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Ceramic pigments obtained by sol-gel techniques and by mechanochemical insertion of color centers in Al_2O_3 host matrix

Riccardo Ricceri[a], Silvia Ardizzone[b], Giovanni Baldi[c], Paolo Matteazzi[a,*]

[a]*Department of Chemical Sciences and Technologies and C.S.G.I, University of Udine, via Cotonificio 108, I-33100 Udine, Italy*
[b]*Department of Physical Chemistry and Electrochemistry, University of Milano, via Golgi 19, I-20133 Milano, Italy*
[c]*Colorobbia S.p.A., via Pietramarina 19, I-50053 Sovigliana—Vinci (Firenze), Italy*

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Abstract

Nanocrystalline pigments for ceramic glazes have been obtained by mechanochemical insertion of Fe and Ti in an α-Al_2O_3 host matrix (Fe and Ti oxides were reduced by high energy milling with metallic Al with subsequent formation of additional Al_2O_3 by oxidation of Al(0)). The powders have been characterized by X-ray diffraction, laser granulometry and by surface area and porosity measurements. Sol-gel techniques have also been used in order to obtain pigments with pure Al_2O_3 and Cr or Fe/Ti-doped Al_2O_3. Pigments have been prepared using Al(III)-alkoxides or Al(III)-inorganic salts, obtaining products with different characteristics in the two cases. Pigments have been studied by X-ray diffraction, surface area and porosity measurements and by the analysis of electrochemical reactivity in aqueous suspensions. Coloring properties of pigments obtained by mechanomaking and by sol-gel techniques have been tested in ceramic glazes; their properties have also been analyzed by insertion in ceramic bodies for glazed gres (porcelain) technology. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Al_2O_3; Mechanochemical processing; Milling; Pigments; Sol-gel processes

1. Introduction

Ceramic pigments like oxides, spinels, zirconates, aluminates, are prepared with blends of oxides and silicates as starting compounds, with the proper particle size distribution of powders, employing also mixtures of salts like halides, borates, etc., that have a "mineralizing" function. The mixture of these substances, that has been obtained by reactions in solutions or solid-state reactions or even by milling, undergoes a proper thermal treatment in order to obtain a substance with a well-defined crystalline structure that can possess a color of its own (idiochromic) or that can be colored by insertion of metallic chromophores (allochromic). The substance must also possess a high thermal and chemical stability in the conditions of use. Ceramic pigments are thus inorganic substances, that are employed in glazes, ceramic bodies, sanitaries, gres, etc. and they have to withstand high temperature effects (even above 1100 °C) together with chemical aggression due to fused glass, in certain cases even for long periods. Research in the field of ceramic pigments is nowadays oriented towards the enlargement of the chromatic set of colors together with an increased thermal and chemical stability. The present work aimed at the development of new ceramic pigments employing new technologies of production. Pigments have been prepared by mechanomaking[1–6] and sol-gel techniques by insertion of color centers (Cr, Fe and Ti) in an α-Al_2O_3 host matrix in order to obtain new color tonalities for chemically and thermally stable substances.

The "doping" of an oxide powder by metal species, different from the reticular ions, is one of the most frequently adopted practices to provoke modifications both of the bulk features of a material and of its surface composition and reactivity.[7–17] The substitution of Al^{3+} for Si^{4+} in zealots, for example, is well known to affect the environment of the zeolite cavity, generate Broensted acid sites and rule consequently the material selectivity and catalytic activity.[14–17] Oxide based allochromic ceramic pigments are another large class of materials obtained by framework substitution of guests metal species in the host lattice of an oxide. The struc-

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[*] Corresponding author. Fax. +39-0432-558803.
E-mail address: ricceri@dstc.uniud.it (P. Matteazzi).

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tural features of the oxide matrix (e.g. TiO_2, ZrO_2, Al_2O_3, etc.) play a primary role in imposing the chromatic performance of the pigment which is a complex function of reticular accomodation and metal ion valence-dimension. As for zeolites, also in the case of these materials, the framework incorporation of the metal may provoke modifications of several properties of the phase, for example of the particle morphology, the surface composition and the interfacial reactivity.[13,18–20] The possibility to control and modulate these latter aspects is very relevant in the case of a ceramic pigment. The particle size distribution and porosity rule the packing capability of the powders in the green body and the actual surface state and interfacial electrification features impose the interparticle interactions in their turn affecting the conditions of stability of the aqueous concentrated suspensions precursors of the ceramic.[21]

