phase of the perovskite structure.

2.3 Characterization

Phases analysis of powders calcined at 800 and 1000 °C were performed by X-ray diffraction with a Shimadzu diffractometer XRD-6000 model, operating with CuKα radiation. The diffractograms were obtained with angle of 2θ ranging from 10 to 80 degrees. The diffraction patterns were adjusted and refined through the Rietveld method [19] making use of the MAUD software [20]. The morphologies of the powders were obtained through a scanning electron microscope (SEM) of the brand JEOL, JCM-5700 model. The colorimetric measurements of the CIE-L*a*b* was performed by using the colorimeter Gretag Macbeth color-eye 2180. The reflectance spectra were measured using a UV-Visible spectrophotometer Shimadzu, with accessory reflectance UV-2550 with a wavelength in the region of 200-900 nanometers.

3. RESULTS AND DISCUSSION

Fig. 1 shows the X-ray diffraction (XRD) patterns of $LnCrO_3$ (Ln= La, Pr, Nd) at 800 and 1000 °C, respectively. All compounds of $LnCrO_3$ (Ln= La, Pr, Nd) were synthesized as well-crystallized single-phase powders. The identification of crystalline phases through Rietveld refinement, revealed the single phase powders with orthorhombic perovskite structure according to 2104121 ($LaCrO_3$), 156319 ($NdCrO_3$), 331072 ($PrCrO_3$) ICSD database. The effectiveness of the synthesis method to obtain the perovskite is proven when we compare the results obtained in this work with others reported in the scientific literature [21-24].

Based on the XRD data, lattice parameters were calculated and presented in Table 1. It was observed that the crystallite size increased as the calcination temperature increased, ranging from 19.72nm to 36.32nm, 15.73nm to 24.08nm and 15.74nm to 17.73 nm to the samples $LaCrO_3$, $PrCrO_3$ and $NdCrO_3$, respectively. This result demonstrates that the average size of the crystallite increases with temperature, which is an expected behavior due to the fact that temperature is the driving force that causes the particles to grow and coalesce [25]. The goodness of fitted (GoF) values of all the fitted patterns lie between 1.58 and 1.86, suggesting a good agreement between the experimental and refined diffraction data [26].

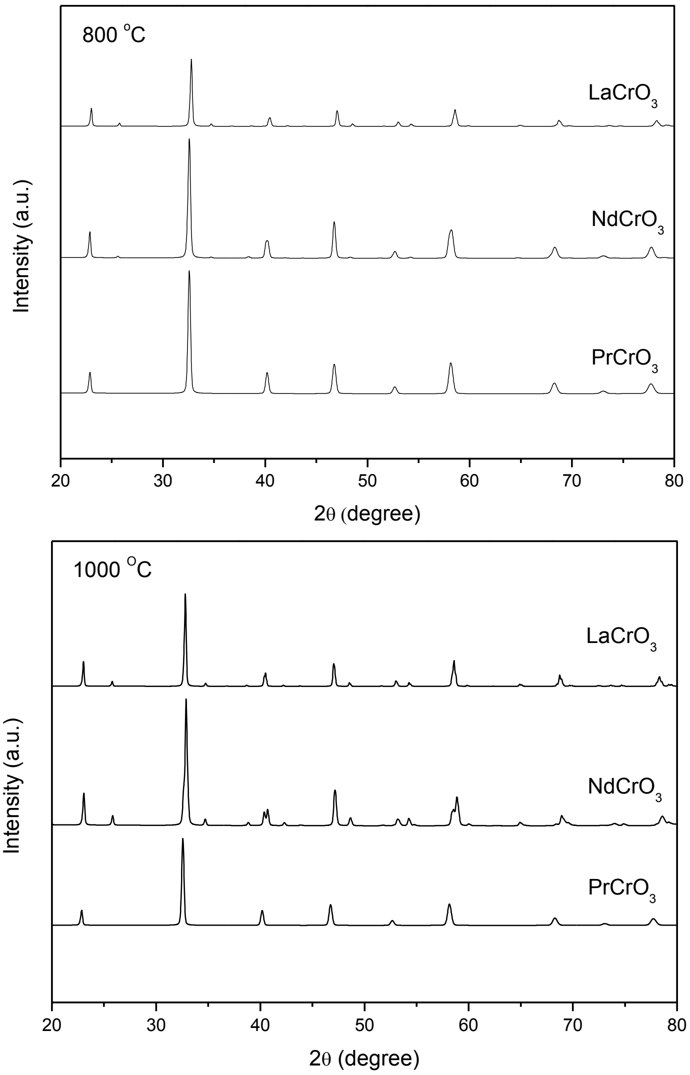


Figure 1: XRD patterns of $PrCrO_3$, $NdCrO_3$ and $LaCrO_3$ a) at 800 °C and b) at 1000 °C.

