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Lanthanum cobaltite black pigments with perovskite structure

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ABSTRACT

In this work $La_{1-x}Ca_xCoO_3$ ($x = 0$–0.4) pigments were synthesized by the polymeric precursor method with heat treatments at 700, 800 and 900 °C for 4 h. The powders were characterized by colorimetry, UV–vis spectroscopy and powder X-ray diffraction (XRD). The X-ray diffraction patterns showed the presence of a single phase perovskite, changing its structure from rhombohedral to cubic, when calcium was added to the lattice. All of the pigments had a black colour with a strong absorption over the whole of the visible spectrum as a consequence of the different oxidation states of cobalt and the high short-range disorder. The substitution of Ca^{2+} for La^{3+} did not influence the pigment colour but decreased its final cost.

1. Introduction

The ceramic industry is always interested in developing more stable pigments that display intense colours and meet the technological specifications and are non-toxic and environmental friendly [1].

Black pigments are generally substituted oxide compounds, usually containing cobalt, iron, chromium and nickel, some of them being considered as toxic. Moreover, the concomitant use of different ions make the control of the colour more difficult as it is related to the chromophore ion itself, its oxidation state and its coordination number [2]. For instance, pigments containing only cobalt usually display either yellow or blue colours [3–6].

In relation to black pigments containing cobalt, Calbo et al. have synthesized the pigments $(Co_{0.5}Mg_{0.5})(Fe_{1.9}Cr_{0.1})O_4$ and $(Co_{0.5}Mg_{0.5})(Fe_{1.74}Cr_{0.06}Al_{0.2})O_4$ [7] by three different methods: co-precipitation, solid state reaction and polymeric gel and observed that all of the pigments have displayed a black colour. Eliziário et al. [8] have synthesized pigments based on cobalt–chromium spinels, $CoCr_2O_4$, Co_2CrO_4 and $Co_{2.75}Cr_{0.25}O_4$, using the polymeric precursor method, with heat treatment between 600 and 1000 °C. The authors have observed that cobalt-rich spinels, Co_2CrO_4 and $Co_{2.75}Cr_{0.25}O_4$, have been much darker showing a black colour, while the spinel with the highest chromium content, $CoCr_2O_4$, has a green colour. The colours of these spinels have been directly related to the occupation of tetrahedral and octahedral sites by the chromophores, as well as to the different oxidation states of chromium and cobalt. Gouveia et al. [9] have synthesized $Co_xZn_{7-x}Sb_2O_{12}$ pigments ($x = 0$–7) by the polymeric precursor method and have obtained black pigments for higher cobalt amounts.

In relation to pigments based on the perovskite structure, cobalt usually occupies octahedral sites, presenting different oxidation states that may lead to different colours. Moreover different dopants can be added, changing the final color of the pigment [6]. As an example of perovskites tested as pigments, $LaFeO_3$ [10] and $BaSn_{1-x}Tb_xO_3$ [11] can be cited.

The present work aims to synthesize cobalt-based black pigments with the perovskite structure, containing La^{3+} ions. $LaCoO_3$ is a cobalt-based perovskite usually applied as a catalyst in reactions, as a membrane for gas separation processes and in a solid oxide fuel cell (SOFC) [12]. To our knowledge $LaCoO_3$ has not been studied as a ceramic pigment. In the present work La^{3+} was

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partially replaced by Ca^{2+}, with the purpose of decreasing the pigment cost, as calcium oxide is about 10 times cheaper than lanthanum oxide and calcium carbonate is about 4 times cheaper than lanthanum carbonate.

2. Materials and methods

$La_{1-x}Ca_xCoO_3$ powder samples were synthesized by the polymeric precursor method [12], with $x = 0$, 0.2 and 0.4 and calcination between 700 and 1000 °C for 4 h. In the synthesis, the following reagents were used, with purities ranging from 98 to 99.9%: citric acid (Cargill), lanthanum nitrate (Sigma), calcium nitrate (Vetec), cobalt nitrate (Vetec) and ethylene glycol (Vetec). During synthesis, stoichiometric amounts of citric acid (CA) and of the metal salts were dissolved in an aqueous solution, under constant stirring, at a temperature of about 70 °C, with a ratio of 3 mol of CA to 1 mol of the metal. After complete dissolution, ethylene glycol (EG) was added into the solution, with a mass ratio of 60% AC to 40% EG. After addition of all of the reagents, the solution was heated up to a temperature of approximately 90 °C, in order to promote the polyesterification reaction to form a gel. Each resin was heat treated at 300 °C for 2 h to obtain the respective powder precursor. This precursor was desaglomerated with the aid of a mortar and sieved through a sieve of 100 mesh. The powder precursors were ground in an alcoholic medium for 4 h, using an attritor mill. After drying, the powder precursor was heat treated between 700 and 900 °C for 4 h.

In order to evaluate the colour stability of the pigments, the sample $La_{0.6}Ca_{0.4}CoO_3$ calcined at 800 °C was mixed with an industrial enamel and applied onto a tile. The ceramic enamel was prepared by adding 3 wt% of the pigment into a boron-based frit, with dispersion in water and deflocculation with 0.1 wt% of sodium tripolyphosphate. The enamel was homogenized in a ball mill for 2 h leading to a stable suspension with a viscosity of about 400 mPa s. This material was applied onto a white earthenware, dried in air for 8 h and in an oven at 80 °C for 24 h. The enameled tiles were heat treated with a heating range of 3 °C min^{-1} up to 1080 °C for 7 h and at 1150 °C for 15 min. Cooling was done with a rate of 5 °C min^{-1}, the colour of the enameled pigment was evaluated by colorimetry.

