

## **New chromium doped powellite (Cr-CaMoO<sub>4</sub>) yellow ceramic pigment.**

R. Galindo, C. Gargori, N. Fas, M. Llusar, G. Monrós\*.

Dpt. of Inorganic and Organic Chemistry, Jaume I University, Av. de Vicent Sos Baynat, s/n. 12071, Castellón (Spain).

### **Abstract.**

A new chromium doped powellite (Cr-CaMoO<sub>4</sub>) yellow ceramic pigment alternative to yellow of praseodymium-zircon has been synthesised and characterised in order to analyse: a) the stoichiometry of the solid solution, b) the effect of the dopant concentration under the pigmenting properties, c) the effect of the chromium precursor and mineralizers addition, d) the effect of the synthesis method. The composition Cr<sub>x</sub>CaMo<sub>1-x</sub>O<sub>4</sub> x=0.075 using K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> or Cr<sub>2</sub>O<sub>3</sub> as chromium precursors fired at 1000-1100°C produces a yellow colour, slightly lower in intensity than the commercial praseodymium-zircon yellow pigment in double (1000°C) or single firing (monoporosa-1080°C or porcelainized stoneware-1200°C) ceramic glazes. By a coprecipitation method with ammonia, and firing at 950°C, the yellow ceramic pigment glazed in a conventional CaO-ZnO-SiO<sub>2</sub> glaze (monoporosa glaze, 1080°C) shows a yellow colour similar to the commercial praseodymium-zircon yellow pigment. However the release and possible mobilization of the Cr (VI) should be controlled in order to get its industrial implementation.

**Keywords:** ceramic pigment, powellite, molybdenum, chromium.

\*Corresponding author: Tl.: 34-(0)964 728250; Fax. 34-(0)964 728214, E-mail address: monros@qio.uji.es

## 1. Introduction.

ABO<sub>4</sub> family of ternary oxides contain many compounds since cation A with valences +1, +2, +3, and +4 can be accommodated with cation B with valences +7, +6, +5, and +4, respectively. They show interesting technological properties and have been used during the last years as solid-state scintillators (CaWO<sub>4</sub> and PbWO<sub>4</sub>), laser-host or solid state lasers (YVO<sub>4</sub>). A number of crystal structures in ABX<sub>4</sub> compounds, consist of BX<sub>4</sub> tetrahedra and AX<sub>8</sub> eight-coordinated polyhedral, which can be seen as two interpenetrating tetrahedra, known as bidisphenoids or dodecahedra [1,2]. Among these structures some important mineral structures as scheelite or zircon are included where A and B cations form two interpenetrating diamond structures in a tetragonally distorted fcc array. Zircon is the mineral ZrSiO<sub>4</sub> and also the general name of the compounds crystallizing in the tetragonal I41/amd phase, like many ABO<sub>4</sub> silicates, vanadates, phosphates and arsenates (HfSiO<sub>4</sub>, YVO<sub>4</sub>, YPO<sub>4</sub>, and YAsO<sub>4</sub>). The Scheelite is the mineral CaWO<sub>4</sub> and the general name of the compounds crystallizing in the tetragonal I41/a phase, like other alkaline-earth tungstates (SrWO<sub>4</sub> and BaWO<sub>4</sub>), PbWO<sub>4</sub>, alkaline-earth molybdates, PbMoO<sub>4</sub>, CdMoO<sub>4</sub>, and a number of fluorites (YLiF<sub>4</sub>, LuLiF<sub>4</sub>, CaZnF<sub>4</sub>). Zircon and scheelite structures are superstructures of the rutile structure common in AX<sub>2</sub> compounds and the following pressure-driven phase transitions sequence can be predicted on the light of recent advances: I41/amd (zircon) → I41/a (scheelite) → I2/a (fergusonite) → P21/n (BaWO<sub>4</sub>-II-type) → orthorhombic phases (BaMnF<sub>4</sub>-type, Cmca) → amorphous [3]. The fergusonite YNbO<sub>4</sub> occurs as different polymorphs depending on the temperature of crystallization [4]: a high-T tetragonal polymorph (space group I41/a) isostructural with scheelite (CaWO<sub>4</sub>) and powellite (CaMoO<sub>4</sub>); and a low-T monoclinic polymorph with the fergusonite-type structure (known also in the mineralogical literature as fergusonite-beta, space group I2/a, no. 15).

Powellite crystallizes in the scheelite structure with the space group I41/a in which the central Ca<sup>2+</sup> ion is coordinated by eight singly-bound molybdate MoO<sub>4</sub><sup>2-</sup>-tetrahedra groups. The point symmetry of the Ca site in this structure has been reported as D<sub>2d</sub> as well as S<sub>4</sub> in synthetic samples. The structure is ideally suited for the formation of solid solutions, as it exhibits significant compositional flexibility. When trivalent ions are substituted for the divalent Ca<sup>2+</sup> ion charge compensation has been found to proceed via coupled substitution with monovalent cations e.g. alkali metal ions. This mechanism has been identified for other solid solutions as well. In other Ln<sup>3+</sup>-molybdates defect structures have been identified where two trivalent cations substitute for three divalent calcium ions. The observation of a homogeneous composition throughout the full series range suggests an ideal solid solution behaviour. This behaviour will be beneficial for the immobilization of radionuclides in a waste repository scenario, as trace contaminants can be structurally incorporated even in the presence of large excess of other trivalent ions [5].

The classical yellow ceramic pigment used before the revolution of the European discovery of the white porcelain was the Yellow lead (II) antimonate Pb<sub>2</sub>Sb<sub>2</sub>O<sub>7</sub> cubic pyrochlore, space group Fd3m [6]. The called Naples Yellow arrives to Venice in Italy from the Byzantine Empire. The history of lead antimonate goes back at least 3500 year, but at present, Naples Yellow cannot be prepared and commercialized due to its high toxicity related to the antimony and lead content [7]. The substitution of Naples Yellow by the yellow of praseodymium in zircon was led for the high increase of the cassiterite (SnO<sub>2</sub>) price about 1914. Tin oxide was, par excellence, the glaze's opacifier and withe

stain for glazes since Rome, only antimony oxide and titanium oxide were sometimes used, but antimony release at relative high temperatures and titanium oxide yellowish the glaze when contains traces of iron or chromium. The high refraction index and high melting point of both zirconia and zircon, together their low solubility in glazes was emphasized by american and european researchers [8]. In 1930-1940 the new opacifier was introduced by several manufactures, such as Titanium Alloy Manufacturing Company, which patent the white and brilliant glazes obtained with zirconia and zircon. Zirconia and zircon accomplish the three main characteristics of ceramic pigments (thermal stability, low solubility in molten glazes and high refraction index). Thus yellow of vanadium doped zirconia is developed but unstabilizes by reaction with silica from the glaze, precipitating zircon. On the other hand the direct doping of zircon is not successful. In 1948 Clarence A. Seabright thought that probably it was necessary to change the synthesis strategy and, as it was led with corundum stains where aluminum hydroxides are used instead corundum, use a mixture of silica and zirconia with chromophores. Thus the turquoise of vanadium doped zircon using NaF as mineralizer had a great success [9]. Later, in 1960, Seabright develops the yellow of praseodymium in zircon (although this pigment it had already been handled and cited in Japan) [10].

A useful colorant classification of the chemicals used as ceramic pigments was reached in 1977 from the requirements of the Toxic Substances Act, 94-469 U.S. law, which includes the whole chemical substances used in U.S.A. whether they are toxic or not. The Dry Colours Manufactures Association (DCMA) commends to their Metal Oxide and Ceramic Colour Subcommittee of DCMA Ecology Committee the classification of the commercial ceramic pigments giving a standard terminology. This DCMA committee applied a chemical-structural criterion for the classification of ceramic pigments in fourteen structural families. In 2010 the Color Pigment Manufacturers Association CPMA actualized the classification and chemical description of the complex inorganic color pigments in the fourth edition. CPMA describes the industrial ceramic pigment by a code such as CPMA 1-01-4 for vanadium doped zirconia [10]. The commercial yellow ceramic pigments included into the CPMA classification are the vanadium doped zirconia (CPMA 1-01-4), the Naples yellow of lead antimonate pyrochlore (CPMA 10-14-4), the yellows based on doped rutile or cassiterite (CPMA 11-15-4 for Ni,Sb-TiO<sub>2</sub>, CPMA 11-16-4 for Ni,Nb-TiO<sub>2</sub>, CPMA 11-52-4 for Ni,W-TiO<sub>2</sub> and CPMA 11-22-4 for V-SnO<sub>2</sub>) and the yellow of praseodymium in zircon (Pr-Zircon, CPMA 14-43-4) [11].