2. Experimental details

2.1. Pigments by mechanomaking

Commercial α-Al_2O_3 powder (purity >99.8%), Fe_2O_3 (hematite, purity >99%) were purchased from Aldrich, metallic Al (purity >99.4%) was provided by Metalpolveri S.r.l. (Italy), TiO_2 (purity >99.9%) was provided by Fischer. Nanocrystalline powders pigments were obtained by mechanomaking[6] in a high energy high capacity ball mill (grinding balls to powder ratio of 7:1, allumina balls diameter of about 25 mm) in Ar atmosphere (the vial was filled up to a pressure of 1.4 bar after evacuation to 10^{-4} bar).[6] The insertion of color centers (Fe/Ti) was performed according to the reaction:

$$xFe_2O_3 + 2xTiO_2 + 14/3xAl + wAl_2O_3$$

$$= 2x[Fe + Ti] + (w + 7/3x)Al_2O_3$$

$$([Fe + Ti] = 5\%\ v/v;\ Al_2O_3 = 95\%\ v/v)$$

The redox reaction is performed by mechanical attrition, the metallic Al is oxidized and Al_2O_3 is formed simultaneously: Fe and Ti oxides are reduced and the ions Fe(II) and Ti(III) are intended to be inserted in α-Al_2O_3 lattice. α-Al_2O_3 has been added to the reagents in order to reach the volumetric fraction of 95% v/v for the matrix and 5% v/v for the chromophores.

The powders were milled for 10 h.

XRD patterns were collected using an INEL diffractometer equipped with a CPS-120 position-sensitive detector and a germanium monochromator using CoK_α ($\lambda = 0.1789$ nm) radiation. The mean crystallite size was calculated from the method described elsewhere[5,22] using the full width at half maximum (FWHM) of the X-ray peaks corrected for instrumental broadening and taking into account strain effects.

Particle size distribution analysis of the powders were performed using a Coulter LS100 Laser diffractometer (0.4–900 μm simultaneous range): the measurements were performed in a water medium.

Specific surface areas were determined by the classical BET procedure using a Coulter SA 3100 apparatus.

2.2. Pigments by sol-gel technique

All the chemicals were of reagent grade purity and were used without further purification; doubly distilled water passed through a Milli-Q apparatus was used to prepare solutions and suspensions. Structural characterization of the powders was performed by XRD technique, using a Siemens D500 diffractometer. Specific surface areas were determined by the classical BET procedure using a Coulter SA 3100 apparatus.

The alumina samples were obtained by heating at different temperatures precursors prepared by a sol-gel procedure using two different starting salts: (a) aluminum tri-sec-butoxide [Al $(OC_4H_9)_3$]; (b) aluminum chloride [$AlCl_3$].

At the beginning of the reaction the water-alcoxide solution (alcoxide/water ratio = 1/100) was kept under stirring at 75 °C for about 30 min.; the temperature was subsequently raised to 85 °C and HNO_3, the reaction catalyst (HNO_3/alcoxide ratio = 0.05) was added to the mixture which was left under stirring for a further 3 h. The product, cooled to room temperature, was then first dried over $CaCl_2$ for 160 h and subsequently heated at 150 °C for 2 h. The samples doped with Ti and Fe were obtained by following the same procedure as for the alumina samples with the exception of dissolving the salts ($FeSO_4$; $TiCl_3$; [Fe + Ti] = 0.8% v/v, Al_2O_3 = 99.2% v/v, Fe/Ti molar ratio = 4) in the aqueous phase before the addition of the aluminum butoxide (in the case of Fe and Ti salts the solution was saturated with nitrogen in order to reduce oxidation of Fe(II) and Ti(III) ions and thus favor the insertion of these ions in the host matrix in their lower oxidation state).

At the beginning of the reaction the water-inorganic salt solution was treated with ammonia solution in order to obtain polycondensation with a fast heatingless reaction. The NH_4OH solution was added dropwise to the solution of the salt (buffered pH = 8.5) and pH was kept under control during all the process. After the addition of ammonia solution, the system was aged for 24 h. The precipitate was then washed by centrifugation-resuspension cycles and was subsequently transferred into a dialysis membrane, to complete purification (at the end of the process, the conductance of the water in contact with the precipitate was less than 15 µS). The sample was then heated at 100 °C to remove excess water.

3. Results and discussions

3.1. Pigments by mechanomaking

The XRD diffraction spectrum of powders (Al_2O_3 95% v/v + Fe_2O_3/TiO_2 5% v/v) after 10 h milling is reported in Fig. 1. The main diffraction peaks of α-Al_2O_3 are present; a value of 22 nm for the α-Al_2O_3 crystallites is obtained by the Scherrer method. The presence of chromophores causes a decrease in α-Al_2O_3 cell volume (249.8 Å^3 against 254.7 Å^3 for pure in α-Al_2O_3),[23] that could show a successful doping of corundum lattice.

The powder size distribution for this sample is reported in Fig. 2. The size distribution is very wide, and covers a large part of the range of the experimental apparatus (from 0.4 up to 400 µm). The distribution is bimodal, there is a population of large particles (center of the distribution about 70–80 µm) and one of smaller particles (center of the distribution about 3 µm), are present. SEM micrographs (see Fig. 3) seem to confirm these results: at lower magnification, a wide size distribution of particles is shown, ranging from a few microns to several hundred µm, the larger particles seeming to be formed by aggregation of smaller particles. This is confirmed by SEM images at higher magnification: in fact, powders look like aggregates of small particles with dimensions up to 2–3 µm.

