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Synthesis of CoAl_2O_4 by double decomposition reaction between LiAlO_2 and molten KCoCl_3

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Abstract

Submicronic CoAl_2O_4 powders were prepared by double decomposition reaction between solid LiAlO_2 and molten KCoCl_3 at 500°C for 24 h. The reaction mechanism involves the dissolution of LiAlO_2 shifted by the precipitation of CoAl_2O_4 until complete transformation and the reaction leads to powders with a very homogeneous chemical composition. The powders obtained were mainly characterized by XRD, FTIR, ICP, X.EDS, electron microscopy and diffraction and diffuse reflexion. The blue pigments obtained exhibit a high thermic stability allowing their use for the colouring of ceramic tiles.

Keywords: Molten salt preparation; A. Firing; B. Spectroscopy; C. Colour; CoAl_2O_4

1. Introduction

In the ceramic industry, natural and synthetic pigments find applications as, the colouring agent in glasses, enamels and unglazed bodies. Currently, many synthetic ceramic inorganic pigments are prepared and widely used, in particular for the production of coloured traditional glazed and unglazed tiles. Cobalt is a very efficient colouring agent in glasses and ceramic glazes,¹ having a particularly mobile 3d electron shell which favours two or three valence states, and coordination numbers four and six in oxide bonds. Because of their expense, cobalt blues were not used extensively in ordinary paints. Early uses were limited to ceramic applications. Later, the cobalt blues were involved in artists' colours.²

The formulation of an inorganic ceramic pigment for colouring porcelains and stonewares is a very complicated problem because of the multitude of specific characteristics required for the final product: suitable decorative parameters such as bril-

liance or opacity, chemical resistance towards alkaline fluxes, colouring and thermal stability around 1250°C as well as thermal endurance.³

The colouring performance of cobalt pigments is strongly dependent upon their thermal stability, their chemical reactivity towards vitreous compounds and also upon the coordination of Co^{2+} ions, the tetrahedral one being preferred to the octahedral one. For the colouring of tiles, cobalt aluminate, CoAl_2O_4 , which has the normal spinel structure, was prepared in order to obtain a blue more intense and brilliant than that produced by Co_2SiO_4 .³ Indeed, in the normal spinel structure stable at high temperature, Co and Al are respectively tetrahedrally and octahedrally coordinated, whereas in Co_2SiO_4 , a change of the coordination of Co^{2+} , from tetrahedral to octahedral, occurs during the firing of tiles. For cobalt-based pigments, the Co^{2+} ions can be incorporated as colouring in all kinds of enamels where they adopt the tetrahedral coordination, though the octahedral one is also possible. A shift from octahedral to tetrahedral is obtained by increasing the basicity of the enamel and the firing temperature.⁴

Although the ceramic pigments are constituted of oxide crystals which are thermally stable at the firing temperature of

enamels and exhibit a very low reactivity towards molten enamels, the reaction and/or the dissolution of the pigment in the liquid enamel cannot be completely prevented. Consequently, the same pigment can produce different colours in different enamels.⁵ The blue colour of the ceramic enamel, containing the cobalt-based ceramic pigments, does not come from only the pigment crystals dispersed in the enamel, but also from cobalt ions dissolved in the enamel.

CoAl₂O₄ powders are often prepared by mixing the corresponding oxides, followed by a calcination step.⁶ Recently, wet-chemical techniques have been applied to prepare CoAl₂O₄ spinel such as chemical co-precipitation,⁷ sol-gel,⁸ polymeric precursor⁹ and hydrothermal treatment.^{10,11} They have led to the development of the pigment-grade CoAl₂O₄ spinel characterized by a fine particle size and uniform distribution.

Molten salts have been reported to be one of the simplest means to prepare pure and stoichiometric powders of multicomponent oxides.^{12,13} When starting materials are mainly simple oxides, but also transition metal carbonates, sulfates, hydroxides or oxyhydroxides, the molten salts acting as flux are often constituted by alkali-metal chlorides, sulfates or hydroxides and reactions are carried out at high temperatures in the range 800–1200 °C. Recent papers give evidence of the interest of this technique for the preparation of various simple or multicomponent oxides: α -alumina,¹⁴ mullite,¹⁵ barium-zinc niobates and tantalates,¹⁶ barium-strontium niobates,¹⁷ lithium nickel manganites,¹⁸ hexagonal barium-cobalt ferrites,¹⁹ anisotropic bismuth titanate.²⁰ The metal sources (simple oxides or salts), are weakly dissolved in the molten flux and the precipitation of the final mixed oxide shifts the dissolution equilibrium until complete transformation. Thus the mixed oxides can be obtained at temperatures a few hundred degrees lower than that required for solid-state diffusion reactions and with shorter thermal treatment durations.

