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Thermal, structural and optical properties of Al_2CoO_4-Crocoite composite nanoparticles used as pigments

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Abstract Al_2CoO_4–$PbCrO_4$ and Al_2CoO_4–Pb_2CrO_5 crystalline powders in different proportions were obtained by the polymeric precursor method. Differential scanning calorimetry (DSC) and thermogravimetry (TG) techniques were used to accurately characterize the distinct thermal events occurring during synthesis. The TG and DSC results revealed a series of overlapping decomposition reactions due to different exothermal events, which were identified as H_2O and NO_x elimination and polymer pyrolysis. The X-ray diffraction patterns of the xAl$_2$CoO$_4$–(1 − x)PbCrO$_4$ and xAl$_2$CoO$_4$–(1 − x)Pb$_2$CrO$_5$ mixed compounds, with $x = 1$, 0.75, 0.5, 0.25 and 0, were obtained in the crystalline form with their respective phases, and proved consistent with the nominal compositions. The synthesis of these two systems yielded nine different colors and shades.

Keywords Al_2CoO_4–Pb_2CrO_5 · Al_2CoO_4–$PbCrO_4$ · Nanoparticles · Polymeric precursors

Introduction

$PbCrO_4$ is a crocoite, normally with a monoclinic $P21/n$ structure, which is used as a yellow pigment and as a photosensitizer [1]. Dilead pentaoxochromate, Pb_2CrO_5, is a phoenicochroite of the PbO-CrO_3 system [2] used as a photoconductive dielectric material because of its centrosymmetry in the monoclinic $C2/m$ space group. Pb_2CrO_5 has been found to have a wide band gap energy (2.1–2.3 eV), a high absorption coefficient in the visible and ultraviolet light-spectrum (10^4–10^5 cm^{-1}), and a high-speed photo-response in this spectral region. The photoresponse and performance of Pb_2CrO_5 devices suggest that Pb_2CrO_5 may be classified as a new type of optoelectronic dielectric material that could potentially be used in room temperature photoconductors in the visible and ultraviolet regions [3–8].

Various methods have been employed to synthesize lead chromate as thin film [9] and ceramic disks [10], including the solid solution reaction and calcination of PbO and Cr_2O_3 mixed powder. On the other hand, $PbCrO_4$ nanocolloids have been prepared in H_2O/sodium bis(2-ethylhexyl)sulfosuccinate, (AOT)/n-heptane, water-in-oil microemulsion medium [11]. $PbCrO_4$ nanorods and Pb_2CrO_5 microparticles were synthesized separately by a hydrothermal method in the presence of polyvinylpyrrolidone surfactant at pH ~7 and pH > 14 at 140 °C for 20 h [12]. Manipulation of the thermodynamic and kinetic control processes plays a key role in crystal growth, which determines the final crystal habit, phase, shape, and structures [13, 14]. To our knowledge, a simple solution method has not been used to discriminate different phases and polymorphs of lead chromate at room temperature. Xu et al. [15] reported a systematic synthesis of lead chromates nanocrystals with different polymorphs and phases, such as monoclinic $PbCrO_4$, orthorhombic $PbCrO_4$, Pb_2CrO_5, and $K_2Pb(CrO_4)_2$ by a simple precipitation reaction with no additives at room temperature. They showed that the pH value and the molar ratio of Pb^{2+} and ${CrO_4}^{2-}$ exert a significant influence on the discrimination of polymorphs and phases of lead chromate.

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The $CoAl_2O_4$ spinel phase, called Thénard's blue, has long been known and extensively studied [16, 17]. This phase may be considered as deriving from Co(II)Co(III)O_4 by replacing all the Co(III) with Al.

This work involved the synthesis of Al_2CoO_4-Crocoite composite nanoparticles and a study of their thermal behavior as a function of the structural and optical properties for pigment applications. Al_2CoO_4-Crocoites samples were prepared by the polymeric precursor method. This method, also called the Pechini method [18], allows for the production of nanocrystalline powder samples at relatively low temperatures. This synthesis produces a polymer network starting from a polyhydroxy alcohol and an alpha-hydroxycarboxylic acid, with metallic cations homogeneously distributed throughout the matrix [19]. The samples were characterized by thermal analysis, thermogravimetric and differential scanning calorimetry, X-ray diffraction, diffuse reflectance and colorimetric coordinate techniques.

