Synthesis of CoAl$_2$O$_4$ by double decomposition reaction between LiAlO$_2$ and molten KCoCl$_3$

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Abstract

Submicronic CoAl$_2$O$_4$ 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$_2$O$_4$ 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.
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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$_2$O$_4$, which has the normal spinel structure, was prepared in order to obtain a blue more intense and brilliant than that produced by Co$_2$SiO$_4$.[3] Indeed, in the normal spinel structure stable at high temperature, Co and Al are respectively tetrahedrally and octahedrally coordinated, whereas in Co$_2$SiO$_4$, 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

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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.

$CoAl_2O_4$ powders are often prepared by mixing the corresponding oxides, followed by a calcination step.[6] Recently, wet-chemical techniques have been applied to prepare $CoAl_2O_4$ spinel such as chemical co-precipitation,[7] sol–gel,[8] polymeric precursor[9] and hydrothermal treatment.[10,11] They have led to the development of the pigment-grade $CoAl_2O_4$ 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 oxosalts. Finely divided yttria stabilized zirconia was obtained by simultaneous reaction of zirconium oxychloride and yttrium chloride with molten alkali-metal nitrates (mixture $NaNO_3$–KNO_3) at 450 °C for a few hours.[21,22] The oxoanion, NO_3^- in this case, reacts as a Lux-Flood base, i.e. donor of oxide anion O^{2-}, whereas the transition metal cations, ZrO^{2+} and Y^{3+} in this case, react as a Lux-Flood acid, i.e. acceptor of O^{2-}. Other simple or mixed oxides were also prepared: TiO_2 anatase,[23] CeO_2,[24] 3 mol%Y_2O_3–HfO_2,[25] $PbTiO_3$,[26] Al_2O_3–ZrO_2 dispersions.[27] For the synthesis of cobalt aluminate $CoAl_2O_4$, the reactions of $CoCl_2$ and $AlCl_3$ towards alkali-metal nitrates, at 450 °C for a few hours, does not lead directly to $CoAl_2O_4$ but to the precipitation of an intimate mixture of the oxides Co_3O_4 and γAl_2O_3 which is then calcined at 1000 °C at a rate of 180 °C h^{-1} without any dwell to give $CoAl_2O_4$.[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: $M(II)TiO_3$, $M(II)SnO_3$, $M(II)Fe_2O_4$, $M(II)Cr_2O_4$, MnP_2O_7, $BaO–16/3Fe_2O_3$.[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 $Al(NO_3)_3\cdot9H_2O$ (Acros), γ-alumina Al_2O_3 (Aldrich) and lithium carbonate Li_2CO_3 (Merck), for the preparation of lithium aluminate $LiAlO_2$, cobalt chloride $CoCl_2\cdot6H_2O$ and potassium chloride KCl for the preparation of the molten medium.

2.2. Synthesis procedures

Cobalt aluminate $CoAl_2O_4$ was prepared by reaction between solid lithium aluminate $LiAlO_2$ and molten cobalt potassium chloride.

2.2.1. Synthesis of $LiAlO_2$

The XRD analysis evidencing the presence of non-negligible amount of $LiAl_5O_8$ beside $\gamma LiAlO_2$ 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 Li_2CO_3 and γAl_2O_3 or Li_2CO_3 and $Al(NO_3)_3$ powders were prepared by dry ball milling in an agate container for 1 h. For the second mixture, the nanohydrated 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 Co^{2+} ions with a melting point lower than that of $CoCl_2$ (724 °C), the double chloride $KCoCl_3$ was chosen. It is a definite compound in the binary phase diagram exhibiting a non-congruent melting at 362 °C. KCl and $CoCl_2\cdot6H_2O$ in equimolar ratio were quickly mixed, by means of a spatula, in a pyrex container. The mixture was ovendried 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 $KCoCl_3$. The solidified block was milled (agate balls and container) for 1 h and finally the powder was ovendried at 100 °C for 1 h and kept inside a closed glass vessel.