The bismuth vanadate BiVO<sub>4</sub> with fergusonite structure is also used as yellow pigment in plastic and ceramic industries. This structure can be considered derived from fluorite CaF<sub>2</sub> lattice substituting Ca by both A and B cations in 1:1 atomic ratio, A occupies a very deformed dodecahedral environment and B is in tetrahedral coordination [12,13]. It can be synthesised by solid state route, but more glossy colours are obtained using hydrothermal and coprecipitation routes; depending of the synthesis conditions zircon or powellite phases crystallize. DTA-TG and XRD analysis indicate that firstly zircon crystallizes and transforms with the thermal treatment into a fergusonite phase which stabilizes in the cooling. The quality of the colour depends of the microstructure developed by the thermal treatment [14]. The stabilization by solid state reaction has made many patents that try to do it by alkaline or earth alkaline cations doping bismuth or substituting vanadium by molybdenum or tungsten. Using alkaline or earth alkaline dopants the monoclinic form of fergusonite or  $\beta$ -fergusonite [15] is stabilized. Gotic et al. [16] have obtained the pigment by solid state reaction at 700°C which is integrated by

compact and irregular particles which relative high size (around 15  $\mu\text{m}$ ) with brown-yellow colourations. By hydrothermal or coprecipitation routes fine and regular particles of 0.3-1.2  $\mu\text{m}$  are obtained which produce lemon-yellow pigments.

From the sequence of pressure-driven phase transitions above described for  $\text{ABX}_4$  compounds [1] ( $\text{I41/amd}$  (zircon)  $\rightarrow$   $\text{I41/a}$  (scheelite)  $\rightarrow$   $\text{I2/a}$  (fergusonite)), it can be observed that the extremes (zircon and fergusonite) produce some known stable ceramic pigments but as far we are concerned, there is not any known ceramic pigment based in scheelite. Only recently and related to powellite, isostructural with scheelite, ceramic pigments with the general formula  $\text{Pr}_{2-x}\text{Ca}_x\text{Mo}_2\text{O}_9$  ( $x$  between 0 and 1) have been obtained [17] which develop colorations from yellow to green with easily application in plastics and in low reactive ceramic glazes. The performance of pigments enamelled in a lead free double firing ceramic glaze produces light yellow colours not better than  $b^*=19$ . Using  $\text{NH}_4\text{Cl}$ ,  $\text{NaF}$  and  $\text{Na}_2\text{SiF}_6$  as flux agents in the  $(\text{Pr}_{2-x}\text{Ca}_x)\text{Mo}_2\text{O}_9$   $x=0.1$  composition with the same molar addition of halogens (0.84 mole per formula weight), a structural effect of fluoride ion is observed but the yellow colour on enamelled samples does not improve. Finally, using an ammonia coprecipitation method in the  $x=0.6$  sample, more regular and higher crystal size crystallization are produced. The microstructure obtained from CO method gives more intense yellow coloured powders and improve their resistance against glaze, producing significantly best yellow colours than ceramic samples [18].

Chromium doped powellite  $\text{Cr-CaMoO}_4$  samples have prepare prepared in order to analyse: a) the stoichiometry of the solid solution, b) the effect of the dopant concentration and temperature on the pigmenting properties, c) the effect of the chromium precursor and mineralizers addition, d) the effect of the synthesis method. Finally the Cr-Powellite ceramic pigment is compared with Pr-Zircon yellow ceramic pigments in its pigmenting properties and environmental limitations.

## 2. Experimental.

The samples were synthesised using the ceramic (CE) method from the indicated precursors in each case. In the CE method (solid state reaction) the precursors were homogenised in acetone media using a planetary mill and when acetone was evaporated, the resulting powders were fired at the considered temperature and soaking time. For the analysis of the effect of the synthesis method, a coprecipitation method (CO) using  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  as soluble precursors was followed. In this method the precursors for 5 g. of final product were solved in 200 ml of water and the solution was precipitated by slow addition of drops of concentrated ammonia solution (12 wt. %  $\text{NH}_3$  in water).

Samples were characterized by the following techniques:

a) X-Ray Diffraction (XRD) carried out on a Siemens D5000 diffractometer using  $\text{Cu K}_\alpha$  radiation,  $20^\circ$ - $70^\circ 2\theta$  range, scan rate  $0.05^\circ 2\theta/\text{s}$ , 10 s per step and 40 kV and 20 mA conditions.

b) Microstructure characterisation of powders was carried out by Scanning Electron Microscopy (SEM), using a Leo-440i microscope supplied by LEYCA.

c) UV-Vis-NIR spectra of fired powder samples and of 5 wt.% glazed samples in

different conventional ceramic glazes were collected using a Jasco V670 spectrometer through diffuse reflectance technique.  $L^*a^*b^*$  colour parameters of glazed samples were measured following the CIE- $L^*a^*b^*$  (Commission International de l'Eclairage) colorimetric method [19] using a X-Rite SP60 spectrometer, with standard lighting D65 and 10° observer. On this method,  $L^*$  is a measure of brightness (100=white, 0=black) and  $a^*$  and  $b^*$  of chroma ( $-a^*$ =green,  $+a^*$ =red,  $-b^*$ =blue,  $+b^*$ =yellow).

### 3. Results and discussion.

#### 3.1. The stoichiometry of the solid solution.

The powellite lattice is raised by a relatively big  $\text{Ca}^{2+}$  ion in dodecahedral coordination (Shannon-Prewitt radius: 1.26 Å) and a small  $\text{Mo}^{6+}$  in tetrahedral environment (Shannon-Prewitt radius: 0.55 Å) [20]. Considering the crystal site coordination since  $\text{Cr}^{3+}$  cannot be accommodated in cubic or tetrahedral sites the best strategy for chromium incorporation into powellite network is the replacement of  $\text{Ca}^{2+}$  or  $\text{Mo}^{6+}$  by chromium (VI) (Shannon-Prewitt radius for IV coordination: 0.40 Å) [5,12]. In order to analyse the stoichiometry of the solid solution the following samples were prepared:

(A)  $\text{Cr}_x\text{Ca}_{1-3x}\text{MoO}_4$   $x=0.075$  stoichiometry, considering the replacement of  $\text{Ca}^{2+}$  by  $\text{Cr}^{6+}$ , it supposes the formation of  $2x$  vacancies of the Ca-dodecahedral positions in powellite network.

(B)  $\text{Cr}_x\text{CaMo}_{1-x}\text{O}_4$   $x=0.075$  stoichiometry, considering the replacement of  $\text{Mo}^{6+}$  by  $\text{Cr}^{6+}$ .

The samples were synthesised using the ceramic (CE) method from  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{CaCO}_3$  and  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  as precursors, all supplied by Panreac S.A. (PA quality). The precursors were homogenised in acetone media using a planetary mill and when acetone was evaporated, the resulting powders were fired at 1000°C with a soaking time of 3 hours.

XRD (X Ray Diffraction) patterns of powders are shown in Figure 1 and UV-Vis-NIR spectra of 5 wt.% of powders added to a conventional CaO-ZnO-SiO<sub>2</sub> glaze (monoporosa glaze 1080°C) are shown in Figure 2. The CIEL $^*a^*b^*$  parameters of glazed samples are shown in Table 1.