Table 1: Microstructural parameters of $LnCrO_3$ (Ln= La, Pr, Nd)

SAMPLE	TEMPERATURE (°C)	LATTICE PARAMETERS (Å)			CRYSTALLINE SYSTEM	CRYSTALLITE SIZE (NM)	GOF(Σ^2)
		a	b	c			
$LaCrO_3$	800	5.450	5.478	7.715	Orthorhombic	19.72	1.15
$LaCrO_3$	1000	5.452	5.474	7.717	Orthorhombic	36.32	1.17
$PrCrO_3$	800	5,499	5,547	7,696	Orthorhombic	15.73	1.55
$PrCrO_3$	1000	5,499	5,547	7,696	Orthorrombic	24.08	1.26

$NdCrO_3$	800	5.474	7.759	5.515	Orthorhombic	15.74	1.24
$NdCrO_3$	1000	5.484	7.694	5.420	Orthorhombic	17.73	1.25

SEM images in Figure 2 shows the sample the $NdCrO_3$ at 800 and 1000 °C, respectively. The sample presented a spongy aspect, highly porous structure and a rough surface. The combustion reaction with urea presents a great evolution of gases, results in porous structures with smaller particle size [27]. Spherical particles (< 200 nm) could be seen in HR-TEM images in Figure 3. Nanoparticles result in less flocculation on the glaze surface and better color distribution due to high surface area [28].

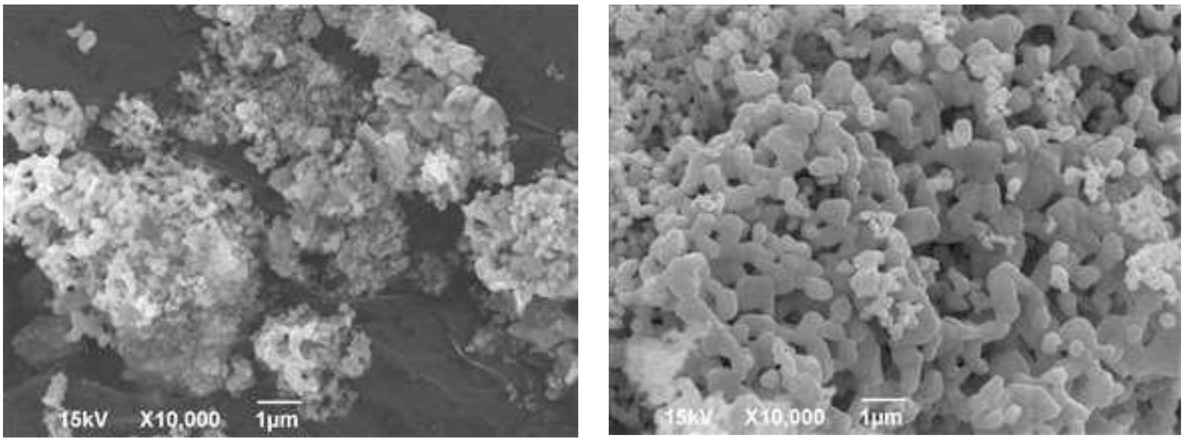


Figure 2: SEM images of the $NdCrO_3$ calcined at (a) 800 °C and b) 1000 °C.

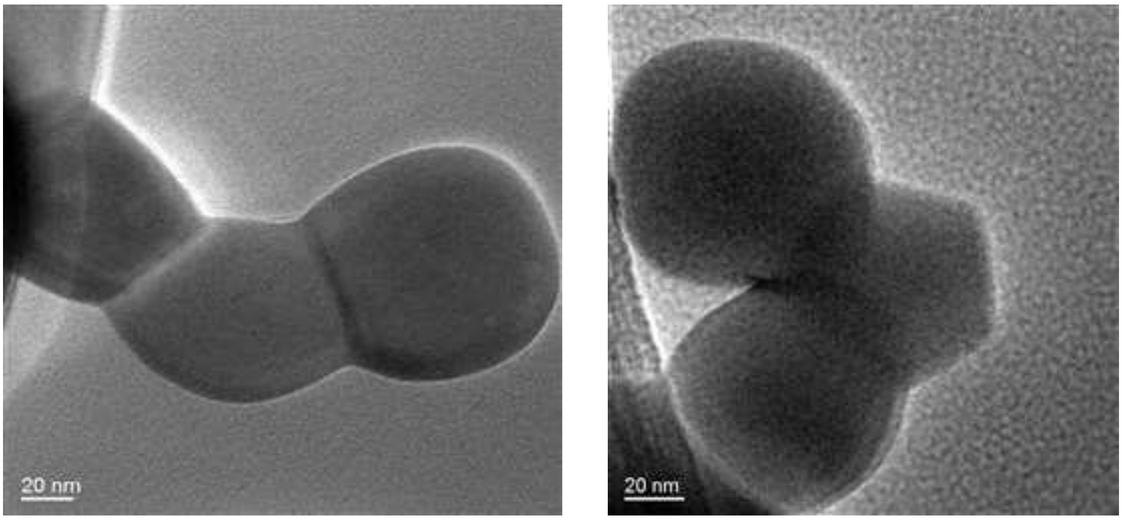


Figure 3: TEM images of the $LaCrO_3$ calcined at 1000 °C.