BET measurements gave a specific surface area of 2.65 m^2 g^{-1}, which is a very low value for these materials and is due to the high energy milling technique that causes particles agglomeration; as confirmed by particle size distribution analysis and by pore volume analysis, that provided a value of 0.019 cm^3/g (practically very low porosity).

3.2. Pigments by sol-gel technique

The XRD diffraction analysis provided different phases composition for the two procedures (a) and (b). As for procedure (a), samples obtained by the sol-gel technique using $Al(OC_4H_9)_3$ as the starting salt (shown as Al1) the diffraction spectra of uncalcined and undoped samples are reported in Fig. 4 and show the presence of the AlOOH phase. For samples obtained by the sol-gel procedure (b), using $AlCl_3$ as starting the salt (shown as Al2), the diffraction peaks of $Al(OH)_3$ phase, bayerite (B) and gibbsite (G) are present in the XRD spectra of the uncalcined and undoped samples (see Fig. 5). For Al1, the mean crystallite size is 2.4 nm, while for Al2 the crystallite size is 18 nm (Scherrer method), the crystal growth is thus much larger using procedure (b); the presence of chromophores does not modify appreciably the phase composition and the crystal size. These struc-

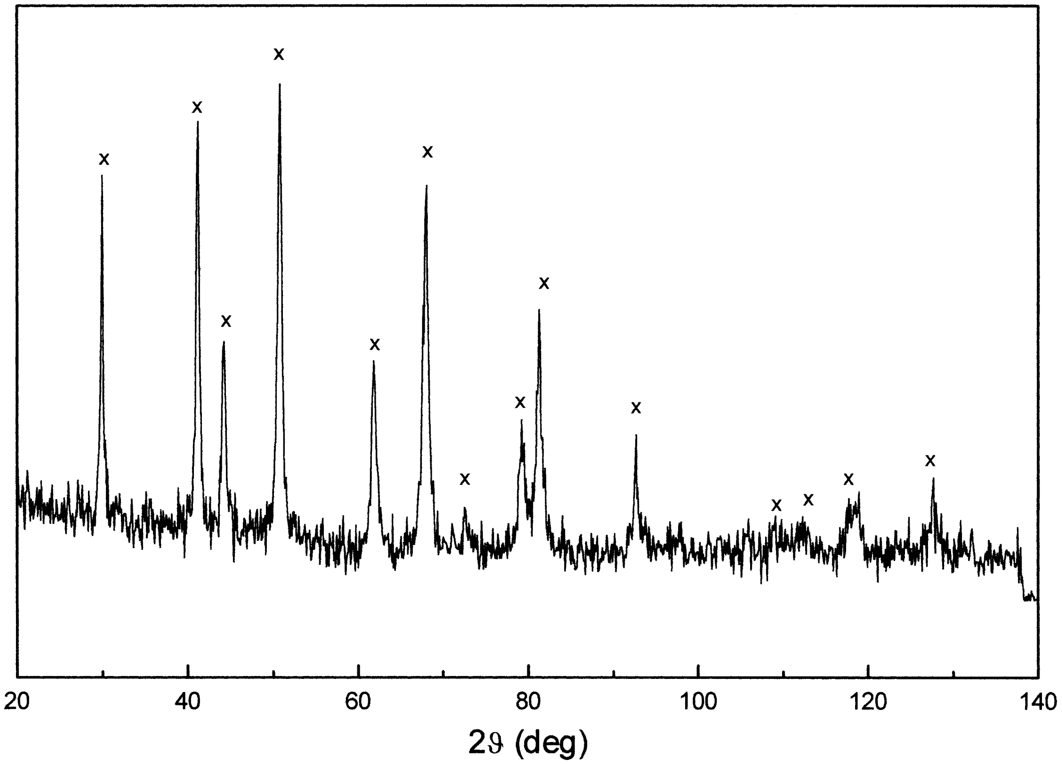


Fig. 1. XRD spectrum of pigments obtained by mechanomaking [α-Al_2O_3, (x)].