Powders of fired A sample are colourless but B show an intense yellow colour. The XRD analysis on Fig. 1 indicates the crystallization of powellite in both powders but in the A sample, poor in calcium, peaks of very weak intensity associated to eskolaite  $\text{Cr}_2\text{O}_3$  were detected as well. When the fired powders were 5 wt.% glazed in a conventional CaO-ZnO-SiO<sub>2</sub> glaze (monoporosa glaze, 1080°C) produce wrong beige colour in A sample and intense yellow colour in B. The CIEL $^*a^*b^*$  parameters of sample B are comparable to the obtained using a commercial Pr-Zircon yellow pigment, the best yellow pigment usually used in conventional ceramics applications. The UV-Vis-NIR spectra of 5 wt.% glazed powders fired at 1000°C, in the monoporosa conventional glaze (Figure 2), show the presence of  $\text{Cr}^{3+}$  in octahedral coordination in the beige A sample, indicating that chromium is solved by the glaze [21]. The yellow sample shows a UV-Vis-NIR spectrum feature composed by a transfer band centred at 270 nm and a shoulder at 500 nm assigned to  $\text{Cr}^{6+}$  in solid solution into powellite lattice. The yellow pigment shows the minimum absorbance in the range of 550-1100 nm, similar to Pr-Zircon commercial sample (supplied by Alfarben S.A.) used as reference.

The above results indicate that the  $\text{Cr}_x\text{CaMo}_{1-x}\text{O}_4$  stoichiometry considering the replacement of  $\text{Mo}^{6+}$  by  $\text{Cr}^{6+}$  (B sample) produces the yellow pigment. The ionic radius of  $\text{Mo}^{6+}$  and  $\text{Cr}^{6+}$  are similar (Shannon-Prewitt radius for IV coordination: 0.55 Å and 0.40 Å for  $\text{Mo}^{6+}$  and  $\text{Cr}^{6+}$  respectively), allowing the solid solution of  $\text{Cr}^{6+}$  replacing  $\text{Mo}^{6+}$  in the powellite lattice.

### 3.2. Effect of the dopant concentration and temperature on the pigmenting properties.

Progressive compositions  $\text{Cr}_x\text{CaMo}_{1-x}\text{O}_4$   $x=0.075$ , 0.1 and 0.125, with stoichiometry considering the replacement of  $\text{Mo}^{6+}$  by  $\text{Cr}^{6+}$  were obtained using the same precursors and ceramic method as described in section 3.1. The powders were fired at 1000°C and successively at 1100°C with a soaking time of 3 hours.

XRD diffraction patterns of  $\text{Ca}(\text{Cr}_x\text{Mo}_{1-x})\text{O}_4$   $x=0.1$  and 0.125 powders fired at 1000°C/3h are shown in Figure 5. These diffraction patterns and its homologous for  $\text{Cr}_x\text{CaMo}_{1-x}\text{O}_4$   $x=0.075$  sample fired at 1000°C/3h presented in Fig. 1 show powellite  $\text{CaMoO}_4$  as the only detected crystalline phase.

CIEL\*a\*b\* values of glazed samples (5 wt. % of pigment addition) in a conventional  $\text{CaO-ZnO-SiO}_2$  glaze (monoporosa glaze 1080°C), are shown in Table 2. The increase of temperature produces a slight increase of the yellow shade ( $b^*$  increases) but the intensity of the colour decreases ( $L^*$  increases). The increase of chromium amount in the composition does not increase the yellow shade of the pigmented glaze, indicating that the solid solution of  $\text{Cr}^{6+}$  in powellite  $\text{Cr}_x\text{CaMo}_{1-x}\text{O}_4$  saturates at  $x=0.075$ .

The UV-Vis-NIR spectra of  $\text{Cr}_x\text{CaMo}_{1-x}\text{O}_4$   $x=0.075$ , 0.1 and 0.125 powders are shown in Figure 3. These UV-Vis-NIR spectra are similar for the three powellite samples but show higher absorption in the range of 500-600 nm than the commercial yellow of praseodymium pigment powder that gives  $L^*a^*b^*$  values of 77.9/-1.5/62 when was glazed (5 wt. % of pigment addition) in the monoporosa glaze (1080°C). The sample  $x=0.075$  shows the lowest absorption in the range of 500-600 nm among the Cr-powellite samples on Fig. 3, in agreement with saturation of the solid solution of  $\text{Cr}^{6+}$  in powellite at  $x=0.075$ .

### 3.3. Effect of the chromium precursor and mineralizer addition.

In order to analyse the effect of chromium precursor, the composition  $\text{Cr}_x\text{CaMo}_{1-x}\text{O}_4$   $x=0.075$  was prepared using the ceramic method above described and using different chromium precursors:  $\text{Cr}_2\text{O}_3$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{Cr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ . The powders were fired at 1000°C with a soaking time of 3 hours and its pigmenting properties were checked using a  $\text{Pb}_2\text{O}_3\text{-B}_2\text{O}_3\text{-2SiO}_2$  glaze (double firing borosilicate glaze, 1000°C). The CIEL\*a\*b\* measurements of the 5 wt. % powders addition in the borosilicate glaze are shown in Table 3. The results indicate that the sample with  $\text{K}_2\text{Cr}_2\text{O}_7$  potassium dichromate as precursor look slightly more yellowish (higher  $b^*$  and lower  $L^*$ ).

Halogen mineralizers addition were studied using the composition  $\text{Cr}_x\text{CaMo}_{1-x}\text{O}_4$   $x=0.075$  with the optimum  $\text{K}_2\text{Cr}_2\text{O}_7$  chromium precursor by addition of 0.2 moles of halogens per formula unit; 0.2 moles of NaF, 0.2 moles of  $\text{NH}_4\text{Cl}$  and 0.07 moles of  $\text{Na}_2\text{SiF}_6$  respectively. The powders were fired at 1000°C with a soaking time of 3 hours and their pigmenting properties were analysed using a  $\text{Pb}_2\text{O}_3\text{-B}_2\text{O}_3\text{-2SiO}_2$  glaze (double firing borosilicate glaze, 1000°C). The CIEL\*a\*b\* of the 5 wt. % powders glazed in the borosilicate glaze are shown in Table 3. The results indicate that the mineralizer addition does not improve the yellow colour. On the other hand the CIEL\*a\*b\* of both unmineralized sample and commercial Pr-Zircon increase its brightness  $L^*$  and  $b^*$  parameters when using the lead borosilicate glaze (1000°C) in respect of monoporosa

glaze checked in section 3.2. (see Table 2 and Table 3).

### 3.4. Effect of the synthesis method..

The composition  $\text{Cr}_x\text{CaMo}_{1-x}\text{O}_4$   $x=0.075$  was synthesized using a coprecipitation method (CO) starting from  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  as precursors, all supplied by Panreac S.A. The amounts of precursors in order to produce 5 g. of final product were solved in 200 ml of water and the solution was precipitated by slow addition of drops of concentrated ammonia (12%  $\text{NH}_3$  in water). A greenish-blue precipitated was obtained that produces an intense yellow powder when washed with water.

The XRD diffraction pattern of washed sample indicates the crystallization of powellite as the only crystalline phase with broad diffraction peaks (Figure 6). These washed powders are integrated by spherical particles of 5-15  $\mu\text{m}$  of size at low magnification, but these particles appears as aggregates of nanoparticles of around 200 nm of diameter at high magnification (Figure 7). When washed powder was 5 wt. % added in a borosilicate glaze  $\text{Pb}_2\text{O}_3\text{-B}_2\text{O}_3\text{-2SiO}_2$  (1000°C) it does not produce yellow colour. Nanoparticles of raw yellow powder were solved by the glaze.

The unwashed powder was fired successively at 850, 900, 950 and 1000°C with a soaking time of 3 hours. The XRD pattern of sample fired at 1000°C is shown in Figure 6 and only indicates the presence of powellite with sharp diffraction peaks. This powder was integrated by compact particles of 3  $\mu\text{m}$  of size (Figure 7). On the other hand its homologous CE sample shows bigger particles in the range of 2-15  $\mu\text{m}$  and its composition appears homogeneous (Fig. 8). The CIEL\*a\*b\* parameters of the glazed powders (5 wt. % of addition) in the monoporosa glaze (1080°C) are shown in Table 4: the L\* intensity of glazed samples improve slightly with temperature and the green component a\* diminishes with temperature, at 950°C it is obtained the higher yellow parameter b\* (57.4) that improves the best valor obtained in monoporosa glaze using CE powders (53.2 at 1000°C  $x=0.075$ ) and it is similar to yellow of praseodymium glazed in the monoporosa glaze ( $b^*=62$ ).