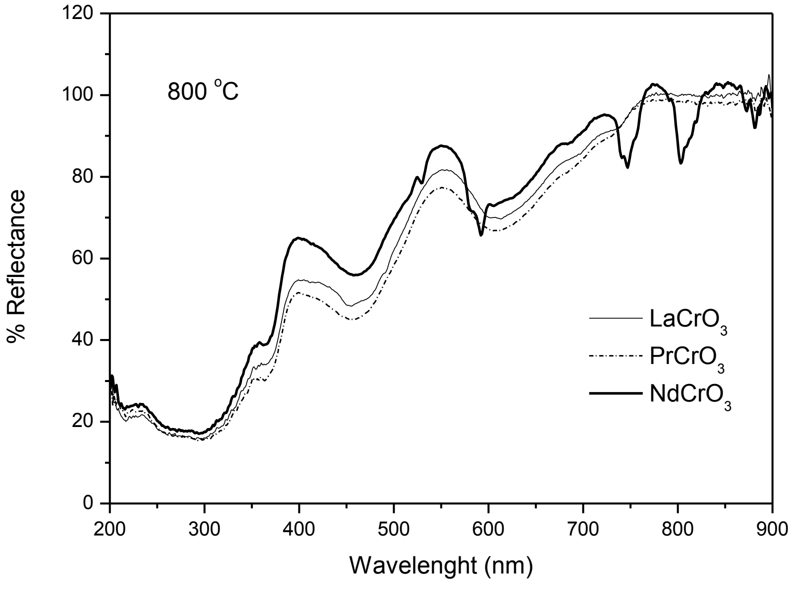
Reflectance spectra in the UV-Visible region of powders synthesized at temperatures of 800 ° C and 1000 ° C are shown in Figure 4 and 5 for the composition of the perovskites $NdCrO_3$, $LaCrO_3$ and $PrCrO_3$ at temperatures 800 and 1000 °C, respectively. In the synthesized perovskite ions there are two chromophores ions, which are transition elements "d" and the lanthanides (transition "f"), in which the color pigment is a result of transitions d-d and f-f, respectively. The lanthanum does not have f-orbital, but is included in the lanthanide series by having chemical properties similar to other elements in the series, hence in the perovskite $LaCrO_3$, the Cr^{3+} ion is the only chromophore.

Comparing the three reflectance spectra and the colorimetric parameters (Table 2), it was observed a difference in the parameters of the three synthesized compounds, which indicates that the contribution of the color is mainly due to the d transition chromophore in the B site of the perovskite. This is proven with the reflectance spectra, since the bands assigned to Cr^{3+} are wider and more intense in the visible region. This could be clearly seen from compounds of lanthanum and praseodymium, which have quite similar reflectance curves. As the temperature increases, the percentage of reflectance decreases and also decreases the luminescence (lower L value), hence the color becomes slightly darker at higher temperatures. The region between 200 and 370 nm is a region with a low percentage reflectance (high absorption) and does not influence the color, because it occurs outside the visible region (UV); above this, the percentage reflectance starts increasing abruptly. The broad band between 400 and 550 is attributed to the blue region, the intense band near 600 indicates that the material is reflecting in the green region.

In all spectra it was observed spectral bands of the Cr^{3+} ion in the octahedral site. In the region between 410 and 490 nm the band is well defined and it is attributed to the $^4A_{2g}(^4F) \rightarrow {}^4T_{1g}(^4F)$ transition. The band between 500 and 600 nm is attributed to the $^4A_{2g}(^4F) \rightarrow {}^4T_{2g}({}_4F)$ transition. The bands between 660 and 730 nm are less pronounced and they are attributed to $^4A_{2g}(^4F) \rightarrow {}^4T_{1g}(^2G)$ and $^4A_{2g}(^4F)\ {}^2E(^2G)$ transitions [29].

In the chromite praseodymium spectra (Figure 4) were not observed bands attributed to the transitions of the Pr^{3+} ion transitions, once they occur in the same region of Cr^{3+} band. These bands are wider and larger and overlaps the praseodymium bands. In the neodymium chromite spectra (Figure 3), in addition to the chromium ion bands there were also observed some bands of the neodymium ion in the region between 720 and 760 nm, which can be attributed to the $^4I_{9/2} \rightarrow (^4F_{7/2} + {}^4S_{3/2})$ transitions. The band between 790 and 820 nm is attributed to the $^4I_{9/2} \rightarrow (^4F_{5/2} + {}^2H_{9/2})$ transition and it is the reason of some neodymium compound be used as lasers [29].