2.2.3. Preparation of $CoAl_2O_4$

Cobalt aluminate was prepared from a mixture $KCoCl_3$/$LiAlO_2$ in the molar ratio 2.5, i.e. five times the

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

$$2LiAlO_2 + KCoCl_3 \rightarrow CoAl_2O_4 + 2LiCl + KCl \quad (1)$$
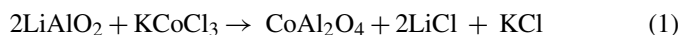
The reagents were quickly blended by rotating movement in a closed bottle, then poured in the pyrex reaction tube of a vertical reactor described elsewhere.[30] The reaction mixture was heated at a rate of $150 \,^{\circ}C \, h^{-1}$ and the reaction temperature was set either at 450 or at $500 \,^{\circ}C$, holding a dwell for 12 h. The thermal treatment was performed under nitrogen flow ($12 l h^{-1}$) 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, $\lambda_{Cu\,K\alpha} = 1.5418 \, \text{Å}$), 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 (Micrometics 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 O (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 Li_2CO_3–γAl_2O_3 at $1000 \,^{\circ}C$ for 4 h showed the presence of αAl_2O_3 and $LiAl_5O_8$ beside $\gamma LiAlO_2$. The increase of the calcination time, up to twelve hours, decreased the proportion of αAl_2O_3 and $LiAl_5O_8$ in the $\gamma LiAlO_2$ powder, but both phases could still be identified on the XRD pattern.
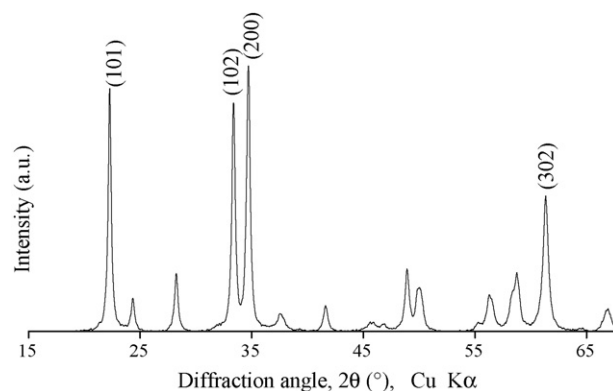

Fig. 1. XRD pattern of LiAlO_2 obtained.

The mixture Li_2CO_3–$2Al(NO_3)_3$ was more reactive. Indeed, from its thermogravimetrical analysis, the end of the weight loss was located below $600 \,^{\circ}C$. Investigating by XRD the phase composition of the powders obtained by thermal treatment of the reaction mixture at temperatures ranging from 600 to $1000 \,^{\circ}C$ (heating rate $180 \,^{\circ}C \, h^{-1}$, dwell for 30 min), it was shown that the powders containing only the $\gamma LiAlO_2$ phase were obtained at $900 \,^{\circ}C$ (Fig. 1). At lower temperatures, α and $\beta LiAlO_2$ were identified beside $\gamma LiAlO_2$. At higher temperatures the phase $LiAl_5O_8$ was revealed beside $\gamma LiAlO_2$.[30]

Consequently the $\gamma LiAlO_2$, obtained from $Li_2CO_3 + 2Al(NO_3)_3$ mixtures calcined at $900 \,^{\circ}C$ 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 $\gamma LiAlO_2$ 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 μm (Fig. 3). The SEM micrograph showed that the particles were agglomerates constituted of grains with sizes in the range 100–300 nm (Fig. 4). The BET specific surface areas and the densities determined by He picnometry were respectively close to $30 \, m^2 \, g^{-1}$ and 2.64.

Such obtained $\gamma LiAlO_2$ powders were reacted, without milling, with molten $KCoCl_3$ in order to prepare $CoAl_2O_4$.
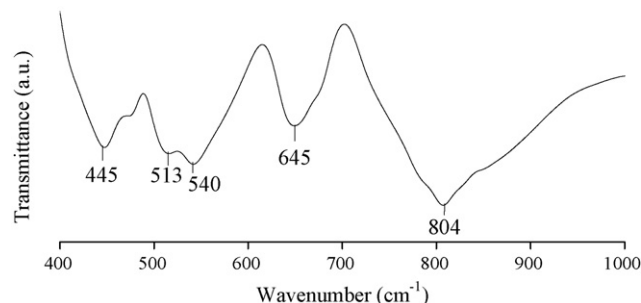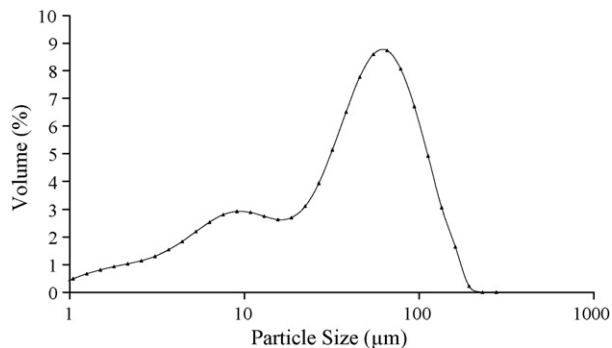