Experimental procedure

Synthesis

The polymeric precursor method involves the polymerization of a metallic citrate using ethylene glycol [20–22]. A hydrocarboxylic acid such as citric acid is normally used to chelate cations in an aqueous solution. The addition of a polyalcohol such as ethylene glycol leads to the formation of an organic ester. Polymerization promoted by heating to around 100 °C results in a homogenous resin in which the metal ions are distributed uniformly throughout the organic matrix.

Lead acetate [$(CH_3CO_2)_2Pb \cdot 3H_2O$], chromium (VI) oxide [$CrO_3$], aluminum nitrate [$Al(NO_3)_3 \cdot 9H_2O$)] and cobalt nitrate [$Co(NO_3)_3 \cdot 6H_2O$)] were used as precursors. Aluminum nitrate, cobalt nitrate, chromium oxide and lead acetate were dissolved in water and then added to an aqueous acid citric solution.

The ethylene glycol ($HOCH_2CH_2OH$) was mixed to promote polymerization of the citrate by a polyesterification reaction. The citric acid:metal molar ratio was 4:1, while the citric acid:ethylene glycol ratio was 3.0:6.1 (molar ratio). The compositions studied here are listed in Table 1 with their respective names.

Table 1 Nominal compositions and respective names used in this work

Composition	Name
$PbCrO_4$	100Pb
$75PbCrO_4$-$25Al_2CoO_4$	25Al75Pb
$50PbCrO_4$-$50Al_2CoO_4$	50Al50Pb
$25PbCrO_4$-$75Al_2CoO_4$	75Al25Pb
Al_2CoO_4	100Al
$25Pb_2CrO_5$-$75Al_2CoO_4$	75Al25Pb2
$50Pb_2CrO_5$-$50Al_2CoO_4$	50Al50Pb2
$75Pb_2CrO_5$-$25Al_2CoO_4$	25Al75Pb2
Pb_2CrO_5	100Pb2

Characterization

The thermal decomposition and crystallization processes were studied by TG (Netzsch STA 409C) and DSC techniques in an oxygen atmosphere at a heating rate of 10 °C min^{-1}. Al_2O_3 was used as reference material during the thermal analysis.

After annealing at 700 °C for 2 h, the powders were structurally characterized using an automatic diffractometer (Rigaku, Rotaflex RU200B) with CuKα radiation (50 kV/100 mA, 1.5405 Å) and a graphite monochromator. The scanning range was between 10° and 70° (2θ) with a step size of 0.02° and a step time of 1 s.

Diffuse reflectance and colorimetric coordinates of the pigments were measured in the 400 and 700 nm range, using a spectrophotometer (Minolta, CM2600d) equipped with standard type D65 (day light) light source, following the CIE-L*a*b* colorimetric method recommended by the CIE (Commission Internationale de l'Eclairage) [23]. In this method, L* is the lightness axis [black (0) → white (100)], b* is the blue (−) → yellow (+) axis, and a* is the green (−) → red (+) axis, and ΔE is defined as the total color difference ($\Delta E^2 = L^{*2} + a^{*2} + b^{*2}$).

Results and discussion

Thermal analysis

It is well known that metal complexation and polymerization reactions occur during synthesis by the polymeric precursor method [24]. In the material studied here, the complexation of aluminum and cobalt with citric acid led to the following reactions:

$$Al(NO_3)_3 \cdot 9H_2O + 3C_6O_7H_8 \rightarrow Al(C_6O_7H_7)_3 + 3HNO_3 + 9H_2O \quad (1)$$

and

$$Co(NO_3)_2 \cdot 6H_2O + 2C_6O_7H_8 \rightarrow Co(C_6O_7H_7)_2 + 2HNO_3 + 6H_2O \quad (2)$$

forming nitric acid and water. The lead complexation reaction occurred as follows:

$$(\mathrm{CH_3CO_2})_2\mathrm{Pb}\cdot 3\mathrm{H_2O} + 2\mathrm{C_6O_7H_8} \rightarrow \mathrm{Pb(C_6O_7H_7)_2} + 2\mathrm{CH_3COOH} + 3\mathrm{H_2O} \quad (3)$$

with the formation of acetic acid and water, while that of chromium was:

$$\mathrm{CrO_3} + 6\mathrm{C_6O_7H_8} \rightarrow \mathrm{Cr(C_6O_7H_7)_6} + 3\mathrm{H_2O} \quad (4)$$