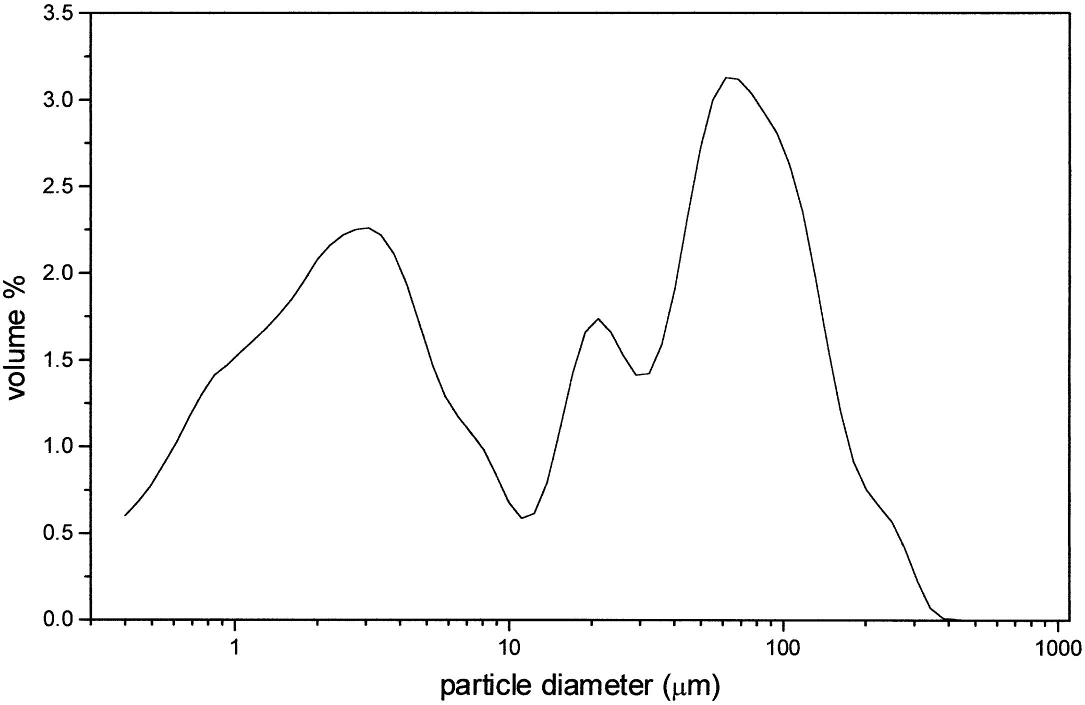
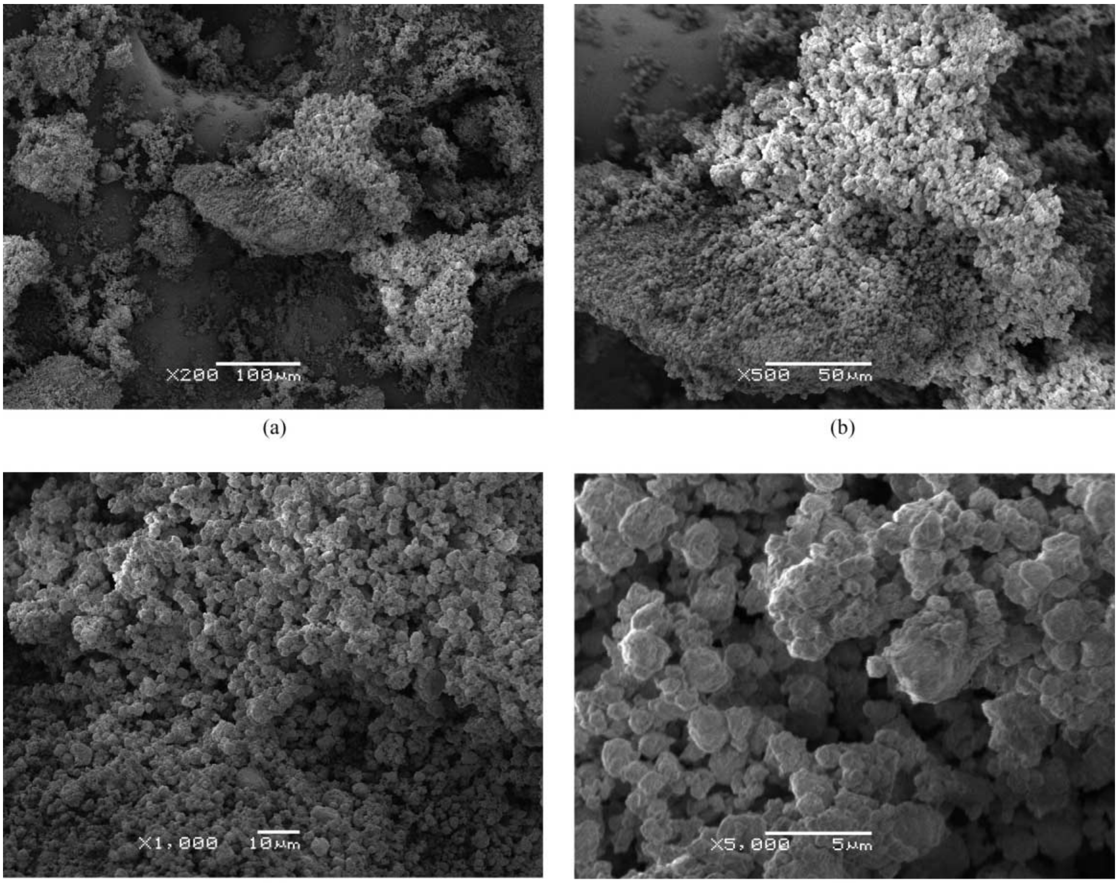


Fig. 2. Particle size distribution for pigments obtained by mechanomaking.