Fig. 2. Infrared spectra of LiAlO_2 obtained.
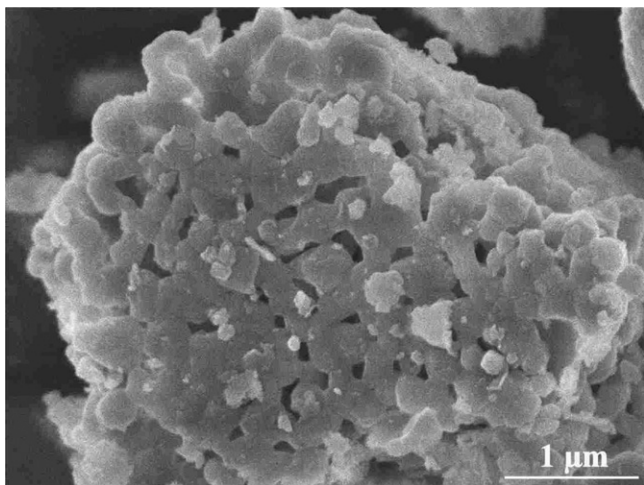
Fig. 3. Size distribution curve of LiAlO$_2$ powder.

Fig. 4. SEM micrograph of an agglomerate of LiAlO$_2$ powder.

3.2. Characterization of CoAl$_2$O$_4$ powders

Beside the peaks of the spinel phase CoAl$_2$O$_4$ (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 γLiAlO$_2$ in the CoAl$_2$O$_4$ powder (Fig. 5). These peaks disappeared when the powder was annealed at 1000 and 1200 °C. They did not appear in the XRD
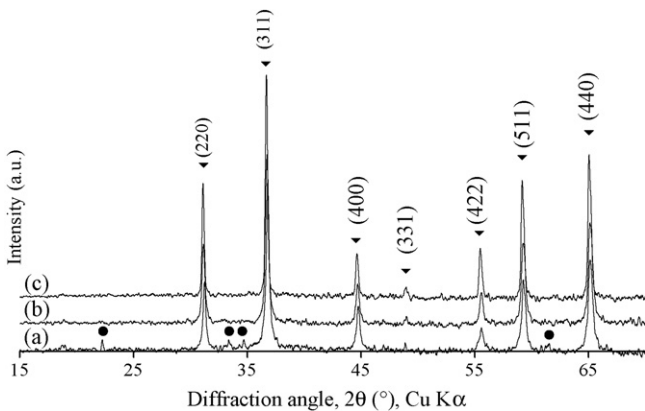

Fig. 5. XRD pattern of CoAl$_2$O$_4$ powder prepared by thermal treatment at 450 °C for 12 h: as prepared (a), annealed at 1000 °C (b), and annealed at 1200 °C (c).
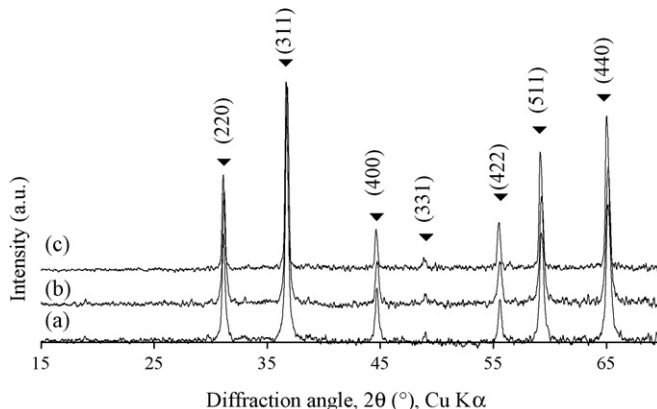

Fig. 6. XRD pattern of CoAl$_2$O$_4$ powder prepared by thermal treatment at 500 °C for 12 h: as prepared (a), annealed at 1000 °C (b), and annealed at 1000 °C (c).
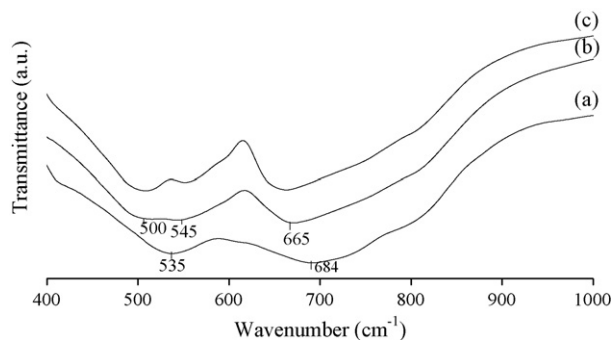

Fig. 7. FTIR spectrum of CoAl$_2$O$_4$ powder prepared at 450 °C for 12 h: as prepared (a), annealed at 1000 °C (b), and annealed at 1200 °C (c).