Mixing these metallic complexes (metallic citrates) above 70 °C triggered the onset of the esterification reaction between metal citrate and ethylene glycol, as follows:

$$\mathrm{M^{n+}[OCOCH_2C(OH)(COOH)CH_2COOH]_x} + 3\mathrm{HOCH_2CH_2OH} \rightarrow \mathrm{M^{n+}[OCOCH_2C(OH)(COOH)CH_2COOCH_2CH_2OH]_x} + \mathrm{x/H_2O} \quad (5)$$

In the compounds studied here, the polyesterification reactions (Reaction 5) occurred continuously until the polymer network was formed. Therefore, the main organic compounds contained in the resin were alcohol, water, acetic acid, nitric acid and polyester.

Figure 1 presents the TG and DSC curves of the mixtures for Al$_2$CoO$_4$–PbCrO$_4$ and Al$_2$CoO$_4$–Pb$_2$CrO$_5$ systems. In the Al$_2$CoO$_4$ crocoites, the molar proportions were 100/0, 75/25, 50/50, 25/75 and 0/100. Although the method is basically semi-quantitative, mass variations can be measured accurately. The TG curves revealed a series of overlapping decomposition reactions due to different exothermal events, which are indicated by the DSC curves.

Samples 100Al, 100Pb, 75Al25Pb2, and 100Pb2 showed low residual mass due to the high content of solvents; they were dried for 4 h at 100 °C. The other samples showed high residual mass due to predrying at 300 °C for 1 h. In general, four thermal events were detected: H$_2$O, NO$_x$; polymer degradation; polymeric degradation (–CH2– groups); and (–CO– and –COO– groups). The addition of Al$_2$CoO$_4$ to the PbCrO$_4$ or Pb$_2$CrO$_5$ compound was found to raise the final decomposition temperature from around 400–500 °C to 800–950 °C. The addition of Al$_2$CoO$_4$ undoubtedly influences the catalytic effect of crocoites on the elimination of organic compounds (mass loss step between ~400 and ~800 °C). This effect was clearly