The images and the UV-Vis-NIR spectra of  $\text{Ca}(\text{Cr}_x\text{Mo}_{1-x})\text{O}_4$   $x=0.075$  coprecipitated powder fired at 1100°C/3h glazed in monoporosa glaze are compared with the glazed commercial Pr-Zircon sample in the same glaze on Figure 9 and 10 respectively; the absorption in the range of 500-600 nm is very similar in both samples (in CE samples the absorbance is lower than Pr-Zircon), indicating that a similar yellow colour is obtained.

### 3.5. Comparison between Cr-Powellite and Pr-Zircon yellow ceramic pigments.

In order to compare the colour yield as ceramic pigments of Cr-Powellite ( $\text{Ca}(\text{Cr}_x\text{Mo}_{1-x})\text{O}_4$   $x=0.075$  obtained from potassium dichromate by CE method) and a commercial Pr-Zircon yellow ceramic pigments (Alfarben S.A), its CIEL\*a\*b\* parameters in four conventional ceramic glazes (5 wt. % addition) are summarized in Table 5. The results indicate that Cr-Powellite and Pr-Zircon yellow ceramic pigments show similar values even though Pr-Zircon look slightly more yellowish (higher b\* and lower L\*) and less greenish (higher negative a\*).

But in order to consider pros and cons, looking at a possible industrial application, not only the positive results should be emphasized. In particular, there are two important



issues that could make questionable the claim that powellite might be an alternative to Pr-zircon: a) health issues:  $\text{Cr}^{6+}$  is highly toxic and moreover easily mobilized, b) environmental issues such as the extent  $\text{Cr}^{6+}$  can be leached.

In order to analyse the above issues, a leaching study was carried out for both Cr-Powellite and the commercial Pr-Zircon yellow ceramic pigments compared in Table 5. The commercial Pr-Zircon yellow ceramic pigment was obtained at 1000°C starting from quartz, zirconia and  $\text{Pr}_6\text{O}_{11}$  as precursors and a mixture of NaF and NaCl added as mineralizer agent (12 wt. %). 1 g of fired pigment placed in a funnel was carefully washed with water until obtaining 100 ml of leaching water. The electrical conductivity, the Cr amount (in Cr-Powellite sample) and the fluoride amount (in Pr-Zircon sample) were measured in the leaching water. The results are summarized in Table 6. Electrical conductivity was measured at 20°C using a CRISON 540 conductivity meter, the chromium amount was measured by colorimetric determination as dichromate ion in the acidified water (adding 10 ml of  $\text{HNO}_3$  0.3M) at 350 nm, finally the fluoride determination was carried out using a fluoride selective electrode (a lanthanum fluoride electrode, doped with europium supplied by CRISON).

The leaching water of Cr-Powellite was yellow colored and the one of Pr-Zircon colorless. In agreement with the results shown in Table 6, the electrical conductivity of the leaching water in Cr-Powellite is higher than in Pr-Zircon. The electrical conductivity of leaching water of Cr-Powellite starting from eskolaite  $\text{Cr}_2\text{O}_3$  precursor (avoiding the potassium release when potassium dichromate is used) is lower (350  $\mu\text{S}$ ). The  $\text{Cr}^{6+}$  is significantly released from the Cr-Powellite pigment and the leaching water should be treated as in other industrial ceramic pigments that present chromium in its composition [11,21]. The usual industrial remediation strategy utilizes reduction reaction of Cr(VI) to Cr(III), an electron donor that commonly drives this reaction is Fe(II). Cr(VI) is far more mobile than Cr(III) and more difficult to remove from water. It is also the toxic form of Cr, approximately 10 to 100 times more toxic than Cr(III) by the acute oral route, presumably owing to the stronger oxidizing potential and membrane transport of Cr(VI). The EPA (U.S. Environmental Protection Agency) classifies Cr(VI) as a known human carcinogen via inhalation, but classify Cr(III) as not known to cause cancer [22]. On the other hand, the observation of a homogeneous composition throughout the samples (see Figures 7 and 8) suggests an ideal solid solution behaviour beneficial for the immobilization of Cr (VI) in powellite lattice which is considered in literature for the immobilization of radionuclides in a waste repository scenario [5]. On the other hand the release of fluoride from the commercial Pr-Zircon is high as well. The toxicity of fluoride at concentration higher than 2 ppm has been supported by documentary evidence. In our body fluoride has the same natural affinity for calcium as it does in the environment and will form preferentially with calcium over all other cations likewise calcium will form preferentially with fluorides over all other anions leading to its health hazard. Attacking bone structure fluoride will leave our bones a weak porous mass; in our blood stream fluorides will rapidly tie up the free calcium electrolytes leading to rapid heart failure. Fluorides can be removed from industrial wastewater streams by precipitation as calcium fluoride ( $\text{CaF}_2$ ) but other methods such as ion exchange, membrane and adsorption are available [23]. Although both wastewater released from Cr-Powellite and Pr-Zircon should be treated, however the release and possible mobilization of the Cr (VI) should be controlled in order to its industrial implementation.

## 7. Conclusions.



From the above discussion the following conclusions can be pointed out:

a) A new chromium doped powellite ( $\text{Cr-CaMoO}_4$ ) yellow ceramic pigment alternative to yellow of praseodymium-zircon has been obtained based on  $\text{Cr}_x\text{CaMo}_{1-x}\text{O}_4$  solid solution of  $\text{Cr}^{6+}$  substituting  $\text{Mo}^{6+}$  in the powellite lattice.

b) Following a solid state reaction method (ceramic method) the composition  $\text{Cr}_x\text{CaMo}_{1-x}\text{O}_4$   $x=0.075$  using  $\text{K}_2\text{Cr}_2\text{O}_7$  or  $\text{Cr}_2\text{O}_3$  as chromium precursor fired at 1000-1100°C produces yellow colour with slightly less intensity than a commercial praseodymium-zircon yellow pigment in different glazes such as: double firing borosilicate (1000°C), single firing monoporosa (1080°C) or single firing porcelainised stoneware (1200°C).

b) Using an ammonia coprecipitation method and firing at 950°C, a yellow ceramic pigment is obtained that 5% added and fired in a conventional  $\text{CaO-ZnO-SiO}_2$  glaze (monoporosa glaze 1080°C) show a yellow colour similar to the commercial praseodymium-zircon yellow pigment.

c) ( $\text{Cr-CaMoO}_4$ ) yellow ceramic pigment release  $\text{Cr}^{6+}$  when washed, and the leaching water should be treated as in other industrial ceramic pigments which present chromium in its composition. The observation of a homogeneous composition throughout the samples suggests an ideal solid solution behavior beneficial for the immobilization of Cr (VI) in powellite lattice which is considered in literature for the immobilization of radionuclides in a waste repository scenario. However the release and possible mobilization of the Cr (VI) should be controlled in order to get its industrial implementation.

**Acknowledgements:** Authors acknowledge the financial support given by MEC (MAT2012-36988-C02-01 project).

## REFERENCES

1. F.J. Manjon, D. Errandonea, Pressure-induced structural phase transitions in materials and Earth sciences. *Physica Status Solidi* 246 (2009) 9–3.
2. R.M. Hazen, L.W. Finger, J.E.E. Mariathasan, High-pressure crystal chemistry of scheelite-type tungstates and molybdates, *Journal of Physics and Chemistry of Solids*, 46, 2 (1985) 253–263.
3. L. E. Depero, L. Sangaletti, Cation Sublattice and Coordination Polyhedra in  $\text{ABO}_4$  Type of Structures, *J. Solid State Chem.* 129 (1997) 82-91.
4. G.M. Wolten, A.B. Chase, Synthetic fergusonites and a new polymorph of yttrium tantalate. *American Mineralogist* 52 (1967) 1536–1541.
5. M. Schmidt, S. Heck, D. Bosbach, S. Ganschow, C. Walther, T. Stumpf, Characterization of powellite-based solid solutions by site-selective time resolved laser fluorescence spectroscopy, *Dalton Trans.*, 42 (2013) 8387-8393
6. C. Cascales, J.A. Alonso, I. Rasines, The new pyrochlores  $\text{Pb}_2(\text{MSb})\text{O}_{6.5}$  ( $\text{M}=\text{Ti}$ ,  $\text{Zr}$ ,  $\text{Sn}$ ,  $\text{Hf}$ ), *J. Mater. Sci. Lett.* 1986, 5, 675-677.
7. J. Dik, Scientific analysis of historical paint and the implications for art history and art conservation: the case studies of Naples yellow and discoloured smalt, Thesis, Faculty of Sciences, University of Amsterdam, 2003, p. 115–120.
8. P.P. Budnikov, A.M. Ginstling, K. Shaw, In *Principles of Solid State Chemistry*, Elsevier Science, 1968.