The synthesis temperature can be decreased up to 450–500 °C on the condition to involve the molten salt in a chemical reaction. To kinds of reaction have to be considered:

- A first kind of reaction is that between transition metal salts and a molten medium constituted of alkali-metal oxoalts. Finely divided yttria stabilized zirconia was obtained by simultaneous reaction of zirconium oxychloride and yttrium chloride with molten alkali-metal nitrates (mixture NaNO₃–KNO₃) at 450 °C for a few hours.^{21,22} The oxoanion, NO₃[–] in this case, reacts as a Lux-Flood base, i.e. donor of oxide anion O^{2–}, whereas the transition metal cations, ZrO²⁺ and Y³⁺ in this case, react as a Lux-Flood acid, i.e. acceptor of O^{2–}. Other simple or mixed oxides were also prepared: TiO₂ anatase,²³ CeO₂,²⁴ 3 mol% Y₂O₃–HfO₂,²⁵ PbTiO₃,²⁶ Al₂O₃–ZrO₂ dispersions.²⁷ For the synthesis of cobalt aluminate CoAl₂O₄, the reactions of CoCl₂ and AlCl₃ towards alkali-metal nitrates, at 450 °C for a few hours, does not lead directly to CoAl₂O₄ but to the precipitation of an intimate mixture of the oxides Co₃O₄ and γ -Al₂O₃ which is then calcined at 1000 °C at a rate of 180 °C h^{–1} without any dwell to give CoAl₂O₄.²⁸

- A second kind of reaction is that of alkali-metal mixed oxides toward molten chlorides containing divalent metal cations. Various divalent metal mixed oxides were prepared in this way such as: M(II)TiO₃, M(II)SnO₃, M(II)Fe₂O₄, M(II)Cr₂O₄, MnP₂O₇, BaO–16/3Fe₂O₃.²⁹

The present paper is concerned with the preparation of cobalt aluminate, involving this second kind of reaction in molten salts.

2. Experimental

2.1. Chemical reagents

The starting materials were reagent grade aluminium nitrate Al(NO₃)₃·9H₂O (Acros), γ -alumina Al₂O₃ (Aldrich) and lithium carbonate Li₂CO₃ (Merck), for the preparation of lithium aluminate LiAlO₂, cobalt chloride CoCl₂·6H₂O and potassium chloride KCl for the preparation of the molten medium.

2.2. Synthesis procedures

Cobalt aluminate CoAl₂O₄ was prepared by reaction between solid lithium aluminate LiAlO₂ and molten cobalt potassium chloride.

2.2.1. Synthesis of LiAlO₂

The XRD analysis evidencing the presence of non-negligible amount of LiAl₅O₈ beside γ -LiAlO₂ in the commercial lithium aluminate (reagent grade Aldrich), this starting material was prepared by solid-state diffusion reactions. Intimate mixtures, with molar ratio Li/Al = 1, of either Li₂CO₃ and γ -Al₂O₃ or Li₂CO₃ and Al(NO₃)₃ powders were prepared by dry ball milling in an agate container for 1 h. For the second mixture, the nano-hydrated aluminium nitrate was previously oven-dried at 100 °C for 12 h. Then the mixtures are introduced in alumina crucibles and calcined inside a muffle furnace, under static air, heating at a rate of 180 °C h^{–1} and maintaining a dwell at the chosen reaction temperature for various times.

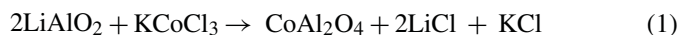
2.2.2. Preparation of the chloride molten medium

In order to obtain a chloride medium containing Co²⁺ ions with a melting point lower than that of CoCl₂ (724 °C), the double chloride KCoCl₃ was chosen. It is a definite compound in the binary phase diagram exhibiting a non-congruent melting at 362 °C. KCl and CoCl₂·6H₂O in equimolar ratio were quickly mixed, by means of a spatula, in a pyrex container. The mixture was oven-dried at 150 °C for 12 h under air and then melted by heating at 400 °C under nitrogen flow (rate 180 °C h^{–1}, dwell for 15 min) and cooled at room temperature for obtaining the compound KCoCl₃. The solidified block was milled (agate balls and container) for 1 h and finally the powder was oven-dried at 100 °C for 1 h and kept inside a closed glass vessel.

2.2.3. Preparation of CoAl₂O₄

Cobalt aluminate was prepared from a mixture KCoCl₃/LiAlO₂ in the molar ratio 2.5, i.e. five times the

stoichiometric ratio, considering that the chemical reaction occurs according to Eq. (1).



The reagents were quickly blended by rotating movement in a closed bottle, then poured in the pyrex reaction tube of a vertical reactor described elsewhere.³⁰ The reaction mixture was heated at a rate of 150°C h^{-1} and the reaction temperature was set either at 450°C or at 500°C , holding a dwell for 12 h. The thermal treatment was performed under nitrogen flow (121 h^{-1}) so as to avoid the partial oxidation of the excess of KCoCl_3 to form the oxide Co_3O_4 . The exhausted gasses were bubbled inside a sodium hydroxide solution. After cooling, the water insoluble oxide phase formed, CoAl_2O_4 , was separated from the excess of chlorides by water extraction followed by multi-step water washing until no chloride ion was detected by AgCl precipitation.