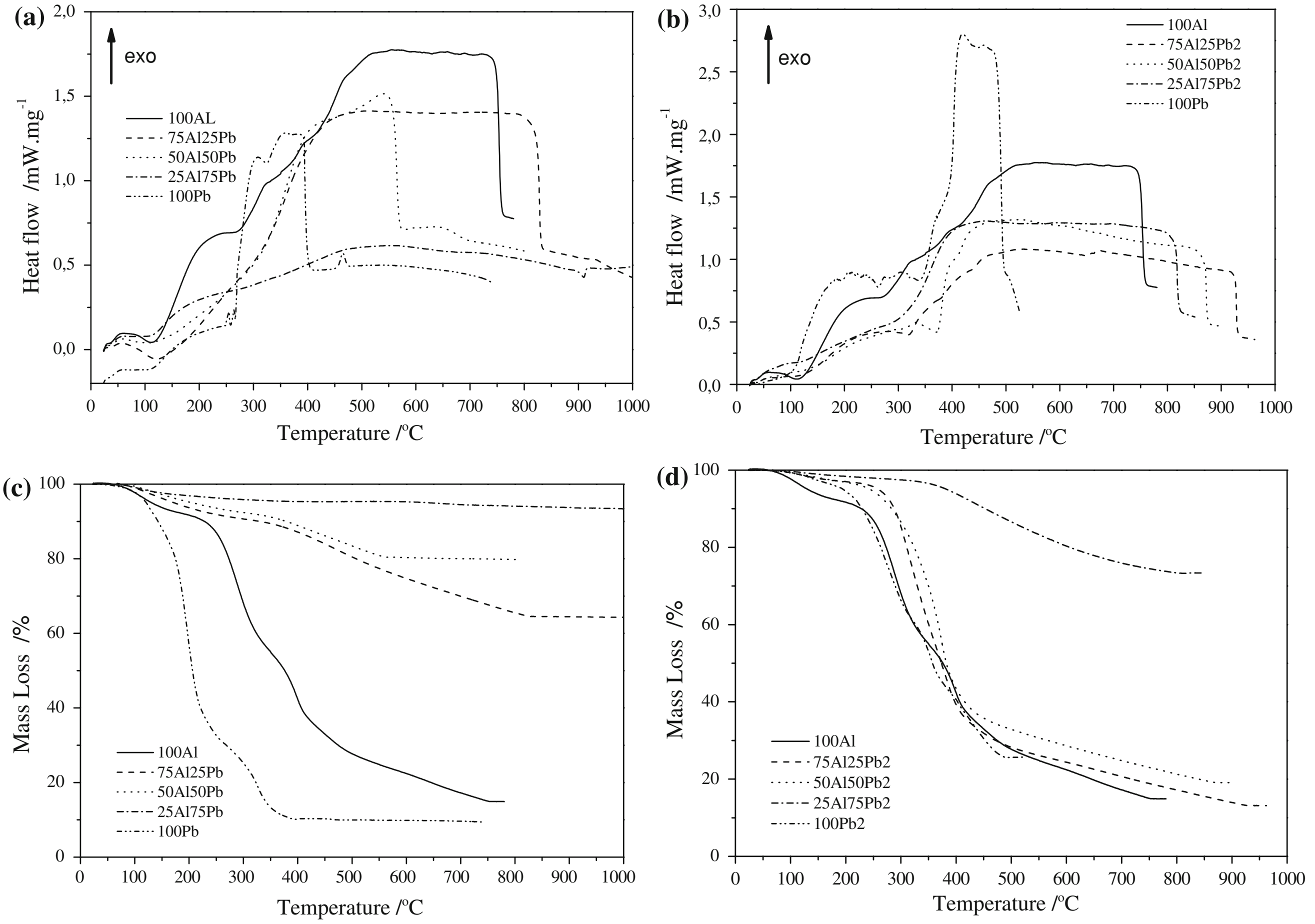

Fig. 1 **a** DSC curves of the Al$_2$CoO$_4$–PbCrO$_4$ systems, **b** DSC curves of the Al$_2$CoO$_4$–Pb$_2$CrO$_5$ systems, **c** TG curves of the Al$_2$CoO$_4$–PbCrO$_4$ systems and **d** TG curves of the Al$_2$CoO$_4$–Pb$_2$CrO$_5$

visible in the DSC results, which showed the exothermic peak between 300 and 400 °C for 100Pb and between 400 and 500 °C for 100Pb2 broadened and shifted to high temperatures. This finding allows us to conclude that the inclusion of Al_2CoO_4 to the crocoites increases the synthesis temperature to obtain crystalline materials without organic compounds.

X-ray diffraction

Figure 2a and b show the X-ray diffraction patterns at room temperature for different samples calcined at 700 °C for 2 h at a heating rate of 10 °C min^{-1}.

In the case of the $PbCrO_4$–Al_2CoO_4 system (Fig. 2a), the composition containing 75% of Al_2CoO_4 presented only the major compound in crystalline form, while the other compound was in the amorphous state. Compositions containing 50% and 25% of Al_2CoO_4 resulted in a mixture of the Pb_2CrO_5 and Al_2CoO_4 crystalline phases. An analysis of the Pb_2CrO_5–Al_2CoO_4 system (Fig. 2b) containing 75% of Al_2CoO_4 revealed that only this major phase crystallized at 700 °C, while the compound remained amorphous. The other compositions containing 50% and 25% of Al_2CoO_4 showed the desired Pb_2CrO_5 and Al_2CoO_4 crystalline phases. In both systems of this study, the Pb_2CrO_5 phase crystallized preferentially. The crocoite phases require less energy (temperature) to crystallize than the Al_2CoO_4 phase. However, the incorporation of large amounts of Al_2CoO_4 delays the formation of crocoites in lower concentrations.