9. C.A. Seabright , Blue turquoise, Ceramic Pigments, U.S. patent, 2,441,407, May 1948.
10. C.A. Seabright , Yellow of Praseodymium, US Pat. 2,992,123, July 11, 1961.
11. (a) CPMA Classification and chemical description of the complex inorganic color pigments, fourth ed. Alexandria, Dry Color Manufacturers Association, 2010. (b) DCMA Safe Handling of Color Pigments, Color Pigments Manufacturers Association Inc., 300 North Washington Street, Suite 102, Alexandria, 1993.
12. L. H. Brixner, Preparation and Properties of Some Novel Rare Earth Compounds of the Types  $\text{LnTi}_{0.5}\text{Mo}_{0.5}\text{O}_4$  and  $\text{LnTi}_{0.5}\text{W}_{0.5}\text{O}_4$ , *Inorg. Chem.*, 3 (4) (1964) 600–602.
13. A. Eremin, G. Kuzmicheva, E. Zharikov, Compounds  $\text{AMO}_4$  ( $\text{A} = \text{Ca}, \text{Sr}, \text{Ba}; \text{M} = \text{W}, \text{Mo}$ ) with scheelite structure: growth, composition, structure peculiarities, *Acta Cryst.* 63 (2007) 275-278.
14. P. Wood, F.P Glasse, Preparation and properties of pigmentary grade  $\text{BiVO}_4$  precipitated from aqueous solution, *Ceramics International*, 30 (2004) 875-882.
15. R. Sullivan, Bismuth vanadate modified pigments in monoclinic crystalline form, European Patent Application EP0443981
16. M. Gotić, S. Musić, M. Ivanda, M. Šoufek, S. Popović, Synthesis and characterisation of bismuth(III) vanadate, *J. of Molecular Structure*, 744-747 (2005) 535-540.
17. G. Gioble , L. Sandhya Kumari, V.S. Vishnu, Synthesis and characterization of environmentally benign calcium-doped  $\text{Pr}_2\text{Mo}_2\text{O}_9$  pigments: Applications in coloring of plastics, *J. of Solid State Chem.*, 181 (2008) 487-489.
18. R. Galindo, C. Gargori, M. Llusar, A. García, J. Badenes, G. Monrós, Ecopigmentos cerámicos verdes y amarillos de  $\text{Pr}_2\text{Mo}_2\text{O}_9$  dopados con calcio obtenidos en presencia de mineralizadores y por coprecipitación química. *Bol. Soc.Esp. Ceram Vidrio.*, 29 (2011) 219-228.
19. CIE Comission International de l'Eclairage, Recommendations on Uniform Color Spaces, Color Difference Equations, Psychometrics Color Terms. Supplement n° 2 of CIE Pub. N° 15 (E1-1.31) 1971, Bureau Central de la CIE, Paris (1978).
20. Shannon, R. D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, *Acta Cryst.* A32 (1976) 751-757.
21. G. Monrós, H. Pinto, J. Badenes, M. Llusar, M.A. Tena, Chromium (IV) stabilisation in new ceramic matrices by coprecipitation method: application as ceramic pigments, *Z. Anorg. Allg. Chem.* 631 (2005) 2131-2135.
22. E. L. Hawley, R. A. Deeb, M. C. Kavanaugh and J. Jacobs R.G, in *Chromium(VI) Handbook* (2004), Chap. 8. Treatment Technologies for Chromium(VI).
23. B. Grzmil, J. Wronkowsky, Removal of phosphates and fluorides from industrial wastewater, *Desalinitation* 189 (2006) 261-269.

**Table 1.** CIEL\*a\*b\* parameters of the 5 wt. %. glazed powders in the monoporosa glaze (1080°C) described in section 3.1.

Sample	L*a*b*
A	60.4/-2.5/16.3
B	74.4/-0.3/53.2
Pr-Zircon	77.9/-1.5/62

**Table 2.** CIEL\*a\*b\* values of powders described in section 3.2.

Temperature (°C)	x=0.075	x=0.1	x=0.125	Commercial Pr-Zircon
1000	73.3/0/52.5	72.6/-0.2/49.7	73.7/-1/47.9	77.9/-1.5/62
1100	75/0.1/53.2	75.7/-0.4/54	74.6/0.7/51.3	-

**Table 3.** CIEL\*a\*b\* parameters of the 5 wt. %. glazed powders in the borosilicate glaze (1000°C) described in section 3.3.

Sample	L*a*b*
<b>Cr-precursor</b>	
Cr <sub>2</sub> O <sub>3</sub>	81.3/-4.7/56.9
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	79.4/-2.3/60
Cr(NO <sub>3</sub> ) <sub>3</sub> ·4H <sub>2</sub> O.	82.5/-2.5/55.6
<b>Mineralizer</b>	
NaF	81.3/-3.8/44.2
NH <sub>4</sub> Cl	80.5/-4.8/56.2
NaSiF <sub>6</sub>	81.2/-3.9/44.2
<b>Commercial Pr-Zircon</b>	77.2/0.1/63.7

**Table 4.** CIEL\*a\*b\* parameters of the 5 wt. % glazed in the monoporosa glaze samples of  $\text{Cr}_x\text{CaMo}_{1-x}\text{O}_4$   $x=0.075$  powders prepared by the coprecipitation method (CO).

T(°C)	L*a*b*
850	79,9/-4,6/53,2
900	79,4/-3,6/56,8
950	78,2/-2,1/57,4
1000	77,6/-1,5/56,8

**Table 5.** Summary of CIEL\*a\*b\* parameters of  $\text{Cr}_x\text{CaMo}_{1-x}\text{O}_4$   $x=0.075$  Cr-Powellite pigment obtained by CE method and a commercial Pr-Zircon ceramic pigment glazed in different glazes.

	Cr-Powellite	Pr-Zircon
powder	73.3/0/52.5	77.9/-1.5/62
borosilicate glaze (double firing 1000°C)	79.4/-2.3/60	77.2/0.1/63.7
monoporosa glaze (single firing 1080°C)	74.4/-0.3/53.2	77.9/-1.5/62
porcelainised stoneware glaze (single firing 1200°C)	78.6/-3.9/41.9	78.5/-3.0/42.5

**Table 6.** Electrical conductivity, Cr amount (in Cr-Powellite) and fluoride amount (in Pr-Zircon) in leaching water (100 ml/g).

	Cr-Powellite	Pr-Zircon
Conductivity ( $\mu\text{S}$ )	1368	865
Cr (mg/g) and (wt.% leached)	11.9	-
F (mg/g) and (wt.% leached)	-	18.4

## FIGURE CAPTIONS

**Figure 1.** XRD diffractogrammes of powders fired at 1000°C: (A)  $\text{Cr}_x\text{Ca}_{1-3x}\text{MoO}_4$   $x=0,075$ , and (B)  $\text{Cr}_x\text{CaMo}_{1-x}\text{O}_4$   $x=0,075$ . CRYSTALLINE PHASES: P (powellite  $\text{CaMoO}_4$ , blue), C (eskolaite  $\text{Cr}_2\text{O}_3$ , red).