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 1200C showed only the CoAl$_2$O$_4$ spinel phase peaks proving the thermal stability of the powders obtained.

In the infrared spectrum of the CoAl$_2$O$_4$ 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 γLiAlO$_2$ beside CoAl$_2$O$_4$ (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 CoAl$_2$O$_4$ powder prepared at 500 °C, but the band at 535 cm^{-1} was no more visible, probably hid-
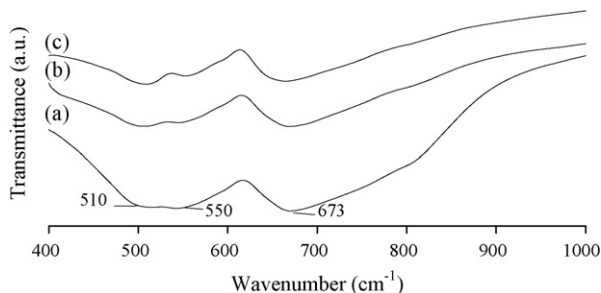

Fig. 8. FTIR spectrum of CoAl$_2$O$_4$ powder prepared at 500 °C for 12 h: as prepared (a), annealed at 1000 °C (b), and annealed at 1200 °C (c).
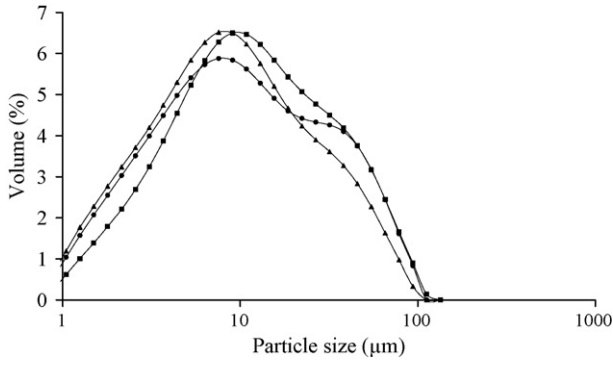
Fig. 9. Size distribution curve of $CoAl_2O_4$ prepared at 450 °C: as prepared (●), annealed at 1000 °C (■), and annealed at 1200 °C (▲).
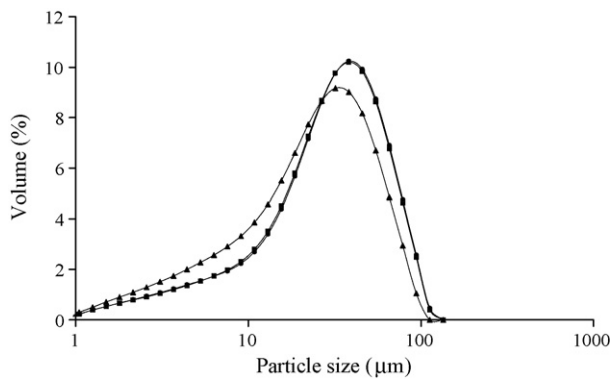