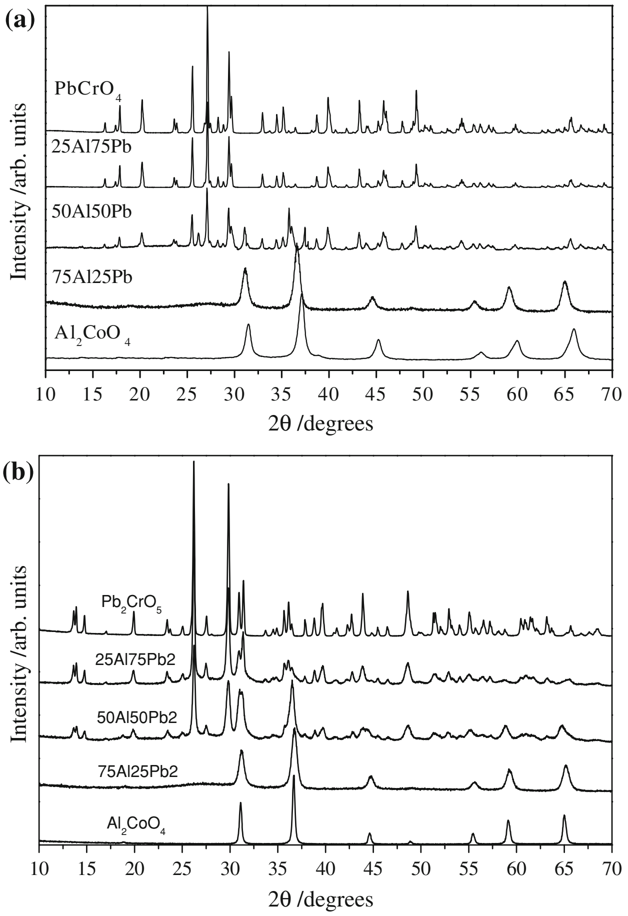

Fig. 2 X-ray diffraction patterns of: **a** $PbCrO_4$–Al_2CoO_4, and **b** Pb_2CrO_5–Al_2CoO_4 systems, heat-treated at 700 °C/2 h

The structures of the phases found in the simple systems were: Al_2CoO_4, $PbCrO_4$ and Pb_2CrO_5, according to the index of the crystallographic cards nos. 38-0814, 74-2304, and 84-0678, respectively. The main aspect of spinels is the presence of two metallic cations, A^{2+} and B^{3+}, in tetrahedral and octahedral positions, respectively. The way in which such sites are occupied depends on the calcination temperature [25, 26].

A complete determination of the crocoite structure and two-dimensional refinement was already done by Quareni and De Pieri [27] in 1964. Based on this early study, it was possible to refine the lead and chromium parameters and to determine the positions of the oxygen atoms. In 1965, the same author confirmed the earlier determination of the structure and refined the atomic parameters, particularly the parameters of the oxygen atoms which could not be determined very accurately by the two-dimensional refinement [28]. The orthorhombic and monoclinic modifications of $PbCrO_4$ have very similar interatomic distances, which confirm the evidence for multiple bonds in the CrO_4^{-2} ions. $PbCrO_4$ powders are monoclinic, with space group $P2_1/n$ (14), and cell parameters of: $a = 7.145(4)$ Å; $b = 7.436(4)$ Å; $c = 6.795(4)$ Å; $A = 0.9609$; $C = 0.9138$; $\beta = 102.420^\circ$, and $Z = 4$. The Al_2CoO_4 powders are cubic, with space group Fd3 m (227): $a = b = c = 8.086(1)$ Å, $Z = 8$, and origin at center, (3-m), and the 24 cations occupy 8 tetrahedral (a) positions, 1/8, 1/8, 1/8, and 16 octahedral (d) positions, ½, ½, ½, while the anions are located in 32 (e) positions, u, u, u [29].

Toda and Morita [30] studied the crystal structure of Pb_2CrO_5. This structure was analyzed under the assumption that the lead, chromium, and oxygen atoms are ionic, in order to use the scattering factors of each ion. The final locations of Pb^{2+}, Cr^{6+} and O^{2-} were determined from a comparison of the calculated relative intensities, the bond lengths and the bond angles against the observed values. Their study resulted in a monoclinic structure: c2/m. The values of the Pb–O bond length were consistent with that in Pb_2SO_5 [31], where the values of the bond angles of O–Cr–O are around 109°. Pb_2CrO_5 powders are monoclinic, with the space group C_2/m (12), and the cell parameters are: $a = 14.018$ Å; $b = 5.683$ Å; $c = 7.148$ Å; $A = 2.4667$, $C = 1.2569$; $\beta = 115.23^\circ$, and $Z = 4$.

Diffuse reflectance

Color generation is known by a mechanism called charge transference. This mechanism consists of the electron movement of an ion to another in response to the absorption of light energy, resulting in a temporary change of the valence state for both ions and originating the material's color [32]. This mechanism is responsible for the color of $PbCrO_4$ and Pb_2CrO_5 compounds. Cr(VI) is not favored energetically. Cr(VI) is a strong attractor of electrons, and the movement of an electron fraction from oxygen to the central ions results in a stable configuration, leading to a transition of charge transference between ligand-metal (anion-cation), which gives rise to the color of the compounds.