**Figure 2.** UV-Vis-NIR spectra of 5 wt.% powders fired at 1000°C glazed in monoporosa glaze (1080°C) compared with the spectrum of Pr-Zircon commercial yellow pigment (Pr-Z): (A)  $\text{Cr}_x\text{Ca}_{1-3x}\text{MoO}_4$   $x=0,075$  and (B)  $\text{Cr}_x\text{CaMo}_{1-x}\text{O}_4$   $x=0,075$

**Figure 3.** UV-Vis-NIR spectra of  $\text{Cr}_x\text{CaMo}_{1-x}\text{O}_4$  powders fired at 1100°C/3h.

**Figure 4.** UV-Vis-NIR spectra of  $\text{Ca}(\text{Cr}_x\text{Mo}_{1-x})\text{O}_4$   $x=0,125$  glazed sample in monoporosa glaze fired at 1100°C/3h compared with a commercial Pr-Zircon commercial pigment in the same glaze.

**Figure 5.** XRD diffraction patterns of  $\text{Ca}(\text{Cr}_x\text{Mo}_{1-x})\text{O}_4$  samples fired at 1000°C/3h. CRYSTALLINE PHASES: P (Powellite  $\text{CaMoO}_4$ ).

**Figure 6.** XRD diffraction patterns of CO raw powders  $(\text{Cr}_x\text{Ca}_{1-x})\text{MoO}_4$   $x=0,075$  fired at 1000°C/3h. CRYSTALLINE PHASES: P (Powellite  $\text{CaMoO}_4$ ).

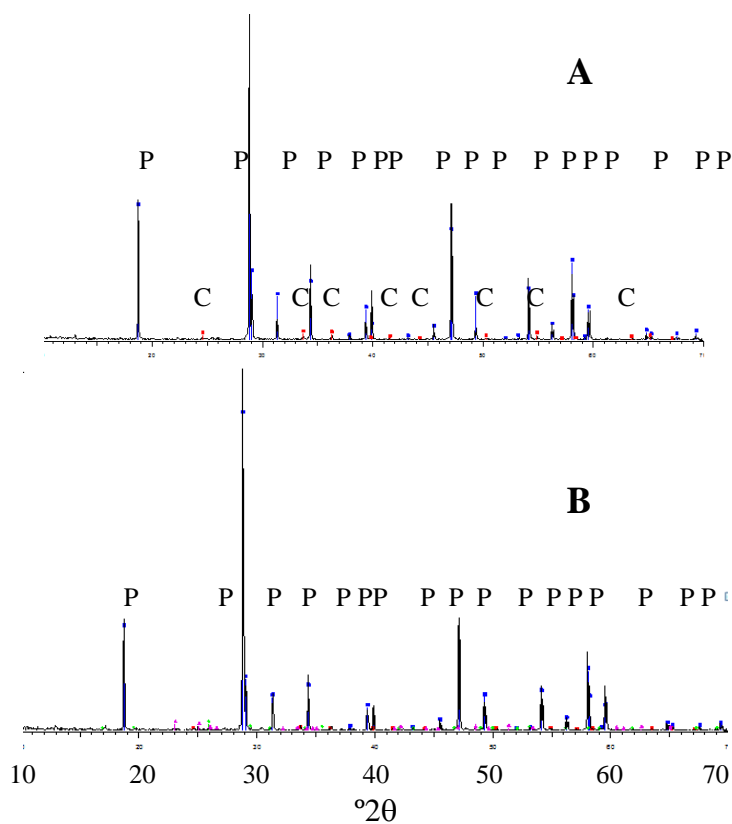
**Figure 7.** SEM micrographs of  $(\text{Cr}_x\text{Ca}_{1-x})\text{MoO}_4$   $x=0,075$  CO washed powders.

**Figure 8.** SEM micrographs of  $(\text{Cr}_x\text{Ca}_{1-x})\text{MoO}_4$   $x=0,075$  CE powders fired at 1000°C/3h and mapping of composition of Ca, Cr and Mo.

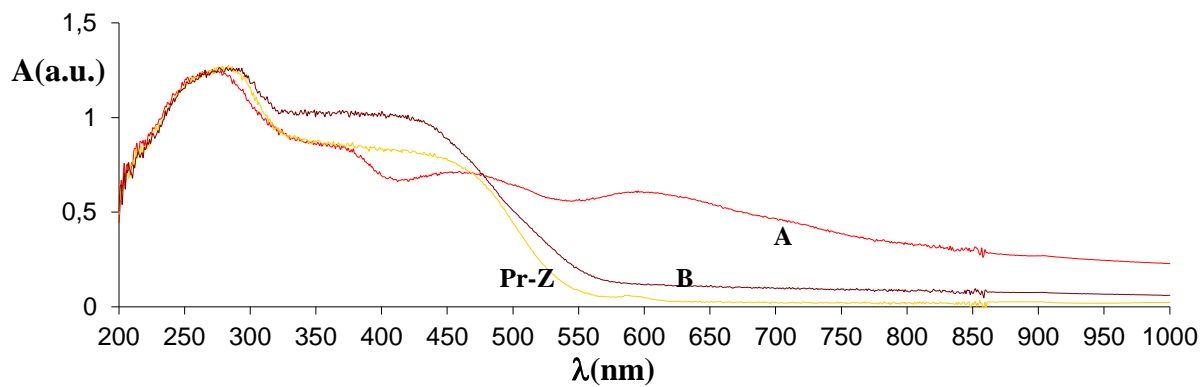
**Figure 9.** Images of 5 wt.% glazed powders in a conventional  $\text{CaO-ZnO-SiO}_2$  glaze (monoporosa glaze 1080°C): (a) Commercial Pr-Zircon, (b)  $\text{Ca}(\text{Cr}_x\text{Mo}_{1-x})\text{O}_4$   $x=0,075$  coprecipitated sample fired at 1000°C/3h and glazed in monoporosa glaze.

**Figure 10.** UV-Vis-NIR spectra of  $\text{Ca}(\text{Cr}_x\text{Mo}_{1-x})\text{O}_4$   $x=0,075$  coprecipitated sample (CO) fired at 1000°C/3h and glazed in monoporosa glaze compared with a commercial Pr-Zircon sample in the same glaze.

**Figure 1.** XRD diffractogrammes of powders fired at 1000°C: (A)  $\text{Cr}_x\text{Ca}_{1-3x}\text{MoO}_4$   $x=0,075$ , and (B)  $\text{Cr}_x\text{CaMo}_{1-x}\text{O}_4$   $x=0,075$ . CRYSTALLINE PHASES: P (powellite  $\text{CaMoO}_4$ , blue), C (eskolaite  $\text{Cr}_2\text{O}_3$ , red).

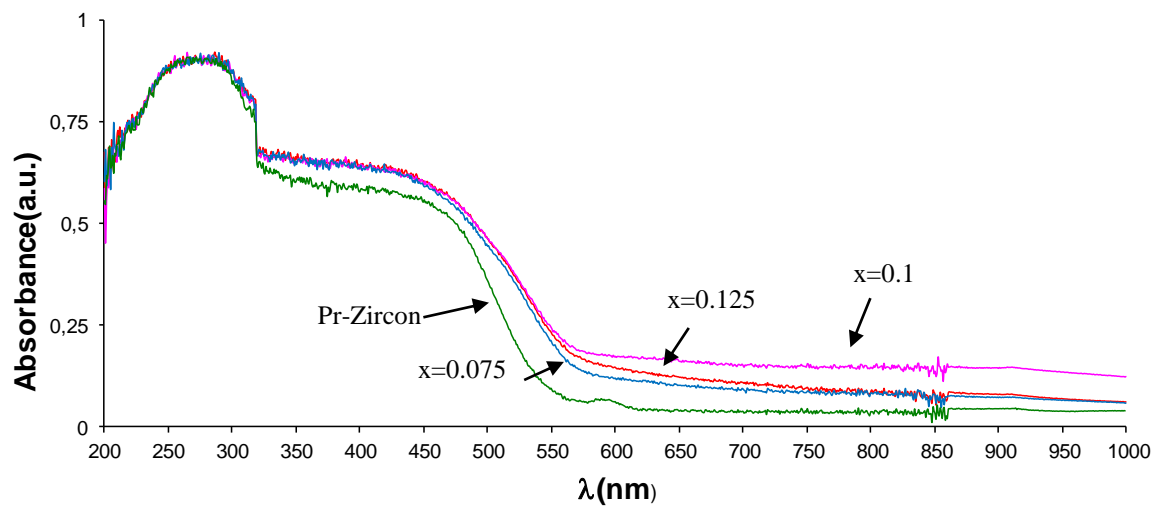


**Figure 2.** UV-Vis-NIR spectra of 5 wt.% powders fired at 1000°C glazed in monoporosa glaze (1080°C) compared with the spectrum of Pr-Zircon commercial yellow pigment (Pr-Z): (A)  $\text{Cr}_x\text{Ca}_{1-3x}\text{MoO}_4$   $x=0,075$  and (B)  $\text{Cr}_x\text{CaMo}_{1-x}\text{O}_4$   $x=0,075$ .