Fig. 10. Size distribution curve of $CoAl_2O_4$ prepared at 500 °C: as prepared (●), annealed at 1000 °C (■), and annealed at 1200 °C (▲).
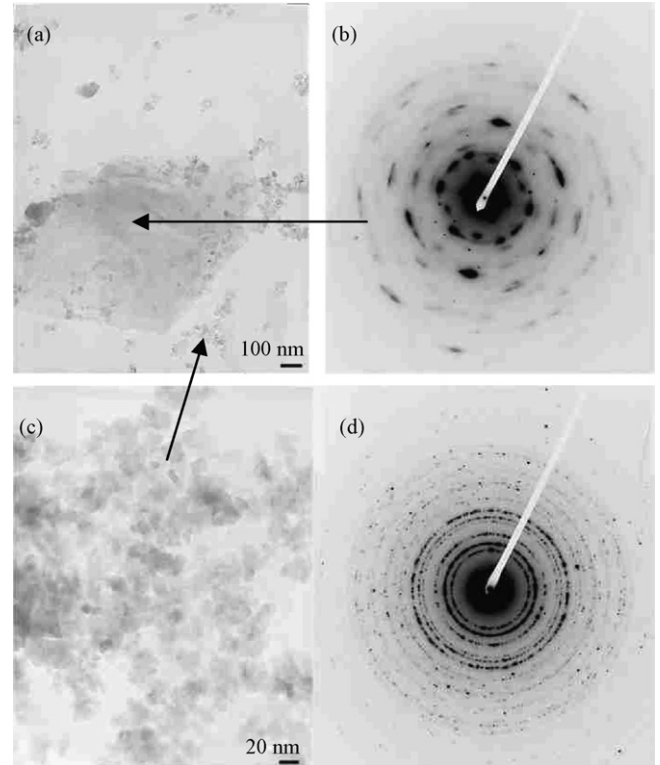
Fig. 11. TEM micrographs and electron diffraction pattern of $CoAl_2O_4$ prepared at 450 °C: γLiAl0$_2$ platelet (a) and its electron diffraction pattern (b), $CoAl_2O_4$ agglomerates (c) and their electron diffraction pattern (d).
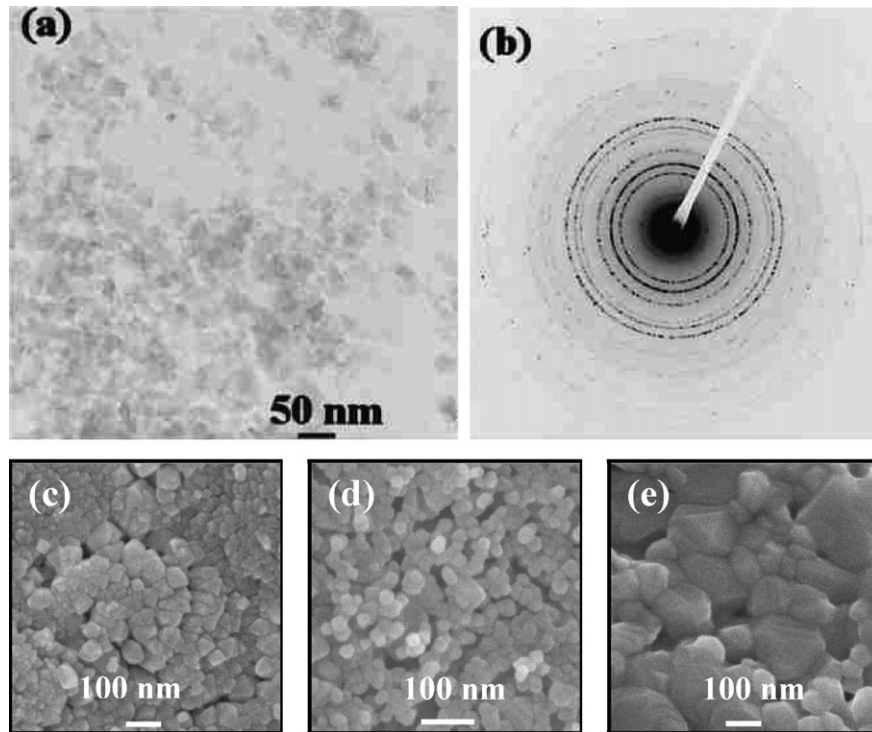

Fig. 12. TEM micrograph (a) and electron diffraction pattern (b) of $CoAl_2O_4$ prepared at 500 °C, SEM micrographs of $CoAl_2O_4$ prepared at 500 °C (c), calcined at 1000 °C (d) and 1200 °C (e).

