



Lanthanum cobaltite black pigments with perovskite structure



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ABSTRACT

In this work $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ ($x = 0-0.4$) 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.

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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 $(\text{Co}_{0.5}\text{Mg}_{0.5})(\text{Fe}_{1.9}\text{Cr}_{0.1})\text{O}_4$ and $(\text{Co}_{0.5}\text{Mg}_{0.5})(\text{Fe}_{1.74}\text{Cr}_{0.06}\text{Al}_{0.2})\text{O}_4$ [7] by three different methods: coprecipitation, 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 $\text{Co}_{2.75}\text{Cr}_{0.25}\text{O}_4$, 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 $\text{Co}_{2.75}\text{Cr}_{0.25}\text{O}_4$, 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 $\text{Co}_x\text{Zn}_{7-x}\text{Sb}_2\text{O}_{12}$ 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 $\text{BaSn}_{1-x}\text{Tb}_x\text{O}_3$ [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

$\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ 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 desagglomerated 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 $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ 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 $K\alpha$ 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

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
$\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$	700	37.33	0.17	0.32
	800	36.16	0.17	0.12
	900	32.60	0.35	0.63
$\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$	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

very small and the modifications in the hues are hardly noticeable (Fig. 1). It is also observed that for the sample $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ 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.

The sample $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ 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.

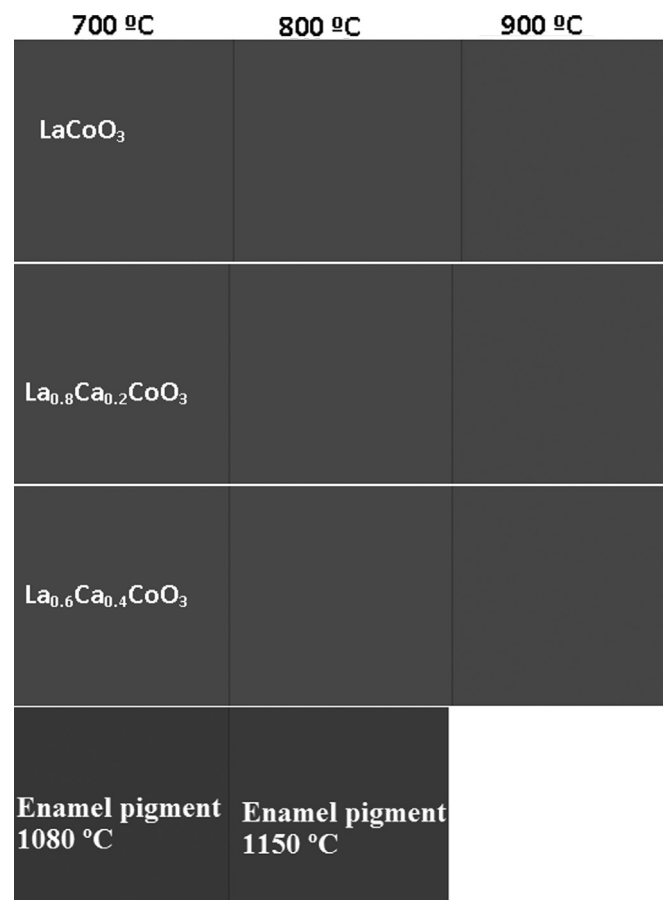


Fig. 1. Colours of the pigments.

As noted previously, the colour of the pigment depends on the chromophore ion itself, its oxidation state and its coordination. In the present case, the studied pigments present very dark colours. In order to understand this behavior, materials were evaluated by X-ray diffraction, infrared spectroscopy and UV–vis spectroscopy.

In the XRD patterns presented in Fig. 2 it is observed that well-crystallized perovskites are readily obtained at 700 °C confirming that the polymeric precursor method is efficient for the synthesis of the $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ system. This material was also obtained by Nakayama et al. [13] who have synthesized LaCoO_3 using the solid state reaction, co-precipitation and thermal decomposition of the heteronuclear complex and have obtained the perovskite phase at 1000, 1200 and 600 °C, respectively.

In relation to the structure, the samples LaCoO_3 and $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ display a rhombohedral structure at all heat treatment temperatures while $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ is cubic after heat treatment at 800 and 900 °C. The rhombohedral distortion from cubic symmetry is mainly caused by tilting of the BO_6 octahedra along one of the four diagonals in the cubic unit cell [14]. Mastin et al. [15] have studied the $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ system and have reported that the increase of temperature and calcium content has favored the formation of the more symmetric orthorhombic and cubic phases.