2.3. Powder characterization

The oxide powders obtained were characterized by X-ray diffraction (XRD, Siemens D501 diffractometer for powders, $\lambda_{\text{Cu K}\alpha} = 1.5418 \text{ \AA}$), Fourier transformed infrared spectroscopy (FTIR, PerkinElmer 1760), scanning and transmission electron microscopies (SEM: JEOL JSM 6400 provided with energy dispersion X-EDS; TEM: JEOL 2010), specific surface area measurements by nitrogen adsorption (Micrometrics Accusorb 2100 E, defined by BET method), size distribution analysis by laser deviation (Malvern mastersizer 2000S), chemical analysis by inductively coupled plasma spectroscopy (ICP Jobin Yvon 24) and thermogravimetric and differential thermal analyses (TGA-DTA, Setaram TAG 24 thermoanalyser).

Diffuse reflection was measured with a lambda 19 PerkinElmer spectrometer equipped with an integrating sphere and monochromators for incoming as well as reflected light. Spectra were recorded in the range 200–800 nm. In addition $L^* a^* b^*$ colour parameters were determined with a Spectraflash SF 300, using standard lighting D65 and an aperture of 10° and following the CIE- $L^* a^* b^*$ colourimetric method recommended by the CIE (Commission Internationale de l'Eclairage).³¹ L^* , is the brightness axis graduated from 0 (black) to 100 (white). It is perpendicular to the chromatic plane defined by axis a^* (green (–) to red (+)) and axis b^* (blue (–) to yellow (+)).

3. Results

3.1. Characterization of LiAlO_2 powders

The X-ray diffraction pattern of the powder obtained by the calcination of the equimolar mixture $\text{Li}_2\text{CO}_3\text{-}\gamma\text{Al}_2\text{O}_3$ at 1000°C for 4 h showed the presence of $\alpha\text{Al}_2\text{O}_3$ and LiAl_5O_8 beside γLiAlO_2 . The increase of the calcination time, up to twelve hours, decreased the proportion of $\alpha\text{Al}_2\text{O}_3$ and LiAl_5O_8 in the γLiAlO_2 powder, but both phases could still be identified on the XRD pattern.

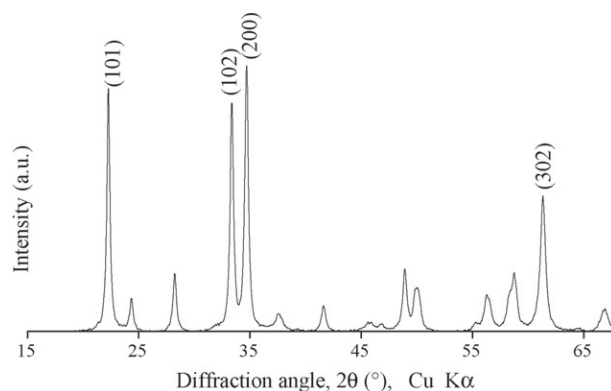


Fig. 1. XRD pattern of LiAlO_2 obtained.

The mixture $\text{Li}_2\text{CO}_3\text{-}2\text{Al}(\text{NO}_3)_3$ was more reactive. Indeed, from its thermogravimetric analysis, the end of the weight loss was located below 600°C . Investigating by XRD the phase composition of the powders obtained by thermal treatment of the reaction mixture at temperatures ranging from 600 to 1000°C (heating rate 180°C h^{-1} , dwell for 30 min), it was shown that the powders containing only the γLiAlO_2 phase were obtained at 900°C (Fig. 1). At lower temperatures, α and βLiAlO_2 were identified beside γLiAlO_2 . At higher temperatures the phase LiAl_5O_8 was revealed beside γLiAlO_2 .³⁰

Consequently the γLiAlO_2 , obtained from $\text{Li}_2\text{CO}_3 + 2\text{Al}(\text{NO}_3)_3$ mixtures calcined at 900°C for 30 min, were selected for the preparation of cobalt aluminate. The absence of LiAl_5O_8 was corroborated by FTIR spectroscopy. The spectra (Fig. 2) exhibited the bands at 804 , 645 , 540 , 513 and 445 cm^{-1} characteristic of the vibrations in the γLiAlO_2 molecule, whereas bands at 490 , 610 , 680 and 725 cm^{-1} characteristic of LiAl_5O_8 were not seen. The chemical analysis, giving a molar ratio Li/Al close to one (0.99 ± 0.02), corroborated also that the phase LiAl_5O_8 was not present in significant proportion in the LiAlO_2 obtained. The granulometric distribution curve evidenced a bimodal repartition with two populations centered around respectively 9 and $65\text{ }\mu\text{m}$ (Fig. 3). The SEM micrograph showed that the particles were agglomerates constituted of grains with sizes in the range $100\text{--}300\text{ nm}$ (Fig. 4). The BET specific surface areas and the densities determined by He pycnometry were respectively close to $30\text{ m}^2\text{ g}^{-1}$ and 2.64 .