The transition metal group, also called iron group, has elements that present an incomplete *3d* electronic sub-level. In the ion formation process, the atom of a transition metal loses its external *4 s* electrons and its configuration becomes: $1\,s^2\,2\,s^2\,2p^6\,3\,s^2\,3p^6\,3d^n$, where n corresponds to the quantity of electrons in the d sub-level, the Co element with electronic configuration has Co^{2+} and Co^{3+} valences and also, albeit less commonly, Co^{1+} and Co^{4+} valences. The diffuse reflectance of the Al_2CoO_4 compound depicted in Fig. 3a and b has characteristic Co^{2+} bands with a $3d^7$ electronic configuration. At around 590 nm there is an absorption band of cobalt in tetrahedral sites (^2E), while another band at around 510 nm corresponds to cobalt in octahedral sites ($^4T_1$), producing powders of intensely blue tones.

The diffuse reflectance spectra show absorption bands at around 560 nm for the $PbCrO_4$ compound (mustard color) and between 500 and 600 nm for the Pb_2CrO_5 (reddish), which shift to red by increasing the thermal treatment temperature. The mustard shade of $PbCrO_4$ (not pure green) is a combination of green and red (650 nm).

Figure 3a and b indicate that the mixtures were effective in generating various colors ranging from blue to red. Three systems yielded nine different colors, whose shades changed upon modifying the calcination temperature.

Colors can be measured by several methods, but in ceramics the most common method to specify the color of a product is CIE-L*a*b*. This method measures the intensity of the diffuse reflectance in the visible region to obtain the three colorimetric coordinates, L*, a*, b*, which determine the black/white lightness, green/red and blue/yellow color intensities, respectively, and also the total color difference, ΔE. Table 2 presents the colorimetric coordinates (L*, a*, b*) and total color difference (ΔE) of Al_2CoO_4–$PbCrO_4$ and Al_2CoO_4–Pb_2CrO_5 powder systems, using type D65-10° (day light) light source, according to the CIE-L*a*b* standard colorimetric method. These colorimetric coordinates must be analyzed jointly to determine the final color of pigments, especially the a* and b* coordinates. The pigment powders are preferred red colored, some compounds are red-yellow colored and others red–blue colored. Also, there are compositions showing green color.

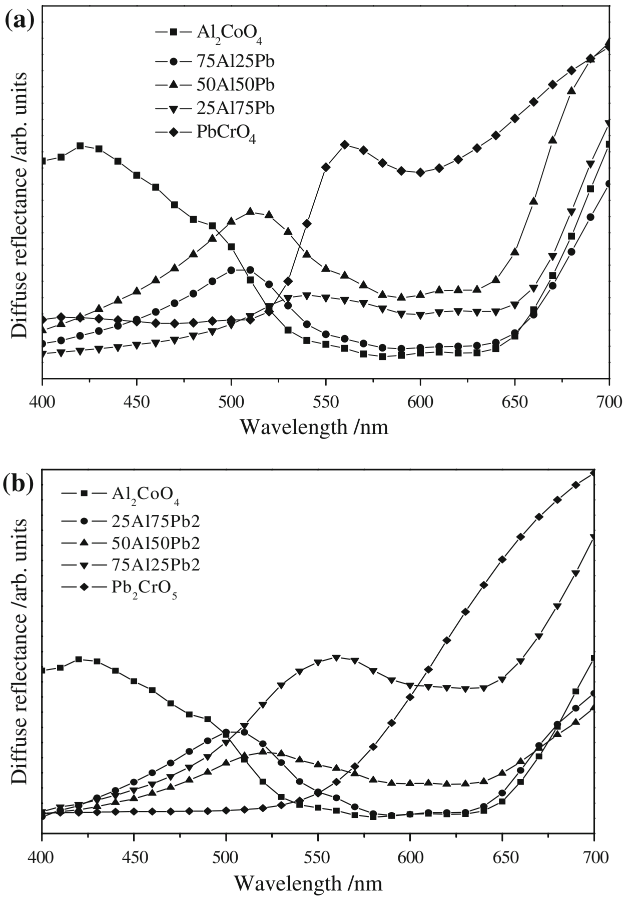

Fig. 3 Diffuse reflectance spectra of the nanometric **a** Al_2CoO_4–$PbCrO_4$, and **b** Al_2CoO_4–Pb_2CrO_5 powders systems, heat treated at 700 °C/2 h