The XRD patterns (Fig. 2c) also show a secondary phase for the sample $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ heat treated at 700 °C. This calcium-rich sample displays a peak assigned to calcite (CaCO_3), since calcium easily forms a carbonate, due to its ionic character. Upon increasing the heat treatment temperature, the carbonate decomposes and this peak disappears.

The infrared spectra, Fig. 3, confirm the presence of carbonate groups in the calcium-rich samples heat treated at low temperatures as indicated by the bands at around 1420 cm^{-1} , 1100 cm^{-1} and 860 cm^{-1} [13,16]. The spectra also show bands at around 1630 and 1100 cm^{-1} , pointing out the presence of water and hydroxyl groups bonded to the metals, respectively [17,18]. Small bands related to the stretching of bidentate carboxyl–metal complexes are also observed at about 1520 cm^{-1} ($\nu(\text{C}=\text{O})$ stretching) and 1420 cm^{-1} ($\nu(\text{CO})$ stretching) [16]. The intensity of these bands decreases with increasing heat treatment temperature.

In relation to metal–oxygen bands, a decrease in the definition with calcium addition is observed indicating that a higher short-range disorder occurs, in spite of the cubic structure. Sharper bands are observed for higher heat treatment temperatures while the calcium-free samples display well-defined bands even at 700 °C. This higher disorder may be one of the reasons for pigment darkening.

According to Predoana et al. [19] and Khalil [20], a band assigned to LaO_{12} has been observed at $560\text{--}570\text{ cm}^{-1}$ in LaCoO_3 perovskites. According to Khalil [20], the intensity of this band diminished and its position shifted toward lower wavenumbers when Ba^{2+} replaced La^{3+} . In the present work, LaO_{12} bands are also found near 560 cm^{-1} with a decrease in intensity of the band and a shift toward lower wavenumbers with calcium addition.

The absorptions attributed to the stretching of the cobalt–oxygen ($\text{Co}-\text{O}$) bonds in an octahedral coordination have been observed near to 600 cm^{-1} and 480 cm^{-1} by Nakayama et al. [13] and at about 625 cm^{-1} by Predoana et al. [19], besides bands at 588 cm^{-1} and 530 cm^{-1} attributed to Co in sevenfold and fourfold coordination, respectively. Berger et al. [21], working in the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ system, have noticed a band at around 670 cm^{-1} and have ascribed this band to the formation of Co^{4+} ions, as a result of electric charge compensation. In the present work bands are observed at 430 cm^{-1} and 600 cm^{-1} , being assigned to CoO_6 . A weak band is also noticed at around 670 cm^{-1} in the calcium-rich samples, indicating that Co^{4+} ions are formed due to La^{3+} substitution, as shown in Eq. 1. This result is in agreement with the