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 °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 °C (Figs. 9 and 10). The $CoAl_2O_4$ powder prepared at 450 °C was characterized by a bimodal population with sizes centered around 10 and 40 μm respectively, the one prepared at 500 °C by a monomodal distribution centered around 35 μm. The specific surface arias reached 54 and 62 m^2 g^{-1} respectively for the powders prepared at 450 and 500 °C, 12 and 18 m^2 g^{-1} after annealing at 1000 °C, 3 and 2.5 m^2 g^{-1} after annealing at 1200 °C. The examination of powders, by transmission electron microscopy and electron diffraction, corroborated the presence of γLiAlO$_2$ in the $CoAl_2O_4$ powder prepared at 450 °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 γLiAlO$_2$ appeared in the form of micronic platelets. In the powder prepared at 500 °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 °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 °C of mixtures of Co_3O_4 and γAl$_2O_3$ obtained by reaction of cobalt and aluminium chlorides in molten alkali nitrates[28] or of mixtures of cobalt acetate and alumina[32] 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
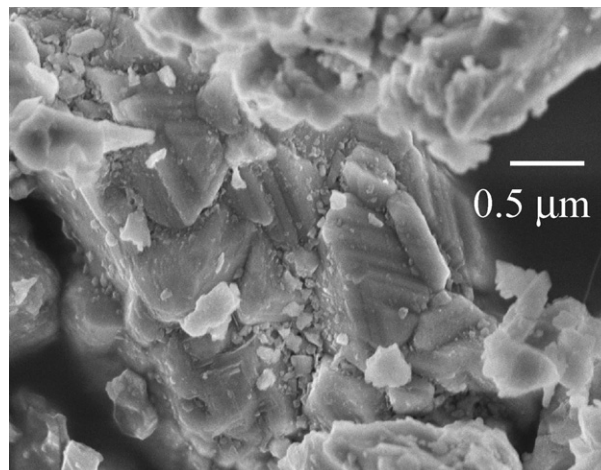

Fig. 14. SEM micrograph of commercial $CoAl_2O_4$ powder.

Table 1
Elementary composition of the transparent glaze HF371 for bifiring (M = alkaline-metal)

Oxides	M$_2$O	(Ca/Mg)O	ZnO	PbO	Al$_2$O$_3$	B$_2$O$_3$	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 °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).
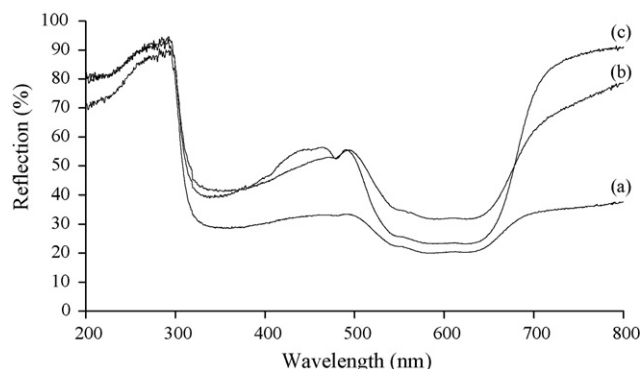

Fig. 13. UV–visible spectrum of $CoAl_2O_4$ prepared at 500 °C: as prepared (a), annealed at 1000 °C (b), and annealed at 1200 °C (c).

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

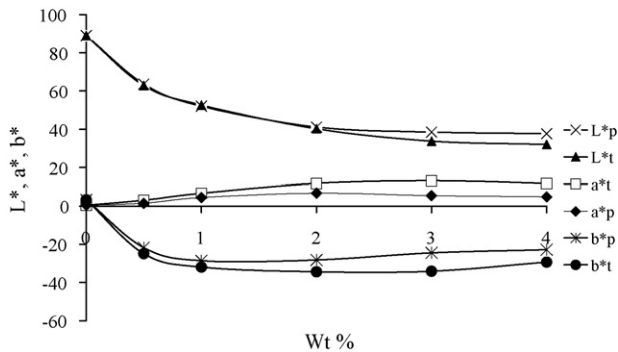| wt%	L^*	a^*	b^*	ΔL	Δa	Δb	ΔE
0	88.95	0.43	3.25				
0.5	63.68	1.48	−21.75	0.83	−1.53	3.2	3.64
1	51.99	4.45	−28.61	−0.63	−2.19	3.38	4.07
2	41.11	6.7	−28.26	0.9	−5.04	6.18	8.02
3	38.49	5.44	−24.51	4.77	−7.7	9.61	13. 20
4	37.65	4.81	−22.85	5.66	−6.93	6.51	11.06

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 $\gamma LiAlO_2$ with an excess of molten $KCoCl_3$ at 450 and 500 °C for 12 h. $\gamma LiAlO_2$ 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 $\gamma LiAlO_2$ and the molten chloride medium containing Co^{2+} ions. $\gamma LiAlO_2$ 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.

$$LiAlO_2 \leftrightarrows Li^+ + AlO_2^- \tag{2}$$

$$KCoCl_3 \rightarrow K^+ + CoCl_3^- \tag{3}$$

$$CoCl_3^- \leftrightarrows Co^{2+} + 3Cl^- \tag{4}$$

$$Co^{2+} + 2AlO_2^- \rightarrow CoAl_2O_4 \tag{5}$$

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.