Such obtained γLiAlO_2 powders were reacted, without milling, with molten KCoCl_3 in order to prepare CoAl_2O_4 .

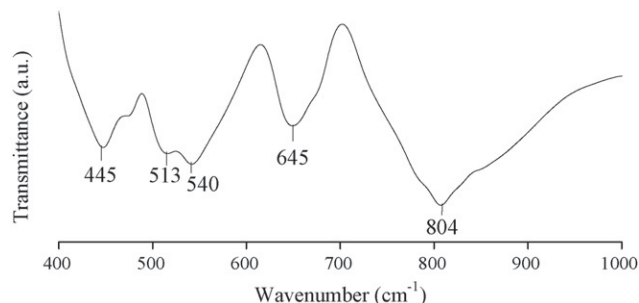


Fig. 2. Infrared spectra of LiAlO_2 obtained.

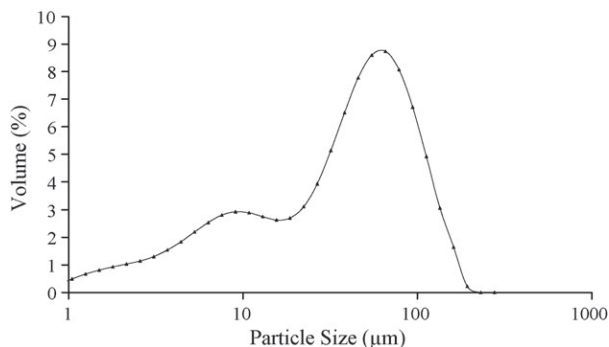


Fig. 3. Size distribution curve of LiAlO₂ powder.

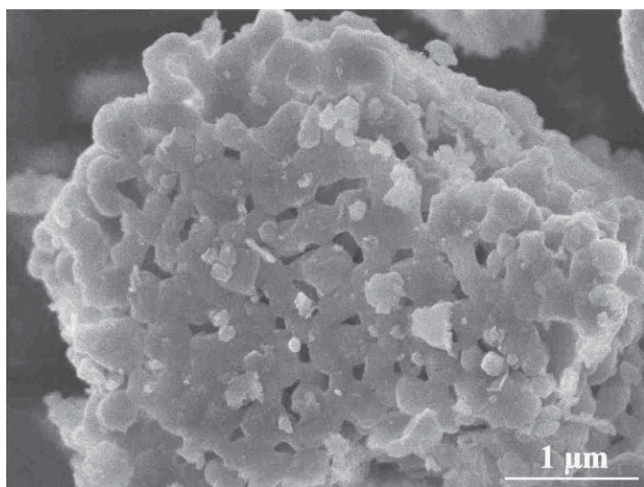


Fig. 4. SEM micrograph of an agglomerate of LiAlO₂ powder.

3.2. Characterization of CoAl₂O₄ powders

Beside the peaks of the spinel phase CoAl₂O₄ (JCPDS file no. 82-2252), the XRD pattern of the powder prepared by thermal treatment at 450 °C for 12 h exhibits small peaks showing the presence of a small proportion of γ LiAlO₂ in the CoAl₂O₄ powder (Fig. 5). These peaks disappeared when the powder was annealed at 1000 and 1200 °C. They did not appear in the XRD

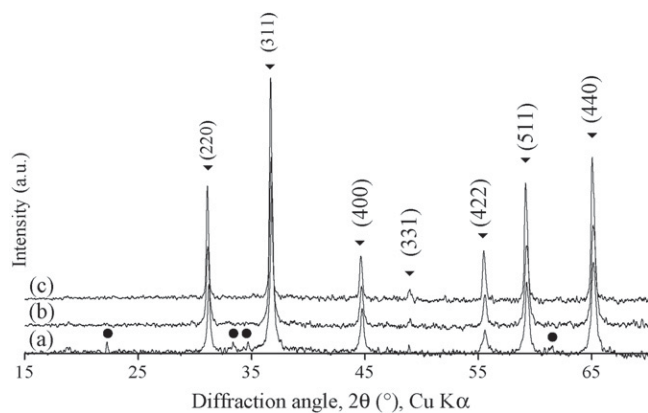


Fig. 5. XRD pattern of CoAl₂O₄ powder prepared by thermal treatment at 450 °C for 12 h: as prepared (a), annealed at 1000 °C (b), and annealed at 1200 °C (c).