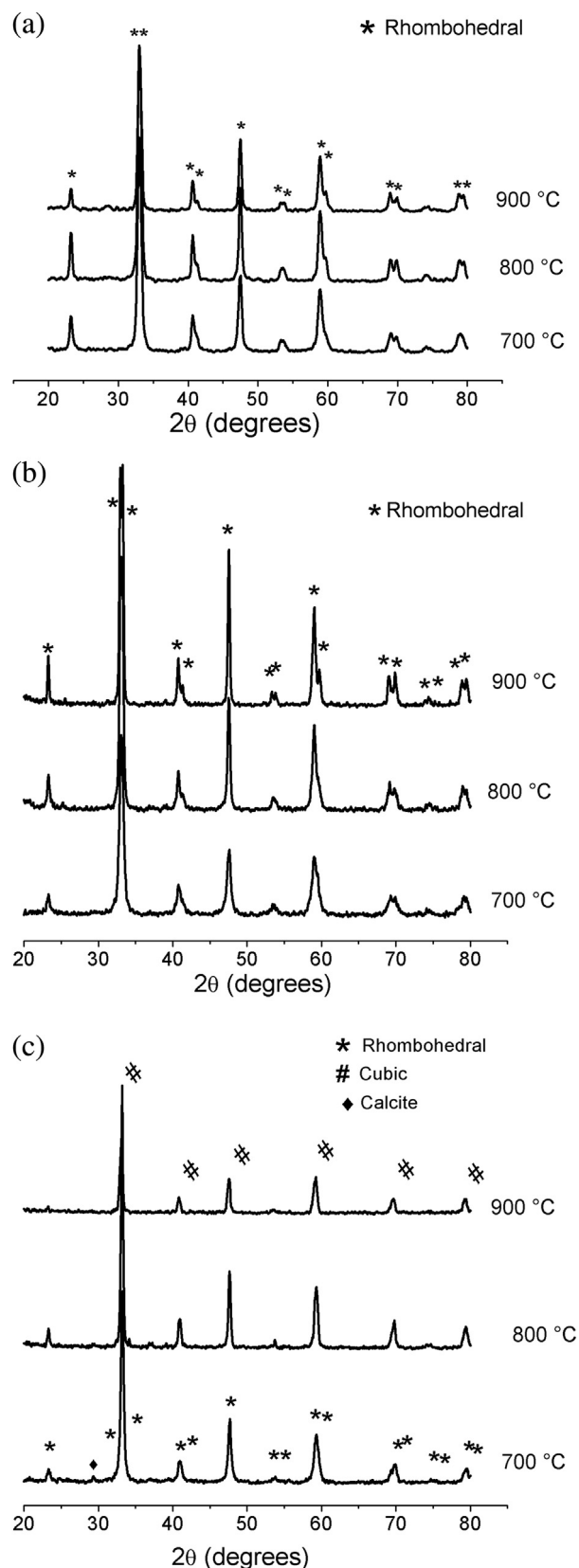


Fig. 2. XRD patterns of the $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ samples, heat treated at 700 °C, 800 °C and 900 °C. (a) LaCoO_3 , (b) $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ and (c) $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$.

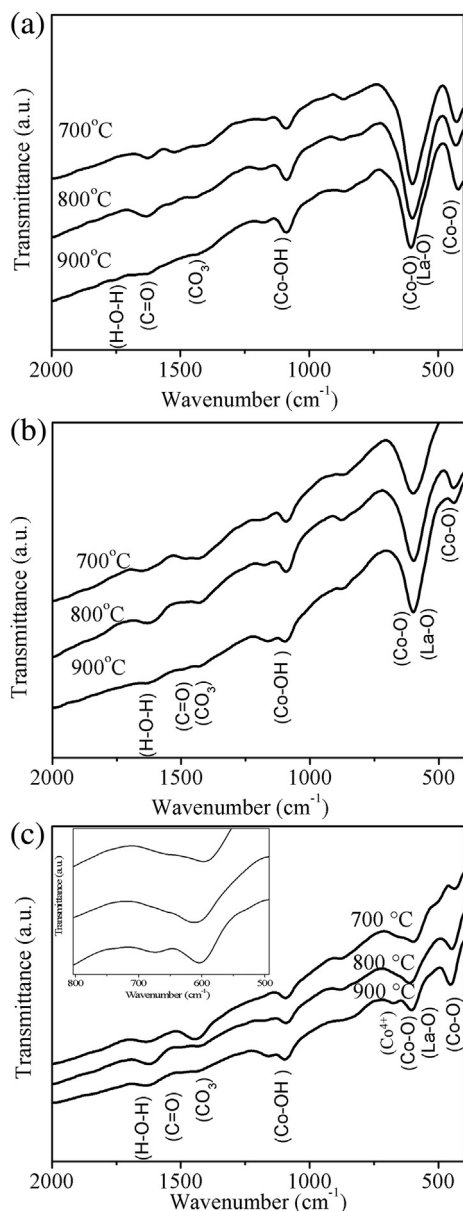
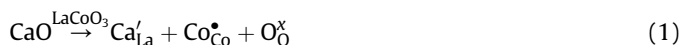


Fig. 3. Infrared spectra of the samples heat treated at 700 °C, 800 °C and 900 °C. (a) LaCoO_3 ; (b) $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$; (c) $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$. Inset: Zoom in the region between 500 and 800 of the infrared spectrum of the sample $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$.

electric charge compensation reported by Berger et al. [21] and Khalil [20] who have stated that the conduction in La–Ba cobaltites has generally been attributed to electronic exchange between Co^{3+} and Co^{4+} . Merino et al. [17] have reported that cobalt can present several oxidation states (Co^{2+} , Co^{3+} and Co^{4+}) in a perovskite structure, as a consequence of defect formation [17]. The simultaneous presence of Co^{3+} and Co^{4+} detected by infrared spectroscopy may be one of the reasons for the darkening of the pigments.



In relation to UV–vis spectra, Fig. 4, results show an almost constant broad band over the whole visible range, pointing out that the colour reflected by the pigments is indeed dark. A broad band between 200 nm and 350 nm can be observed, being ascribed to the ligand–metal charge transfer and does not influence the pigment colour.