(a) (b)

(c) (d)

Fig. 3. SEM micrographs of pigments obtained by mechanomaking at different magnifications.

tural differences are very important in order to study the insertion of the chromophore in the host-lattice, causing different color characteristics in the two cases (see below). The two different kinds of samples have been heated at different temperatures in the 300–1200 °C range: the treatment causes the modification of the samples till the formation of γ-Al_2O_3 at about 1000 °C and α-Al_2O_3 at about 1200 °C. BET measurements for samples treated at different temperatures are reported in Table 1 together with pore volume analysis. The two samples (a) and (b) before thermal treatments are very different: Al1 sample shows a large specific surface area, about three times larger in comparison with that of Al2; the pore volume is also larger for Al2 with respect to

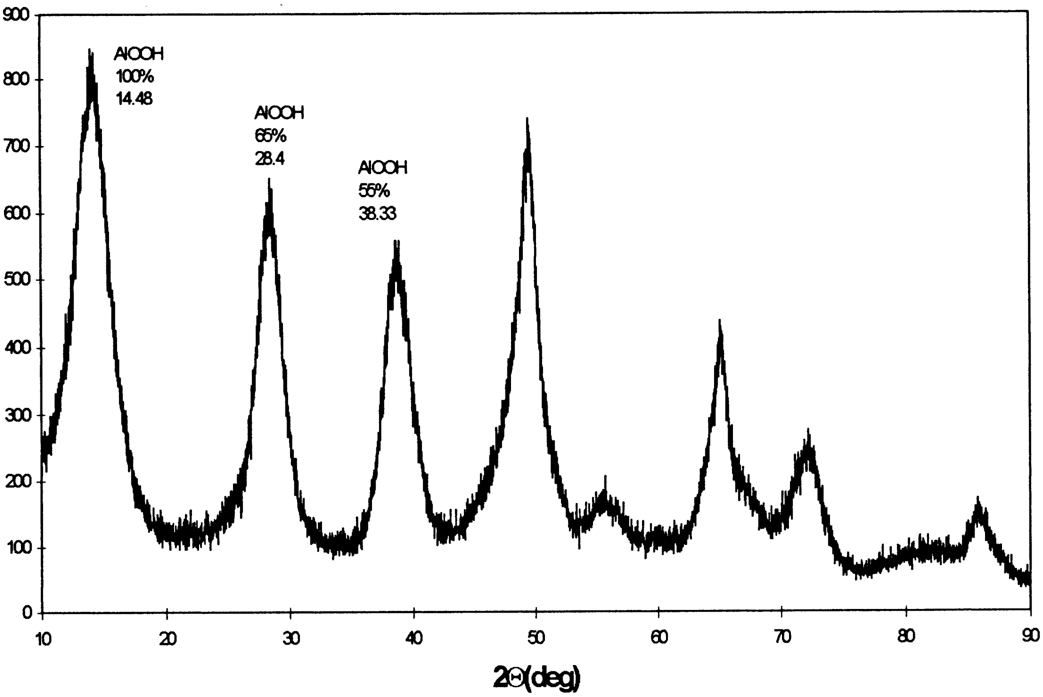


Fig. 4. XRD spectrum of uncalcined and undoped alumina sample obtained by the sol-gel technique [starting salt: $Al(OC_4H_9)_3$].