Table 2 Colorimetric coordinates (L*, a*, and b*) and total color difference (ΔE) of Al_2CoO_4-$PbCrO_4$ and Al_2CoO_4-Pb_2CrO_5 powders systems, using light source type D65-10° (day light), following the CIE-L*a*b* standard colorimetric method

Samples	Light source	a*	b*	L*	ΔE
$PbCrO_4$	D65-10°	10.26	26.85	37.70	47.41
25Al75Pb	D65-10°	25.10	−1.01	13.79	28.66
50Al50Pb	D65-10°	31.23	−6.65	2.78	32.05
75Al25Pb	D65-10°	20.64	−10.90	−6.78	24.30
$AlCo_2O_4$	D65-10°	45.44	−9.77	−51.64	69.48
75Al25Pb2	D65-10°	− 6.95	− 3.88	21.06	22.51
50Al50Pb2	D65-10°	−5.74	5.94	21.18	22.73
25Al75Pb2	D65-10°	−2.32	17.29	29.16	33.98
Pb_2CrO_5	D65-10°	33.78	28.02	38.53	58.40

Conclusions

The powders obtained by the polymeric precursor method are pigments with intense and uniform colors. This effect is attributed to the synthesis that produces reactive nanopowders, confirming the importance of this chemical method to produce materials for different applications. Powders of the pure systems (Al_2CoO_4, $PbCrO_4$, and Pb_2CrO_5) were synthesized as a single phase, with the position of the X-ray diffraction plane showing a good match with the values indexed in crystallographic phase cards. Mixed phases were also obtained successfully, expanding the possibilities of colors from blue to red. The DSC and TG techniques allowed the decomposition and crystallization processes to be described as a function of the mixed composition, and to determine the temperature range of processes: degradation of the polymer (pyrolysis of the organic compounds), and elimination of nitrates and water. In the lead-rich systems, the crystallization process occurred at lower temperatures than in the aluminum-rich systems, and the inclusion of Al_2CoO_4 to the crocoites increased the synthesis temperature required to obtain crystalline materials without organic compounds. Finally, the two systems (Al_2CoO_4–$PbCrO_4$, Al_2CoO_4–Pb_2CrO_5) yielded nine different colors, whose shades can be modified by changing the calcination temperature. The colorimetric coordinates were determined for all the samples.