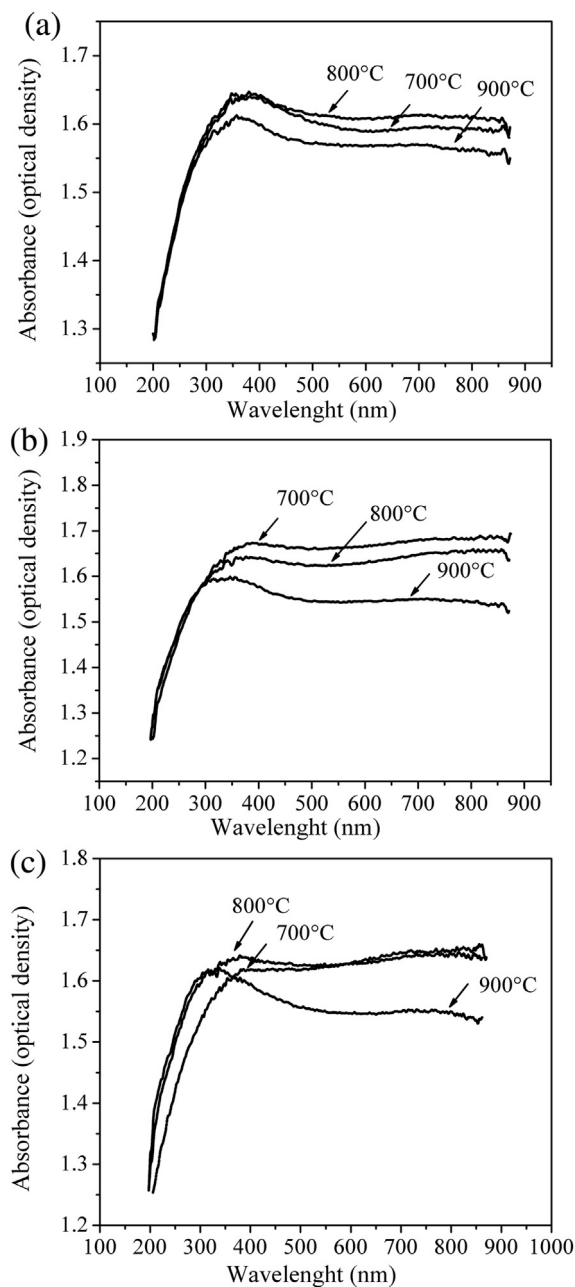


Fig. 4. UV–vis spectra of the samples heat treated at 700 °C, 800 °C and 900 °C. (a) LaCoO_3 ; (b) $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$; (c) $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$.

According to literature data, the presence of Co^{2+} is characterized by an electronic transition at about 600 nm [3], while the presence of Co^{3+} is related to bands at around 400 and 700 nm [22]. Mastin et al. [15] have claimed that some Co^{2+} can be formed by the thermal reduction of Co^{3+} , favored by high temperatures and nonstoichiometry, usually present in perovskites. In the present case, as cobalt is the only chromophore present in the $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$, the broad absorption band between 400 and 700 nm is probably due to the overlapping of different bands assigned to Co cations in different oxidation states in octahedral sites.

The decrease of the absorbance of the samples with the thermal treatment temperature was also observed, especially for samples calcined at 900 °C. This decrease may be assigned to a sintering among particles.

The presence of Co^{4+} could not be confirmed by our UV–vis spectra, as its band usually appears at 100 nm [23], out of the range measured in this work. On the other hand it is confirmed by infrared spectroscopy.

In this sense, the presence of cobalt in three different oxidation states seems to be responsible for the dark colour observed in these pigments.

4. Conclusions

The synthesized pigments are all single phase except for the sample $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$, heat treated at 700 °C that also present the calcite phase. Thus the polymeric precursor method is satisfactory for the synthesis of the $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ system.

All of the pigments display a strong absorption over the whole visible range, leading to a black colour as confirmed by the low values of the three colorimetric parameters. Such a dark color is probably due to the different oxidation states of cobalt and to the defects that increase the short-range disorder of the structure, thus altering the cation coordination.

The substitution of calcium for lanthanum does not influence markedly the parameters L^* , a^* and b^* , thus being an alternative to decrease the cost of the pigment. Such a result is quite interesting, due to the great importance of black pigments. We believe that the sample $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$, heat treated at 800 °C is the most adequate to be used as a pigment as it is single phase with lower cost and lower L^* , a^* and b^* values. When applied on a ceramic tile, no change in the colour of this pigment is observed indicating that it presents chemical and thermal stability.

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