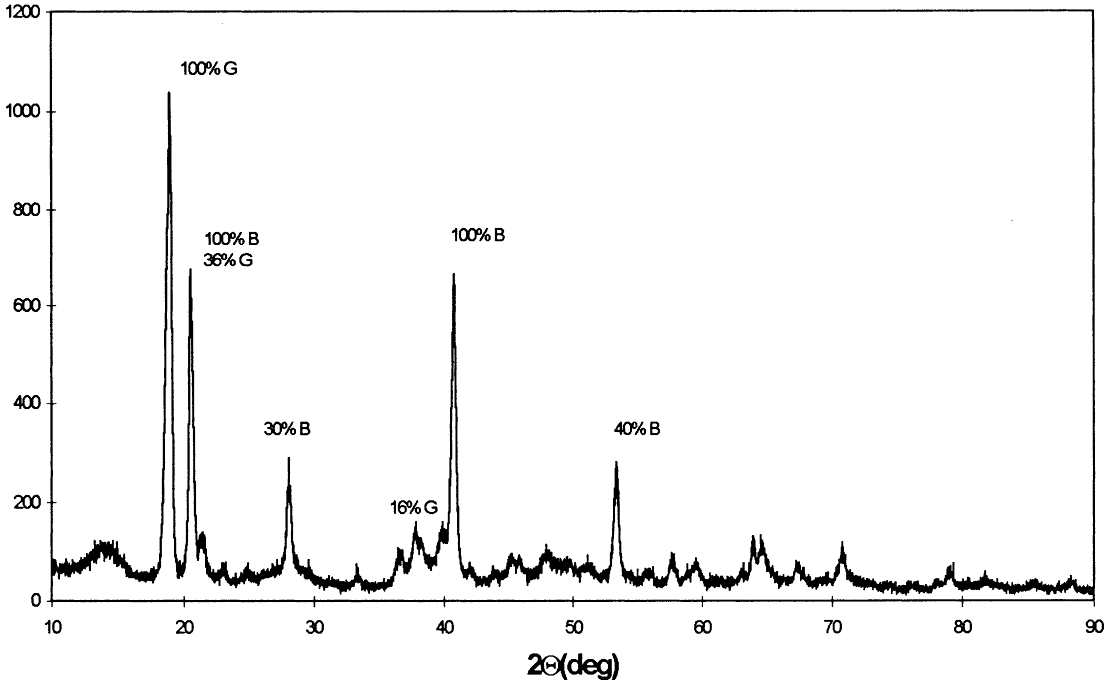


Fig. 5. XRD spectrum of uncalcined and undoped alumina sample obtained by the sol-gel technique (starting salt: $AlCl_3$).

Table 1
BET areas and pores volume for alumina samples obtained by the sol-gel technique

Sample	S (m^2/g)	Pores volume (cc/g)
All n.c.	341.13	0.13246
A11470	355.66	0.36671
A111200	5.636	0.02003
A12 n.c.	118.43	0.26327
A12300	408.46	0.35040
A12470	419.93	0.41521
A121200	5.042	0.02797

All; the presence of the chromophores does not alter the values obtained for the undoped samples. The thermal treatment at 470 °C increases the surface area for Al2, while the values of Al1 do not change appreciably: this could be due to the presence of a crystalline phase (aluminum hydroxides) in the untreated sample Al2, which is not present in Al1. On increasing temperatures, the specific areas and porosities decrease for both samples Al1 and Al2 till α-Al_2O_3 is obtained at about 1200 °C: the surface areas and porosities are very low and the crystal size is, for both samples, about 34–35 nm, the presence of the chromophores did not cause for these samples appreciable changes in α-Al_2O_3 cell volume (about 255 $Å^3$ for all samples, the same found for pure α-Al_2O_3). The powder size distribution for the two samples after thermal treatment at 1200 °C is reported in Figs. 6 and 7: the two distributions are similar, and very wide, (covering the 1–900 μm range) with a large fraction of particles above 50 μm.

By SEM analysis (not shown), the Al1 samples show smooth surfaces as a result of a gel-dehydration; the Al2 samples appear to consist of aggregates formed by small particles; after thermal treatment at 1200 °C difference in morphology between Al1 and Al2 are not so evident, but sintering and agglomeration phenomena cause the formation of aggregates with irregular shape and size (see Fig. 8).

3.3. Glazing tests

Powder pigments obtained by mechanomaking were added to a melting substrate: the pigment (5% w/w of the overall solid content) was added to a 5% w/w aqueous suspension of a transparent frit with a medium lead content (see Tables 2 and 3 for composition and properties of the frit). The suspension was then deposited on a support; then, water was removed at 35 °C using an infrared lamp. The glazing was obtained after a thermal cycle of 1 h, a maximum temperature of 1120 °C was reached and the sample was mantained at that temperature for 5 min (atmosphere during heat treatment: H_2 5% v/v, N_2 95% v/v). The resulting color was bluish-grey: this clearly indicated the presence of free Fe(0) and Ti(0) that were not inserted in the α-Al_2O_3 lattice.

The uncalcined sol-gel pigment obtained from Al alkoxides using Fe(II) and Ti(III) salts as dopants was thermally treated according to the thermal cycle reported in Fig. 9 (atmosphere: H_2 5% v/v, N_2 95% v/v) in order to obtain the corundum structure (the hydrogen atmosphere was employed in order to assure reduction