Characterizations of the heat-treated perovskites were performed by X-ray diffraction (XRD), infrared spectroscopy (IR), UV–vis spectroscopy and colorimetry.

Infrared spectra were obtained in the range from 2000 to 400 cm^{-1} in an MB-102 Bomem spectrophotometer using samples that were previously pressed with KBr. The UV–vis spectra were recorded using an SHIMADZU – UV-2550 Spectrometer, in the 190–900 nm range. The samples were evaluated by X-ray diffraction (XRD) in a D-5000 Siemens diffractometer, with a step size of 0.03 and step time of 1 s, using the Cu Kα radiation ($\lambda = 1.54060$ Å) and 2θ values ranging from 20 to 80°. The results were analyzed by comparison with the JCPDS 36-1388 files. The CIE L^*, a^* and b^* colour parameters were measured by means of a GretacMacbeth Color-eye 2180 colorimeter, following the CIE (Commission Internationale de l'Eclairage) standards, in which L^* varies from black (0) to white (100), a^* from green (−) to red (+), and b^* from blue (−) to yellow (+).

3. Results and discussion

The L^*, a^* and b^* colorimetric parameters of the pigments are shown in Table 1 for the different compositions and heat treatment temperatures. It can be noticed that the values of L^* decrease with the heat treatment temperature. The values of the a^* and b^* coordinates increase with temperature. However, such changes are very small and the modifications in the hues are hardly noticeable (Fig. 1). It is also observed that for the sample $La_{0.6}Ca_{0.4}CoO_3$ the sign of parameter b^* changes from 0.44 to −0.07, as the heat treatment temperature increases. The substitution of calcium for lanthanum does not influence the parameters L^*, a^* and b^* markedly, thus on the basis of colour specification being an alternative to decrease the pigment cost. Such result is quite interesting, due to the great commercial importance of black pigments.

Table 1
The colorimetric parameters L^*, a^* and b^*.

Samples	Temperature (°C)	L^*	a^*	b^*
$LaCoO_3$	700	36.36	0.17	0.20
	800	34.56	0.29	0.58
	900	33.48	0.32	1.19
$La_{0.8}Ca_{0.2}CoO_3$	700	37.33	0.17	0.32
	800	36.16	0.17	0.12
	900	32.60	0.35	0.63
$La_{0.6}Ca_{0.4}CoO_3$	700	35.73	0.29	0.44
	800	36.19	0.11	0.05
	900	35.68	0.20	−0.07
Enamel pigment	1080	27.94	−0.03	2.94
	1150	29.06	0.15	3.03

The sample $La_{0.6}Ca_{0.4}CoO_3$ calcined at 800 °C was applied as pigment in a ceramic tile (Fig. 1 and Table 1) in order to evaluate if this material survives processing conditions. No meaningful change in the colour of the pigment is observed indicating that this perovskite is thermally and chemically stable, not reacting with the enamel.

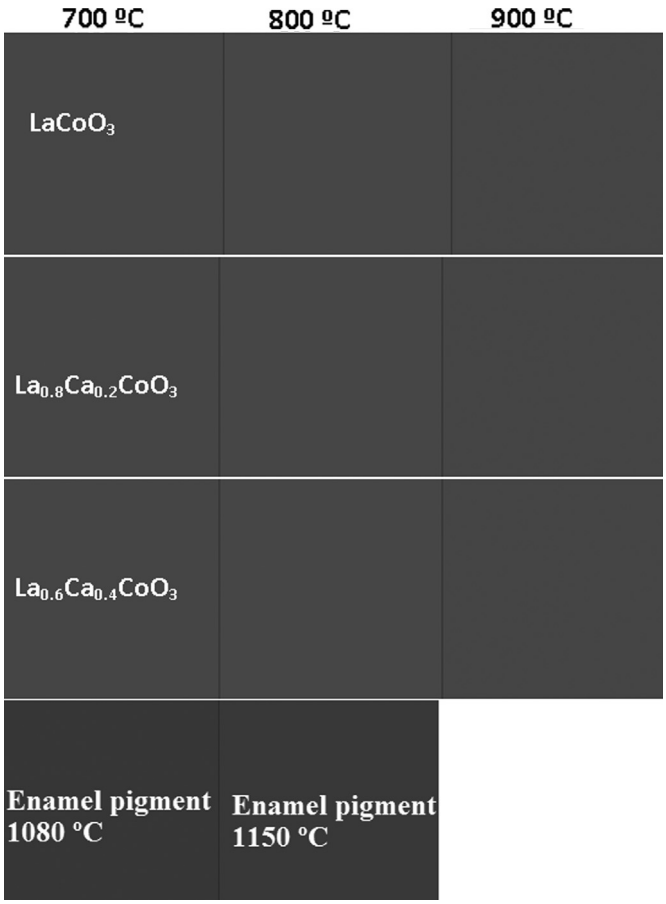

Fig. 1. Colours of the pigments.