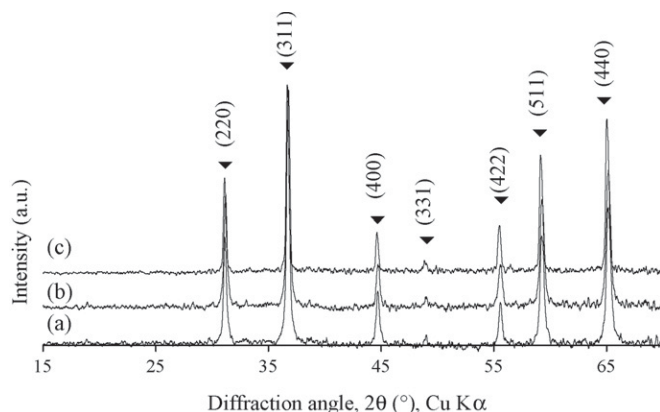


Fig. 6. XRD pattern of CoAl₂O₄ powder prepared by thermal treatment at 500 °C for 12 h: as prepared (a), annealed at 1000 °C (b), and annealed at 1000 °C (c).

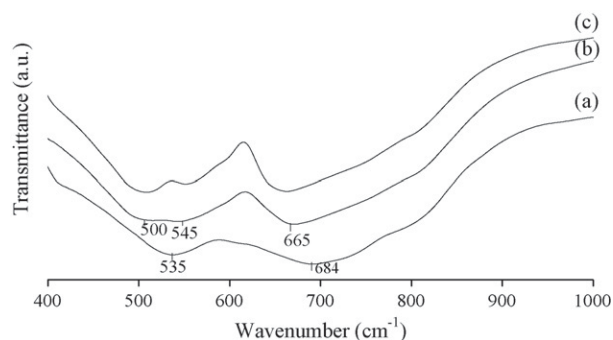


Fig. 7. FTIR spectrum of CoAl₂O₄ powder prepared at 450 °C for 12 h: as prepared (a), annealed at 1000 °C (b), and annealed at 1200 °C (c).

pattern of the powder prepared by thermal treatment at 500 °C for 12 h (Fig. 6). For both preparation temperatures, the patterns of the powder annealed at 1000 and 1200 °C showed only the CoAl₂O₄ spinel phase peaks proving the thermal stability of the powders obtained.

In the infrared spectrum of the CoAl₂O₄ powder prepared at 450 °C, the band at 535 cm⁻¹ and the shoulder at 810 cm⁻¹ could be attributed to the presence of γ LiAlO₂ beside CoAl₂O₄ (Fig. 7). Their intensity strongly decreased in the spectra of powders annealed at 1000 and 1200 °C. Yet, the shoulder at 810 cm⁻¹ remained visible. This shoulder was also present in the IR spectrum of the CoAl₂O₄ powder prepared at 500 °C, but the band at 535 cm⁻¹ was no more visible, probably hid-

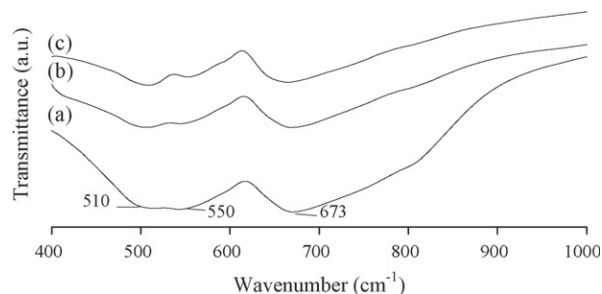


Fig. 8. FTIR spectrum of CoAl₂O₄ powder prepared at 500 °C for 12 h: as prepared (a), annealed at 1000 °C (b), and annealed at 1200 °C (c).

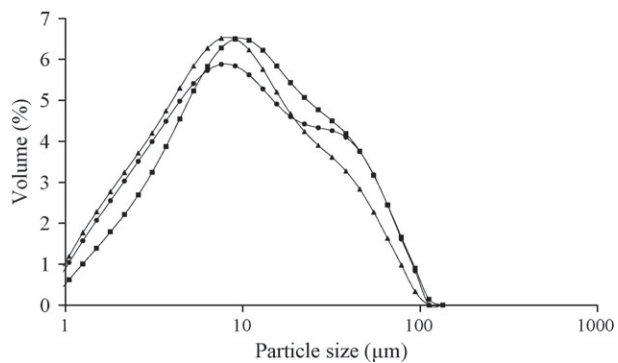


Fig. 9. Size distribution curve of CoAl_2O_4 prepared at 450°C : as prepared (●), annealed at 1000°C (■), and annealed at 1200°C (▲).