The coordinates a* and b* are chromaticity coordinates. When the coordinate a* is low and negative it deviates from the green hue. An important observation is that the pigments on ambient light show green color, but the colorimetric coordinates indicated greenish gray tones, this is probably due to some interaction of samples with the excitation lambda of the colorimeter.



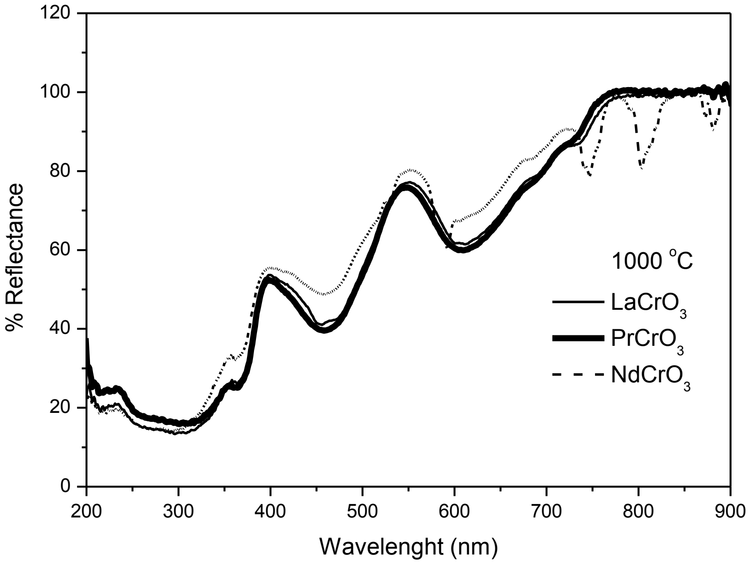


Figure 4: Reflectance spectra of the perovskites $NdCrO_3$, $PrCrO_3$ and $LaCrO_3$ calcined a) at 800 and b)1000 °C.

Table 2: Colorimetric parameters of $LnCrO_3$ (Ln= La, Pr, Nd) at 800 and 1000 °C

SAMPLE	T(°C)	L*	a*	b*
$LaCrO_3$	800	60.11	-2.68	11.70
$LaCrO_3$	1000	58.32	-4.03	13.14
$PrCrO_3$	800	58.62	-2.74	11.67
$PrCrO_3$	1000	58.57	-4.25	12.97
$NdCrO_3$	800	60.47	-3.02	10.74
$NdCrO_3$	1000	59.92	-3.15	10.77

The Table 3 presents the colorimetric parameters of glaze. The chemical composition of transparent glaze consisted of SiO_2 (64.57%), Al_2O_3 (21.25%), CaO (6.61%), K_2O (3.43%), ZnO (3.21%) and traces of SO_3, Fe_2O_3, TiO_2, CuO oxides. It was observed that the parameters a* and b* of the glazes underwent displacement, however, the color of the pigments were not altered. This was due to the high content of silica and alumina combined with the low content of zirconium oxide and impurities of less than 1% (Table 4), conferring the low reactivity, thermal stability and chemical compatibility between pigment and glaze compounds [30]. The brightness values L* of the pigment and the glaze were similar, as compared in Tables 2 and 3. This fact occurred due to the intermediate levels of CaO and K_2O that are responsible for the color development. Glazes with high contents of these compounds have lower luminosity and therefore, the final color is darker [31].

Table 3: CIE-L*a* b* coordinates of glazes calcined at 800 °C and 1000 °C

SAMPLE	T(°C)	L*	a*	b*
$LaCrO_3$	800	61.23	-0.32	18.73
$LaCrO_3$	1000	59.72	0.07	18.83
$PrCrO_3$	800	62.75	-3.15	21.9
$PrCrO_3$	1000	61.4	-7.4	22.8
$NdCrO_3$	800	63.35	-2.95	23
$NdCrO_3$	1000	61.95	-8.15	23.15

4. CONCLUSION

The microwave assisted combustion method used in this work compared to other methods of synthesis, presented a favorable route for obtaining the $LaCrO_3$, $PrCrO_3$ and $NdCrO_3$ perovskites. The oxides obtained at two temperatures of calcination (800 and 1000 °C) were single phase, nanometric with orthorhombic perovskite structure. The chromite lanthanides showed greenish gray shades when subjected to a colorimeter, being darker in the calcined powders at higher temperatures. It was observed that the transition metal d exerts a greater contribution to the color definition of the lanthanides, since there was a little change in the color with the replacement of the A site in the perovskite. The color of the pigment remained practically unchanged in the transparent glaze, revealing a chemical compatibility between the constituents of the pigments and the glaze.

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