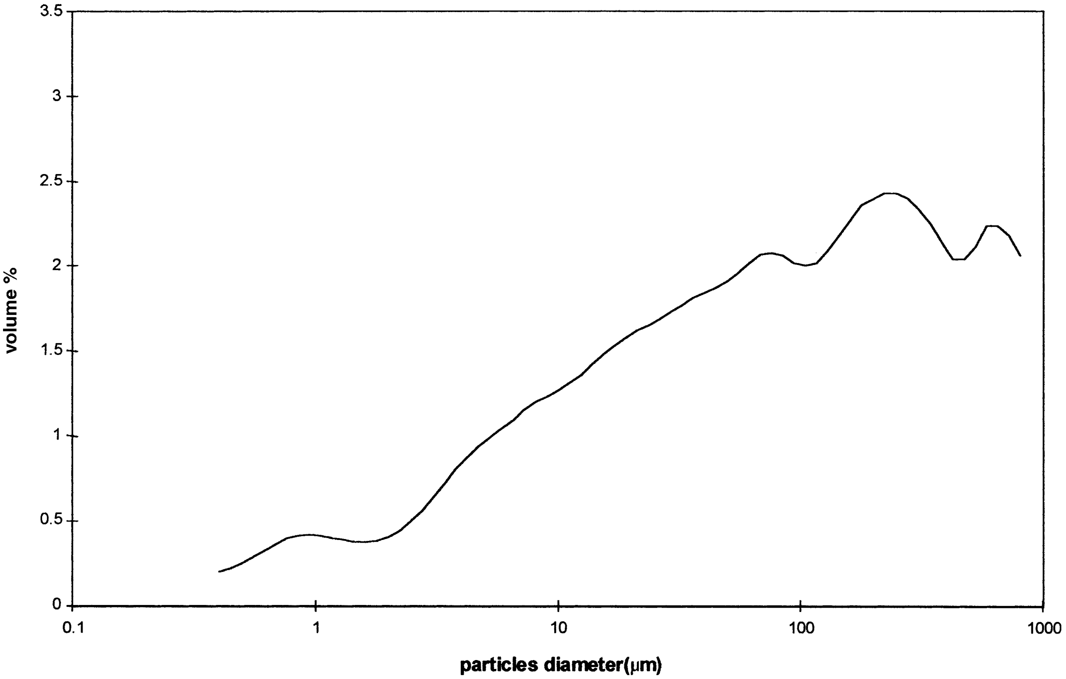


Fig. 6. Particle size distribution for pigments obtained by the sol-gel technique [starting salt: $Al(OC_4H_9)_3$].

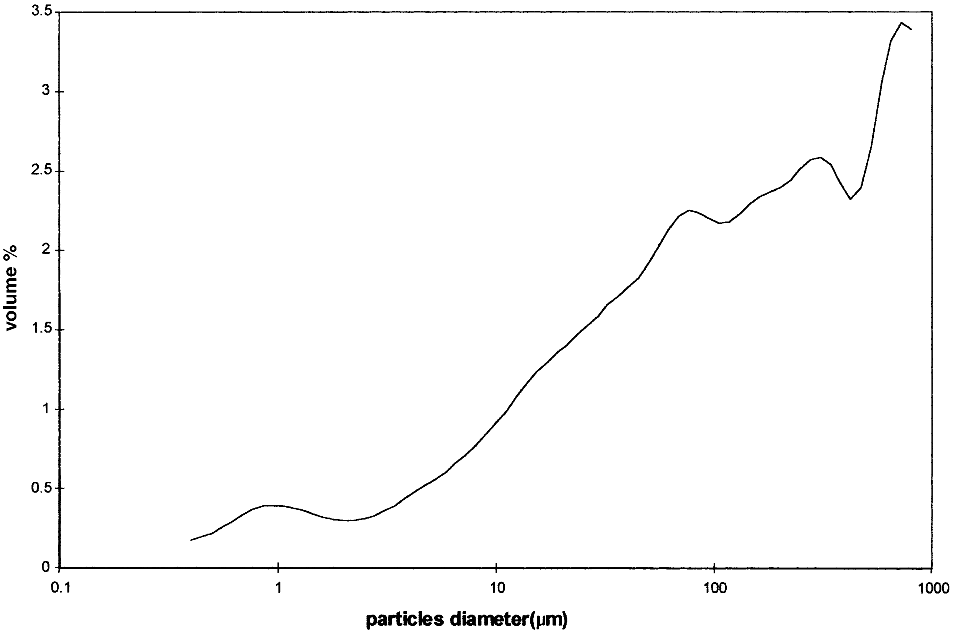


Fig. 7. Particle size distribution for pigments obtained by the sol-gel technique (starting salt: $AlCl_3$; B = bayerite, G = gibbsite).

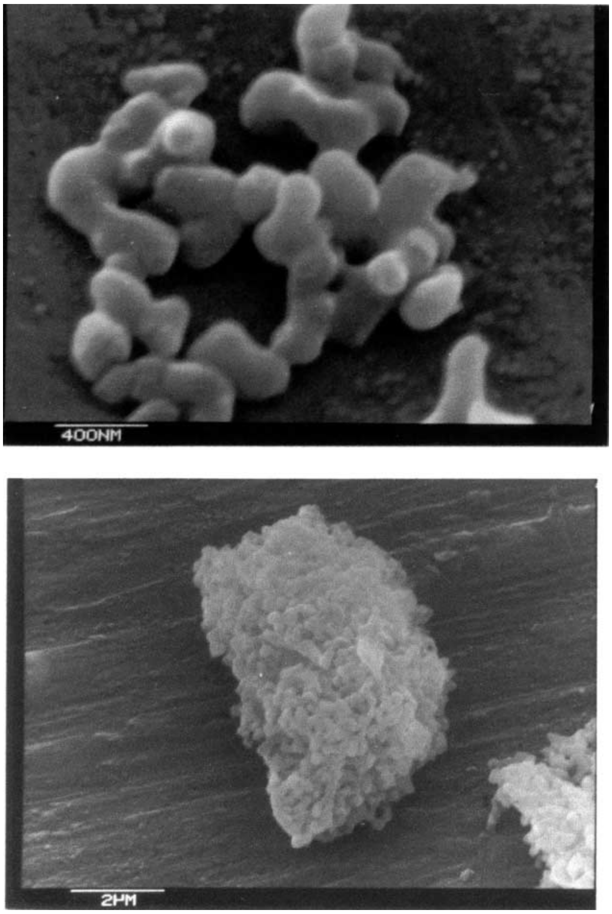


Fig. 8. SEM micrographs of samples obtained by the sol-gel technique [starting salt: $Al(OC_4H_9)_3$] after calcination at 1200 °C.