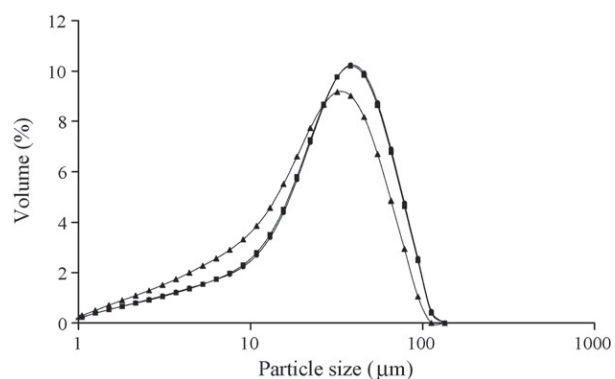


Fig. 10. Size distribution curve of CoAl_2O_4 prepared at 500°C : as prepared (●), annealed at 1000°C (■), and annealed at 1200°C (▲).

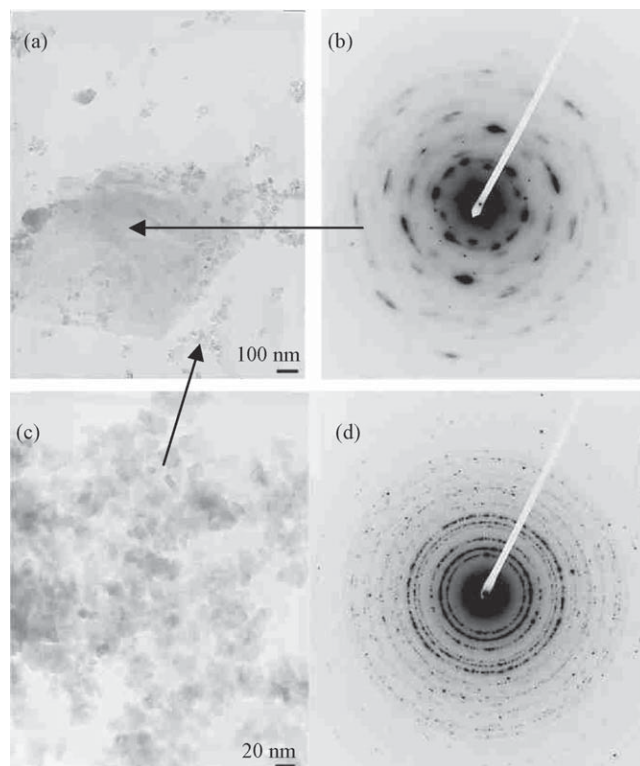


Fig. 11. TEM micrographs and electron diffraction pattern of CoAl_2O_4 prepared at 450°C : γLiAlO_2 platelet (a) and its electron diffraction pattern (b), CoAl_2O_4 agglomerates (c) and their electron diffraction pattern (d).

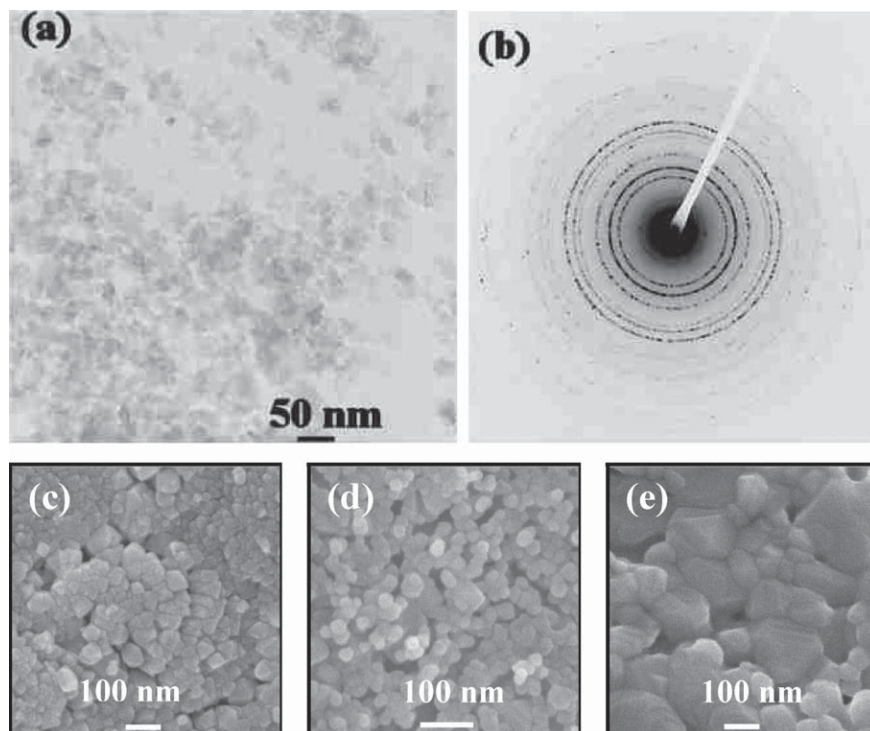


Fig. 12. TEM micrograph (a) and electron diffraction pattern (b) of CoAl_2O_4 prepared at 500°C , SEM micrographs of CoAl_2O_4 prepared at 500°C , calcined at 1000°C (d) and 1200°C (e).

den by the increase of the intensity of bands of CoAl_2O_4 at 510 and 550 cm^{-1} (Fig. 8). The shoulder vanished when the powder was annealed at 1000 and $1200\text{ }^\circ\text{C}$ and the spectra exhibit only the bands at 510, 550 and 673 cm^{-1} characteristic of the spinel CoAl_2O_4 phase.