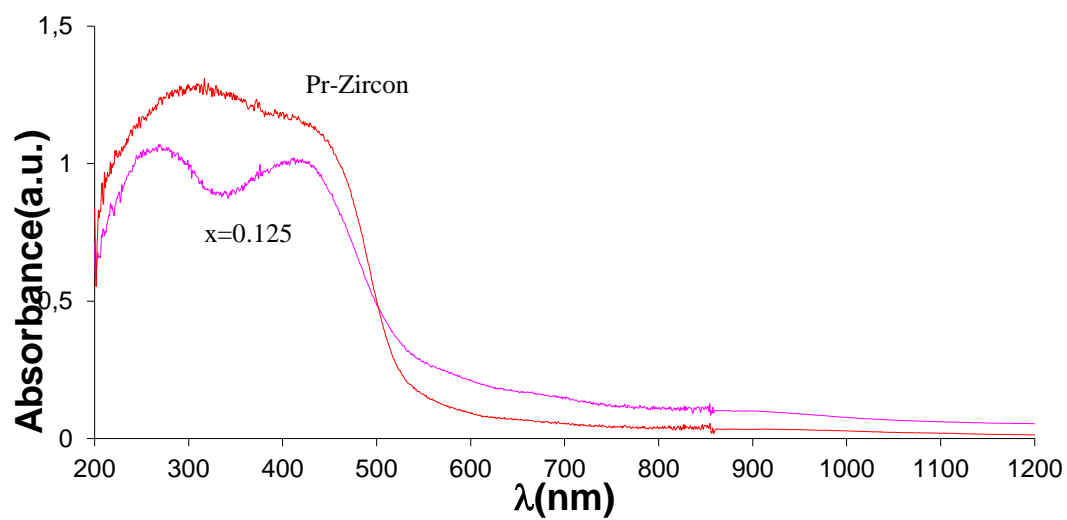




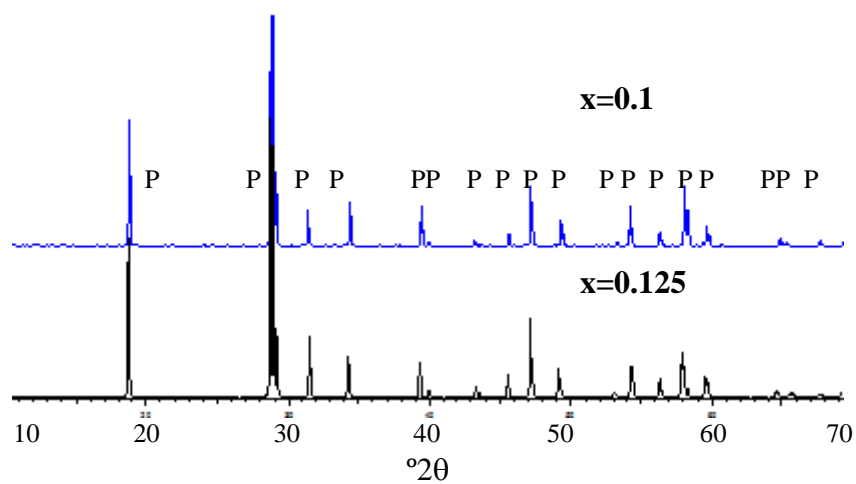
**Figure 3.** UV-Vis-NIR spectra of  $\text{Cr}_x\text{CaMo}_{1-x}\text{O}_4$  powders fired at  $1100^\circ\text{C}/3\text{h}$ .



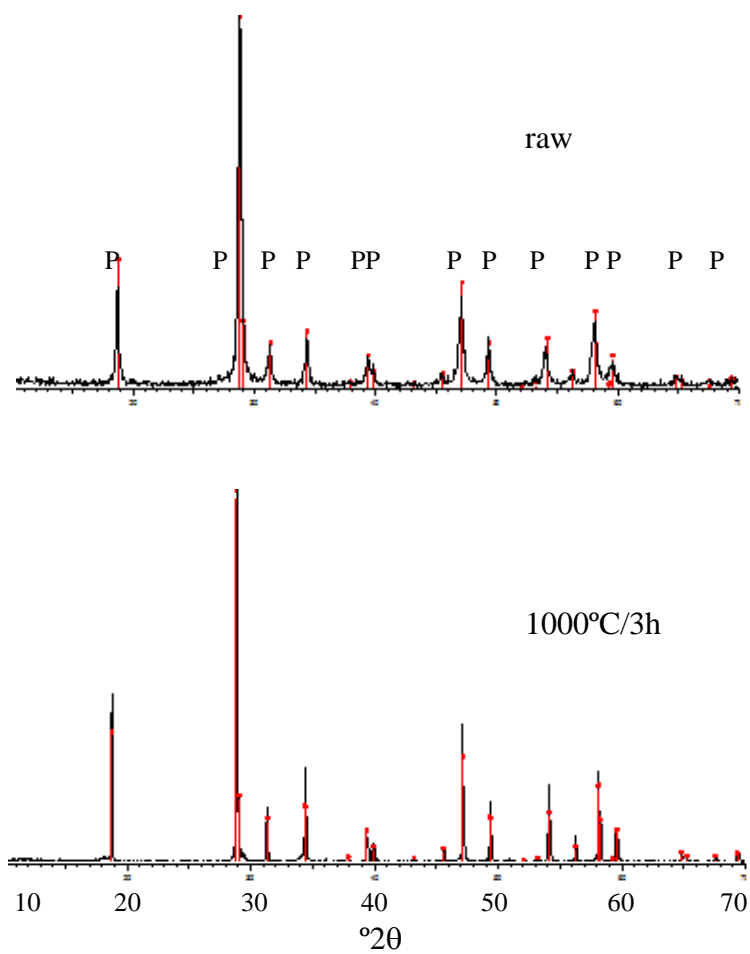
**Figure 4.** UV-Vis-NIR spectra of  $\text{Ca}(\text{Cr}_x\text{Mo}_{1-x})\text{O}_4$   $x=0.125$  glazed sample in monoporosa glaze fired at  $1100^\circ\text{C}/3\text{h}$  compared with a commercial Pr-Zircon commercial pigment in the same glaze.