Acknowledgements

References

1. Bamford, C. R., *Colour Generation and Control in Glass*. Elsevier, Oxford, 1977.
2. Hackman, J. R., Cobalt aluminate blue. In *Processing of the Pigment Handbook*, *vol. 1*, ed. P. A. Lewis. second ed. A Wiley-Interscience Publication, 1988, pp. 389–394.
3. Monari, G. and Manfredi, T., Colouring effects of synthetic inorganic cobalt pigments in fast-fired porcelainises tiles. *Ceram. Eng. Sci. Proc.*, 1996, **17**(1), 167–172.
4. Paul, A. and Douglas, R. W., Optical absorption of divalent cobalt in binary alkali borate glasses and its relation to the basicity of glass. *Phys. Chem. Glasses*, 1968, **9**(1), 21–26.
5. Eppler, D. R. and Eppler, R. A., Relative stability of ceramic pigments. *Ceram. Eng. Sci. Proc.*, 1997, **18**(2), 139–149.
6. Zayat, M. and Levy, D., Blue $CoAl_2O_4$ particles prepared by the sol–gel and citrate-gel methods. *Chem. Mater.*, 2000, **9**, 2763–2769.
7. Bolt, P. H., Habraken, F. H. P. M and Geus, J. W., Formation of nickel, cobalt, copper, and iron aluminates from α- and γ alumina-supported oxides: a comparative study. *J. Solid. State Chem.*, 1998, **135**, 59–69.
8. Chokkaram, S., Srinivasan, R., Milburn, D. R. and Davis, B. H., Conversion of 2-octanol over nickel-alumina, cobalt-alumina, and alumina catalysts. *J. Mol. Catal. A: Chem.*, 1997, **121**, 157–169.
9. Stangar, U. L., Orel, B., Krajnc, M., Korosec, R. C. and Bukovec, P., Sol–gel-derived thin ceramic $CoAl_2O_4$ coatings for optical applications. *Materiali in Thechnologije*, 2002, **36**(6), 387–394.
10. Cho, W. S and Kakihana, M., Crystallization of ceramic pigment $CoAl_2O_4$ nanocrystals from Co–Al metal organic precursor. *J. Alloys Compd.*, 1999, **287**, 87–90.
11. Chen, Z. Z., Shi, E. W., Li, W. J., Zheng, Y. Q., Zhuang, J. Y., Xiao, B. and Tang, L. A., Preparation of nanosized cobalt aluminate powders by a hydrothermal method. *Mater. Sci. Eng.*, 2004, **B107**, 217–223.
12. Chiu, C. C., Li, C. C. and Desu, S. B., Molten salt synthesis of a complex perovskite $Pb(Fe_{0.5}Nb_{0.5})O_3$. *J. Am. Ceram. Soc.*, 1991, **74**, 38–41.
13. Yoon, K. H., Cho, Y. S., Lee, D. H. and Kang, D. H., Powder characteristics of $Pb(Mg_{1/3}Nb_{2/3})O_3$ prepared by molten salt synthesis. *J. Am. Ceram. Soc.*, 1993, **76**, 1373–1376.
14. Jin, X. and Gao, L., Size control of α-Al_2O_3 platelets synthesized in molten Na_2SO_4 flux. *J. Am. Ceram. Soc.*, 2004, **87**(4), 533–540.
15. El Ouatib, R., Guillemet, S., Durand, B., Samdi, A., Er Rakho, L. and Moussa, R., Reactivity of aluminium sulphate and silica in molten alkali-metal sulphates in order to prepare mullite. *J. Eur. Ceram. Soc.*, 2005, **25**, 73–80.
16. Thirumal, M., Jain, P. and Ganguli, A. K., Molten salt synthesis of complex pervskite-related dielectric oxides. *Mater. Chem. Phys.*, 2001, **70**, 7–11.
17. Duran, C., Messing, G. L. and Tralier–Mc Kinstry, S., Molten salt synthesis of anisometric particles in the SrO–Nb_2O_5–BaO system. *Mater. Res. Bull.*, 2004, **39**, 1679–1689.
18. Kim, J. H., Myung, S. T. and Sun, Y. K., Molten salt synthesis of $LiN_{0.5}Mn_{1.5}O_4$ spinel for 5V class cathode material of Li-ion secondary battery. *Electrochim. Acta*, 2004, **49**, 219–227.
19. Hsiang, H. I and Chang, C. H., Molten salt synthesis and magnetic properties of $3BaO.2CoO.12Fe_2O_3$ powder. *J. Magn. Magn. Mater.*, 2004, **278**, 218–222.
20. Kan, Y., Jin, X., Wang, P., Li, Y., Cheng, Y. B and Yan, D., Anisotropic grain growth of $Bi_4Ti_3O_{12}$ in molten salt fluxes. *Mater. Res. Bull.*, 2003, **38**, 567–576.
21. Jebrouni, M., Durand, B. and Roubin, M., Elaboration de zircone yttriée par réaction en milieu nitrate fondu et caractérisation. *Ann. Chim. Science des Matériaux.*, 1992, **17**, 143–154.
22. Descemond, M., Jebrouni, M., Durand, B., Roubin, M., Brodhag, C. and Thevenot, F. J, Characteristics and sintering behaviour of 3 mol% Y_2O_3–ZrO_2 powders synthesized by reactions in molten salts. *Mater. Sci.*, 1993, **28**, 2283–2288.