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References

1. Toda K, Watanabe S. An ultraviolet detector using a Pb_2CrO_5 thin film. J Mater Sci Lett. 1999;18:689–90.
2. Negas T. The system PbO-chromium oxide in air. Am Ceram Soc. 1968;51:716–9.
3. Wishah KA, Abdul-Gader MM. Photoconduction and polarization effects in a heattreated Au/Pb_2CrO_5/SnO_2 film device. Appl Phys A. 1998;66:229–34.
4. Toda K, Abdul-Gaderz MM, Okaday M. Impedance analysis of the AC behaviour of a Au/Pb_2CPO_5/SnO_2 thin-film device. J Phys Condens Mater. 1997;9:3609–23.
5. Toda K, Watanabe SJ. Optoelectronic properties of Pb_5CrO_8 thin-films for application to contact-type line-image sensor. Appl Phys. 1995;77:2786–90.
6. Yoshida S, Toda K. Contact type line image sensor using Pb_2CrO_5 thin film. Appl Opt. 1990;29:1793–7.
7. Morita S, Toda KJ. Determinations of the crystals-structure of Pb_2CrO_5. Appl Phys. 1984;55:2733–7.
8. Toda K, Morita SJ. Photovoltaic effect in Pb_2CrO_5 ceramic. Appl Phys. 1984;55:210–2.
9. Toda K, Morita SJ. Optical properties and photovoltaic effect in Pb_2CrO_5 in thinfilms. Appl Phys. 1985;57:5325–9.
10. Toda K, Yoshida SJ. Photovoltaic mechanism of Pb_2CrO_5 ceramic disk with a pair of planar electrodes. Appl Phys. 1988;63:1580–4.
11. Panda AK, Bhowmik BB, Das AR, Moulik SP. Dispersed molecular aggregates. 3. synthesis and characterization of colloidal lead chromate in water/ sodium bis(2 ethylhexyl)sulfosuccinate/ n-heptane water-in-oil microemulsion medium. Langmuir. 2001;17:1811–16.
12. Liang JH, Li YD. Synthesis and characterization of lead chromate uniform nanorods. J Cryst Growth. 2004;261:577–80.
13. Cölfen H, Mann S. Higher-order organization by mesoscale self-assembly and transformation of hybrid nanostructures. Angew Chem Int Ed. 2003;42:2350–65.
14. Dickinson SR, McGrath KM. Switching between kinetic and thermodynamic control: calcium carbonate growth in the presence of a simple alcohol. J Mater Chem. 2003;13:928–33.
15. Xiang J-H, Yu S-H, Xu Z. Polymorph and phase discrimination of lead chromate pigments by a facile room temperature precipitation reaction. Cryst Growth Des. 2004;6:1311–5.
16. Bonnenberg D, Wijn HPJ. "Further Spineis". In: Hellwege KH, Hellwege AM, editors. Landolt-Bornstein Zahlenwerte und Funktionen aus Naturwissenschaften und Technik, Neue Serie. Berlin: Springer-Verlag; 1970. p. 446, 451.
17. Bonnenberg D, Hempel KA, "Further Spinels". In: Hellwege KH, Hellwege AM, editors. Landolt-Bdmstein Zahlenwerte und Funktionen aus Naturwissenschaften und Technik, Neue Serie. Berlin: Springer-Verlag; 1980. p. 654.
18. Pechini M. Method of preparing lead and alkaline – earth titanates and niobates and coating method using the same to form a capacitor. US Patent 3 330 697. 1967.
19. Kakihana M. Invited review "sol-gel" preparation of high temperature superconducting oxides. J Sol–Gel Sci Technol. 1996;6:7–55.
20. Bernardi MIB, Antonelli E, Lourenço AB, Feitosa CAC, Maia LJQ, Hernandes AC. $BaTi_{1-x}Zr_xO_3$ nanopowders prepared by the modified Pechini method. J Therm Anal Calorim. 2007;87:725–30.
21. de Melo DS, Santos MRC, Santos IMG, Soledade LEB, Bernardi MIB, Longo E, et al. Thermal and structural investigation of SnO_2/Sb_2O_3 obtained by the polymeric precursor method. J Therm Anal Calorim. 2007;87:697–701.
22. Xavier CS, Candeia RA, Bernardi MIB, Lima SJG, Longo E, Paskocimas CA, et al. Effect of the modifier ion on the properties of $MgFe_2O_4$ and $ZnFe_2O_4$ pigments. J Therm Anal Calorim. 2007;87:709–13.
23. CIE. Recommendations of uniform color spaces, color difference equations, phychometrics color terms. Supplement no.2 of CIE Publ. N°. 15 (E1e1.31) 1971, Bureau Central de la CIE, Paris; 1978.
24. Mesquita A, Bernardi MIB, Maia LJQ, Mastelaro VR. Synthesis and characterization of $Pb_{1-x}La_xTiO_3$ nanocrystalline powders. J Therm Anal Calorim. 2007;87:747–51.
25. He T, Becker KD. An optical in-situ study of a reacting spinel crystal. Solid State Ionics. 1997;101–103:337–42.
26. Becker KD. In situ spectroscopy in solid state chemistry. Solid State Ionics. 2001;141:21–30.
27. Quareni S, De Pieri R. La struttura della crocoite $PbCrO_4$. Rend Soc Min Ital. 1964;20:232–50.
28. Quareni S, De Pieri R. A three-dimensional refinement of the structure of crocoite, $PbCrO_4$. Acta Cryst. 1965;19:287–9.
29. Casado PG, Rasines I. The series of spinels $Co_{3-s}AlSO_4$ $(0 < s < 2)$: study of Co_2AlO_4. J Solid State Chem. 1984;52:187–90.
30. Morita S, Toda K. Determination of the crystal-structure of Pb_2CrO_5. J Appl Phys. 1984;55:2733–7.
31. Binnie WP. The crystal structure of lanarkite, PbO.$PbSO_4$. Acta Cryst. 1951;4:471–2.
32. Nassau K. The physics and chemistry of color. New York: Wiley Interscience Publication; 2001. p. 143–53.