Table 2
Composition of the frit

Compound	Mass% oxides
CaO	8.1
MgO	1.2
PbO	2.6
K_2O	4.2
Na_2O	2.1
Al_2O_3	9.15
B_2O_3	8.92
Fe_2O_3	0.1
BaO	1.4
SiO_2	57.2

Table 3
Physical chemical properties of the frit

Linear coefficient of thermal expansion $\alpha_{50\text{–}400\ °C}$	$65\times10^{-7}\ K^{-1}$
Glass trans. temp. T_g	610 °C
Softening point (dilatometric)	720 °C
Sintering point	730 °C
Softening point	870°c
Ball point	1000 °C
Half ball point	1130 °C

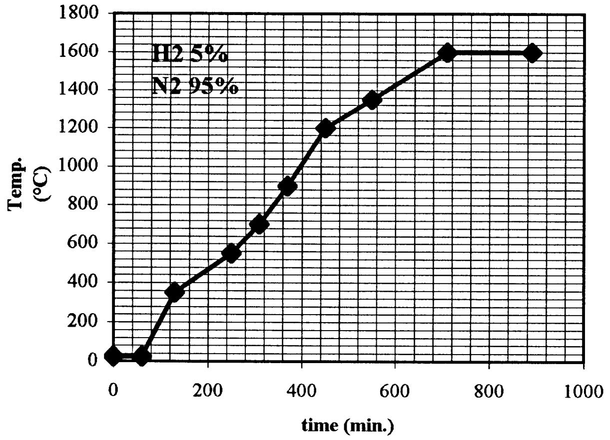


Fig. 9. Thermal cycle under controlled atmosphere for glazing tests.

of dopant ions, that could have undergone oxidation during the final steps of the milling process, to Fe(II) and Ti(III)). XRD data (not shown) showed the presence of a relevant amount of spinel $FeAl_2O_4$, that was not detected by XRD technique in the samples obtained by mechanomaking (only Moessbauer spectra, not shown, showed the possible presence of spinel $FeAl_2O_4$ for samples obtained by mechanosynthesis): these data are very important taking also into account that the amount of dopants, for the pigments obtained by the sol-gel technique, was several times lower that for those obtained by mechanomaking. The pigment was then washed and milled in order to obtain a fine powder (average size about 10 μm) and added to an aqueous suspension of the same frit that was described previously for the other pigments, and also the same procedure was followed except for the gas atmosphere during glazing (99.9% CO_2 was used). The resulting color was in this case deep intense blue, that could be very promising for technological applications. Pigments obtained with precursors deriving from inorganic salts of Al did not provide significant results with the glazing test.

4. Conclusions

α-Al_2O_3 samples, both pure and doped with metallic ions (Fe, Ti), were obtained by a procedure implying sol-gel stages. The presence of the dopant did not introduce any appreciable modification either in structure (cell volume) morphology (surface area and porosity) of the powders. Powders were heated at different temperatures, phase transition between γ- and α-alumina occurred around 1000–1200 °C. The process provided a blue pigment in the case of Fe–Ti doped alumina showing the presence of the compound (spinel) $FeAl_2O_4$, that could be important and responsible for the color of the pigment, although insertion of dopants ions Fe(II) and Ti(III) in the α-Al_2O_3 lattice could also contribute, to a minor extent, to the resulting final color. This new pigment could have a relevant interest in the industrial field, but first process costs have to be evaluated carefully.

The mechanochemical technique also provided intesting results: also in this case the formation of $FeAl_2O_4$ was obtained, although in a much smaller amount with respect to pigments obtained by the sol-gel technique. The final resulting blue color of the pigment was less intense that in the former case: this could be due to the presence of a smaller amount of $FeAl_2O_4$ but also to a less significant insertion of Fe and Ti ions in the corundum lattice (the small effectiveness in both dopant ions insertion and spinel formation are confirmed by the presence of free metallic Fe and Ti in the pigment, responsible for the greyish tonality of the resulting color, although variation in α-Al_2O_3 volume cell for doped pigments obtained by mechanosynthesis could indicate an effective insertion of Fe/Ti ions in the corundum lattice). Only the choice of the proper parameters for the mechanosynthesis process, in particular the applied energy in the attrition, could result in the optimization of the production of nanocrystalline powders with new and industrially exploitable color formulations.

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