23. Harle, V., Deloume, J. P., Mosoni, L., Durand, B., Vrinat, M. and Breysse, M., Elaboration by reaction in molten nitrates and characterization of pure titanium oxide with large surface area. *Eur. J. Solid State Inorg. Chem.*, 1994, **31**, 197–210.

24. Koulikova, E., Deloume, J. P., Durand, B., Mosoni, M. and Vrinat, M., Preparation of cerium(IV) oxide by the method of molten salts. *Eur. J. Solid State Inorg. Chem.*, 1994, **31**, 487–500.

25. Lakhlifi, A., Leroux, C., Satre, P., Durand, B., Robin, M. and Nihoul, G., Hafnia powders (HfO_2): elaboration and characterization by transmission electron microscopy. *Solid State Chem.*, 1995, **119**, 289–298.

26. Aboujalil, A., Deloume, J. P., Chassagneux, F., Scharff, J. P. and Durand, B., Molten salt synthesis of the lead titanate $PbTiO_3$, investigation of the reactivity of various titanium and lead salts with molten alkali metal nitrites. *J. Mater. Sci.*, 1998, **28**, 1601–1606.

27. Hamon, D., Vrinat, M., Breysse, M., Durand, B., Mosoni, L. and des Couri-eres, T., Zirconia-alumina supports for hydrotreatment catalysts, molten salt preparation and characterization. *Eur. J. Solid State Inorg. Chem.*, 1993, **30**, 713–726.

28. Ouahdi, N., Guillemet, S., Demai, J. J., Durand, B., Er Rakho, L., Moussa, R. and Samdi, A., Investigation of the reactivity of $AlCl_3$ and $CoCl_2$ toward molten alkali-metal nitrates in order to synthesize $CoAl_2O_4$. *Mater. Lett.*, 2005, **59**, 334–340.

29. Durand, B., Preparation of fine grained mixed oxides by double decomposition reactions in molten salts. In *Ceramic Powders: Preparation, Consolidation and Sintering*, ed. P. Vincenzini. Elsevier Sci. Publ. Co., Amsterdam, 1983, pp. 413–420.

30. Ouahdi, N., Synthèse de l'aluminate de cobalt par voie sels fondus, caractérisation et application à la coloration des carreaux céramiques industriels. Thesis, Toulouse III, 2005.

31. C.I.E. Recommendations on Uniform Color Spaces, Color Difference Equations, Psychometric Color Terms. Supplement no. 2 of C.I.E. Publ. N. 15 (E1-1.31) 1971. Bureau Central de la C.I.E., Paris 1978.

32. Melo, D. M. A., Cunha, J. D., Fernandes, J. D. G., Bernardi, M. I., Melo, M. A. and Martinelli, F. A. E., Evaluation of $CoAl_2O_4$ as ceramic pigments. *Mater. Res. Bull.*, 2003, **38**, 1559–1564.

33. Merikhi, J., Junk, H. O. and Feldmann, C., Sub-micrometer $CoAl_2O_4$ pigment particles—synthesis and preparation of coatings. *J. Mater. Chem.*, 2000, **10**, 1311–1314.