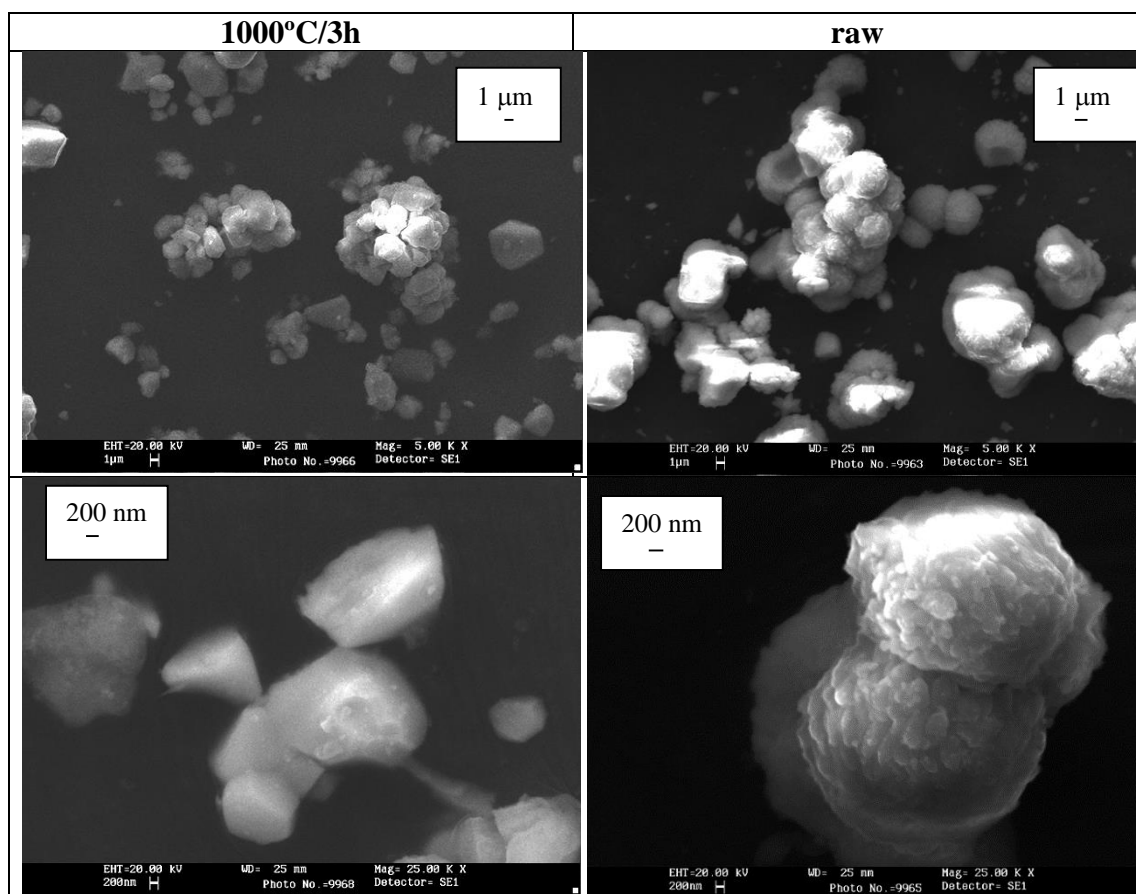
**Figure 5.** XRD diffraction patterns of  $\text{Ca}(\text{Cr}_x\text{Mo}_{1-x})\text{O}_4$  samples fired at  $1000^\circ\text{C}/3\text{h}$ .  
CRYSTALLINE PHASES: P (Powellite  $\text{CaMoO}_4$ ).



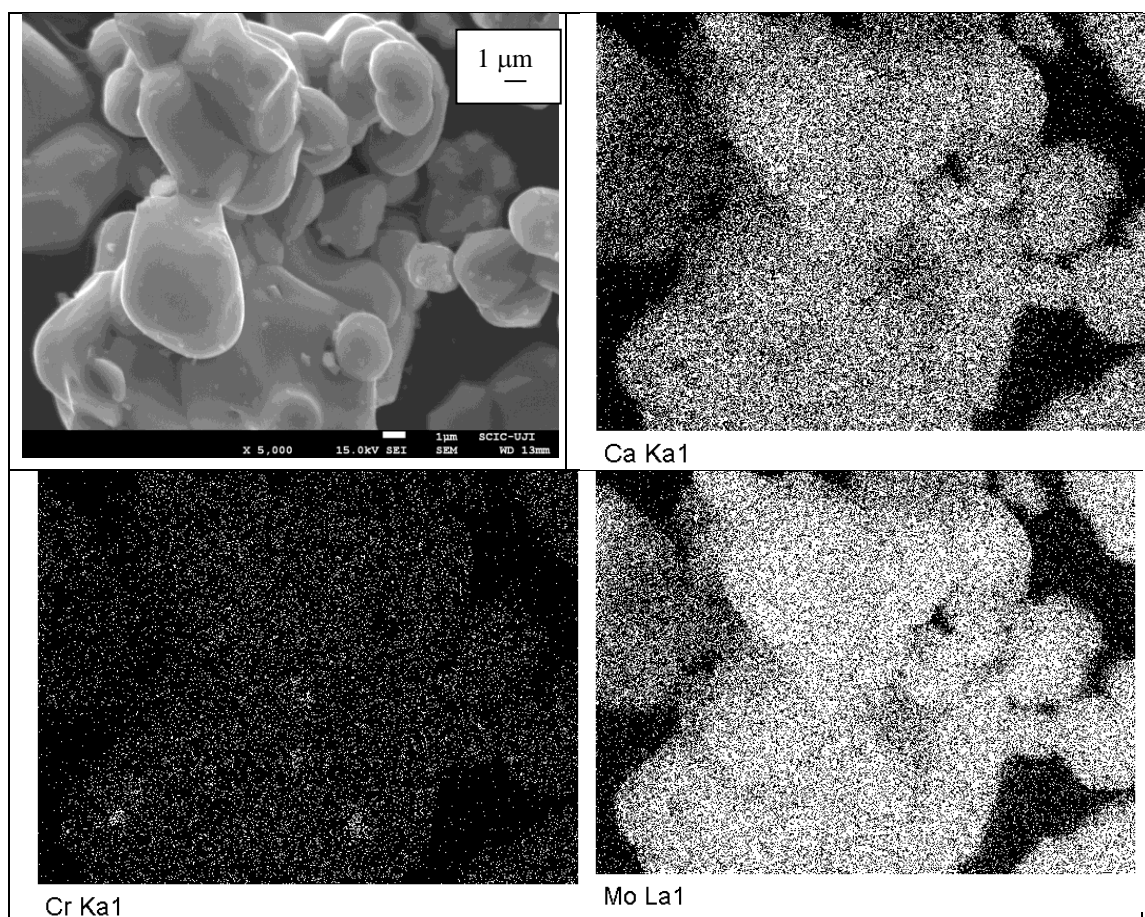
**Figure 6.** XRD diffraction patterns of CO raw powders  $(\text{Cr}_x\text{Ca}_{1-x})\text{MoO}_4$   $x=0,075$  fired at  $1000^\circ\text{C}/3\text{h}$ . CRYSTALLINE PHASES: P (Powellite  $\text{CaMoO}_4$ ).



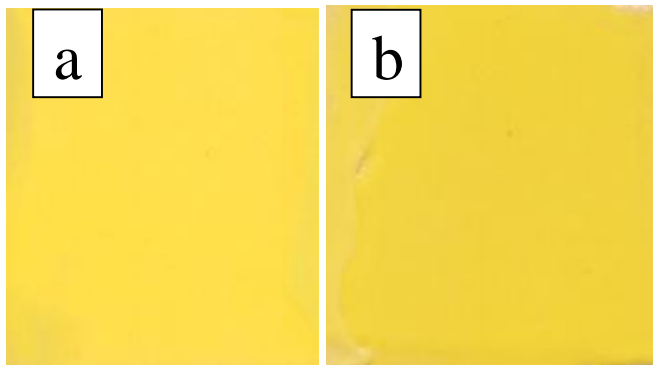
**Figure 7.** SEM micrographs of  $(\text{Cr}_x\text{Ca}_{1-x})\text{MoO}_4$   $x=0,075$  CO washed powders.



**Figure 8.** SEM micrographs of  $(\text{Cr}_x\text{Ca}_{1-x})\text{MoO}_4$   $x=0,075$  CE powders fired at  $1000^\circ\text{C}/3\text{h}$  and mapping of composition of Ca, Cr and Mo.



**Figure 9.** Images of 5 wt.% glazed powders in a conventional CaO-ZnO-SiO<sub>2</sub> glaze (monoporosa glaze 1080°C): (a) Commercial Pr-Zircon, (b) Ca(Cr<sub>x</sub>Mo<sub>1-x</sub>)O<sub>4</sub> x=0.075 coprecipitated sample fired at 1000°C/3h and glazed in monoporosa glaze.





**Figure 10.** UV-Vis-NIR spectra of  $\text{Ca}(\text{Cr}_x\text{Mo}_{1-x})\text{O}_4$   $x=0.075$  coprecipitated sample (CO) fired at  $1000^\circ\text{C}/3\text{h}$  and glazed in monoporosa glaze compared with a commercial Pr-Zircon sample in the same glaze.