For both powders, the granulometric distribution was not significantly affected by the annealing at 1000 and $1200\text{ }^\circ\text{C}$ (Figs. 9 and 10). The CoAl_2O_4 powder prepared at $450\text{ }^\circ\text{C}$ was characterized by a bimodal population with sizes centered around 10 and $40\text{ }\mu\text{m}$ respectively, the one prepared at $500\text{ }^\circ\text{C}$ by a monomodal distribution centered around $35\text{ }\mu\text{m}$. The specific surface areas reached 54 and $62\text{ m}^2\text{ g}^{-1}$ respectively for the powders prepared at 450 and $500\text{ }^\circ\text{C}$, 12 and $18\text{ m}^2\text{ g}^{-1}$ after annealing at $1000\text{ }^\circ\text{C}$, 3 and $2.5\text{ m}^2\text{ g}^{-1}$ after annealing at $1200\text{ }^\circ\text{C}$. The examination of powders, by transmission electron microscopy and electron diffraction, corroborated the presence of $\gamma\text{-LiAlO}_2$ in the CoAl_2O_4 powder prepared at $450\text{ }^\circ\text{C}$ (Fig. 11). The CoAl_2O_4 phase was constituted of agglomerates of more or less spherical elementary grains with sizes in the range 20–50 nm, meanwhile $\gamma\text{-LiAlO}_2$ appeared in the form of micronic platelets. In the powder prepared at $500\text{ }^\circ\text{C}$, only grains of CoAl_2O_4 with sizes in the same range were observed (Fig. 12).

4. Characterization of the colour of CoAl_2O_4 powders prepared at $500\text{ }^\circ\text{C}$

The UV-visible spectrum of annealed and non-annealed powders exhibits a minimum of absorption near 500 nm and a maximum of adsorption from about 540 to 640 nm (Fig. 13). These values are in agreement with those published for CoAl_2O_4 powders prepared by thermal treatment at $1000\text{ }^\circ\text{C}$ of mixtures of Co_3O_4 and $\gamma\text{-Al}_2\text{O}_3$ obtained by reaction of cobalt and aluminium chlorides in molten alkali nitrates²⁸ or of mixtures of cobalt acetate and alumina³² or by the polyol method.³³

The blue pigment prepared in molten KCoCl_3 medium and a commercial pigment (Union Cerame K4618) was comparatively tested for industrial tiles colouring. The XRD pattern of the commercial pigment exhibited very narrow peaks identifying a very well crystallized CoAl_2O_4 spinel phase.³⁰ It was not known how the commercial powder was prepared, but its observation by FEG. SEM revealed a coarse morphology (Fig. 14) very different

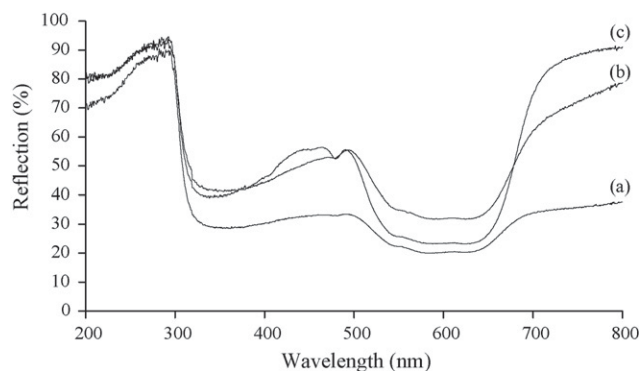


Fig. 13. UV-visible spectrum of CoAl_2O_4 prepared at $500\text{ }^\circ\text{C}$: as prepared (a), annealed at $1000\text{ }^\circ\text{C}$ (b), and annealed at $1200\text{ }^\circ\text{C}$ (c).

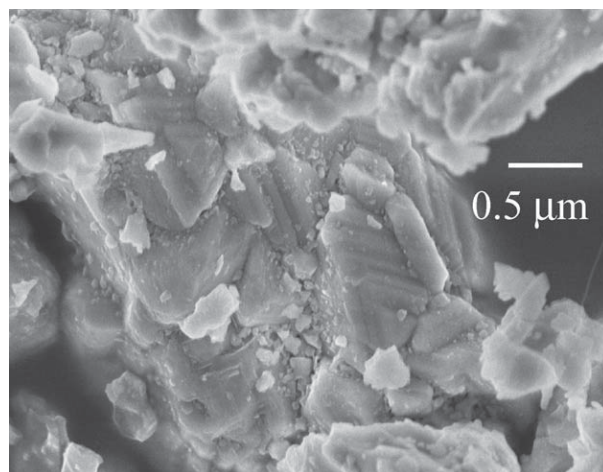


Fig. 14. SEM micrograph of commercial CoAl_2O_4 powder.

Table 1
Elementary composition of the transparent glaze HF731 for bifiring (M = alkaline-metal)

Oxides	M_2O	(Ca/Mg)O	ZnO	PbO	Al_2O_3	B_2O_3	SiO_2
wt%	<15	<15	<15	<15	<15	<15	>45

of that of the powder synthesized by reaction in molten KCoCl_3 (Fig. 12).

Both pigments were incorporated, in a weight ratio from 0.5 to 4.0% in a fast monofiring glaze, transparent and crystallized at the enamel firing temperature ($1075\text{ }^\circ\text{C}$). Yet, a short firing cycle for 37 min eliminated the defects. Some information about the elements entering in the composition of the glaze HF731 are given in Table 1. The changes of the colour of the enameled tiles, due to the variation of the pigment amount, were well evidenced by the evolution of colourimetric parameters (Table 2). It was noticeable that the discrepancy between the values obtained with respectively, the CoAl_2O_4 powder prepared in molten salt medium and the commercial one, was all the more significant as the amount of pigment in the enamel increased. Up to amount of 2 wt%, the L^* values are very similar; beyond, the experimental pigment exhibited a brightness somewhat higher than that of the commercial one. As for the chromatic parameters, a value a^* slightly lower and a value b^* slightly higher for experimental than for the commercial powder, indicated respectively a decrease in the degree of green and blue (Fig. 15).

Table 2
Influence of the pigment wt% on the colorimetric parameters of tiles enameled with the molten salt prepared pigment and discrepancies with the values obtained with the commercial pigment

wt%	L^*	a^*	b^*	ΔL	Δa	Δb	ΔE
0	88.95	0.43	3.25				
0.5	63.68	1.48	-21.75	0.83	-1.53	3.2	3.64
1	51.99	4.45	-28.61	-0.63	-2.19	3.38	4.07
2	41.11	6.7	-28.26	0.9	-5.04	6.18	8.02
3	38.49	5.44	-24.51	4.77	-7.7	9.61	13.20
4	37.65	4.81	-22.85	5.66	-6.93	6.51	11.06

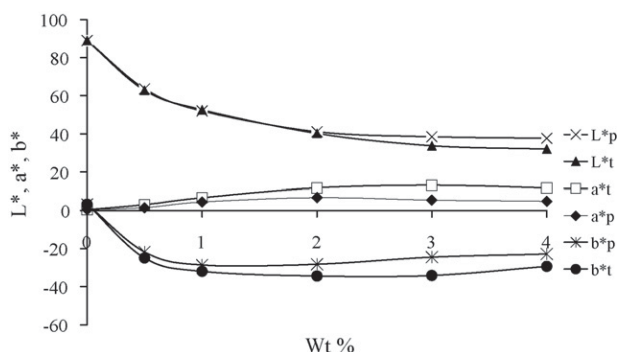


Fig. 15. Influence of the amount of pigment in the enamel on the parameters L^* , a^* and b^* of industrial tiles: (p) prepared pigment; (t) commercial pigment.

5. Discussion and conclusion

CoAl_2O_4 powders have been prepared directly by reaction of solid γLiAlO_2 with an excess of molten KCoCl_3 at 450 and 500 °C for 12 h. γLiAlO_2 is not detected in the ones obtained at 500 °C. Chemical analysis and EDX measurements show, for the latter powders, a good homogeneity of chemical composition with molar Al/Co ratio very close to 2 (1.99 ± 0.02). Their morphology is in the form of agglomerates with sizes regularly distributed mainly in the range 10–100 μm . Each agglomerate is constituted of more or less spherical nanometric crystallites (20–50 nm in diameter).

The chemical composition homogeneity is attributed to the reaction mechanism which is a double decomposition process between the solid γLiAlO_2 and the molten chloride medium containing Co^{2+} ions. γLiAlO_2 is partially dissolved (even if the solubility is very low) in the molten medium according to reaction (2). The molten KCoCl_3 is dissociated via reactions (3) and (4) and CoAl_2O_4 is precipitated via reaction (5). The precipitation shifts the dissolution equilibrium until complete transformation.



Owing to their regular granulometric distribution with nearly spherical nano-sized crystallites, the molten salt prepared CoAl_2O_4 powders are easily dispersed in the glaze and lead to very good quality colouring after enameling.

The reaction of alkali-metal aluminates with a chloride molten medium containing Co^{2+} ions appears as a simple and reproducible method for preparing CoAl_2O_4 -based pigments suitable for the colouring of tiles.

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