

New chromium-calcium titanate red ceramic pigment.

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Abstract: synthesis and characterization of a new chromium- calcium titanate red ceramic pigment is described in this communication. The pigment is based on the solid solution of chromium (IV) in calcium titanate and was characterized as red-brown pigment in a CaO-ZnO-SiO₂ transparent glaze used for ceramic tiles (1080°C). XRD, UV-Vis-NIR spectroscopy and CIE-L*a*b* techniques of characterization have been employed. The L*a*b* valour of the optimal pigment with 0,015 mol/mol of chromium fired at 1100°C with a soaking time of 3 hours and 5% weight added to the transparent glaze is 59.3/12.5/9.5. Likewise 5%w. addition of NHCl used as flux agent increase b* and decrease L* valour (L*a*b*=45.2/15.3/5.3).

Introduction.

Perovskite ABO₃ is an ideally cubic phase, but really becomes a rhombic syngony. A cation (Ca²⁺, Sr²⁺, Cd²⁺, Ba²⁺, Ni²⁺, Co²⁺) ideally occupies vertex of cube, B cation (Ti⁴⁺, Zr⁴⁺, Sn⁴⁺) the centre and oxygens occupy face centres. Several authors have studied perovskite as ceramic pigment structure:

(i) R.A. Eppler (1) develops black pigments from (Sr,Ca)MnO₃ perovskites using oxides and carbonates mixed with conventional mineralizers fired at 730°C with soaking time of 3 hours.

(ii) I. V. Pishch I y E. V. Radion (2) applies the (NiCa)TiO₃ perovskite as yellow pigment and (CoCa)TiO₃ as brown-turkish colorations using precipitation synthesis methods. Yellowish intensification when Ni increase is associated to a shifting of Ni(II) bands absorption in octahedral coordination. Yellow application is limited and cobalt based pigment is really a solution colorant. Likewise these authors use MTiO₃ and MZrO₃ (M=Ca, Sr, Cd, Zn) perovskites obtained from alkaline precipitation with 1M NaOH 1M as white ceramic pigments (3).

(iii) M. Jansen y H. P. Letschert (4) pose an alternative to cadmium sulfoselenide included into zircon pigment based on nitride solid solutions CaTaO_{2+x}N_{1-x} and LaTaO_{2+x}N_{1-x} that change from yellow to orange and red, in function of N amount in perovskite solid solution (as cadmium sulfoselenide in zircon in function of Cd amount). Cadmium sulfoselenide in zircon pigment does not show toxicity due to their low solubility, but it may promote biodisposal cadmium when is deposited as waste or incinerated, is for that because their use has been restricted. Although the use of cadmium sulfoselenide included into zircon pigment, may be considered sure from recently studies, there is high interest to dispose an alternative. Rare earth presence on perovskites is not a problem, but oxynitride synthesis, by ammonolysis of oxide mixture at high temperature and soaking times, is more complicated than for cadmium sulfoselenide in zircon pigment, and stability on ceramic matrices and glazes is lower than cadmium-zircon pigment also, but it is a stable alternative for polymer colouration (5).

Young-II Kim et al. (6) study crystallographic features of AMo_2N ($A = Ba, Sr, Ca; M = Ta, Nb$) oxynitride perovskites: $BaTaO_2N$ structure becomes cubic (distance $Ta-O/N=2.056$ Å), $SrTaO_2N$ and $CaTaO_2N$ show octahedral distortion showing lower distances $Ta-O/N=2.02$ Å. Nb oxynitrides are isostructural with above homologous Ta perovskites with $Nb-O/N$ distances slightly higher. Estimated band-gap from diffuse reflectance studies are: $BaTaO_2N$, 1.8 eV; $SrTaO_2N$, 2.1 eV; $CaTaO_2N$, 2.4 eV; $BaNbO_2N$, 1.8 eV; $SrNbO_2N$, 1.9 eV; $CaNbO_2N$, 2.1 eV. Impedance spectroscopy and electric transport measurements indicates that $BaNbO_2N$ shows metallic conductivity (probably by reduction during sintering) instead tantalates are semiconductors. Likewise, F. Chevire et al. (7) studied optical properties of $La_{1-x}A_xTiO_{2+x}N_{1-x}$ ($A = Sr, Ba$) systems obtained by ammonolysis at 950°C from fused salts as precursors.

(iv) E. Stobierska et al (8) y F. Matteucci et al. (9) obtain Cr and other chromophores doped $YAlO_3$ and characterize their performance in several ceramic matrices and glazes.

This document describes the synthesis and characterization of a new red ceramic pigment based on chromium doped calcium titanate perovskite.

Experimental.

Red ceramic pigments based on $(Cr_xCa_{1-x})TiO_3$ $x = 0.005, 0.01, 0.015, 0.02$ and 0.04 perovskite have been prepared by ceramic method using $Cr_2O_3, CaCO_3, TiO_2$ (anatase) as precursors supplied by PANREAC S.A. (quality analysis). Precursors were milled in acetone media and dried.

Dried powders where successively fired at 1000, 1100 and 1200°C during 3 hours of soaking time and obtained powders were 5% enamelled in a conventional glaze (1080°C). Samples were characterized by several techniques:

(a) DRX analysis carried out on a Siemens D5000 diffractometer using $Cu K_{\alpha}$ radiation, $20^{\circ}-70^{\circ} 2\theta$ range, scan rate $0.05^{\circ}2\theta/s$, 10 s per step and 40 kV and 20 mA conditions, show that perovskite is the only crystalline phase detected (Fig. 1).

(b) 5% weight enamelled samples in a conventional glaze (1080°C) show the visual red-brown colour associated to $CIEL^*a^*b^*$ colour measurements (Table 1), which were measured following the CIE (Commission International de l'Eclairage) colorimetric method using a Perkin-Elmer spectrophotometer, with standard lighting C. On this method, L^* is a measure of brightness (100=white, 0=black) and a^* and b^* of chroma ($-a^*=green, +a^*=red, -b^*=blue, +b^*=yellow$). From Table 1 can be stated that $x=0.05$ sample produces the best red shade (higher a^* and lower L^*).

(d) UV-Vis-NIR spectroscopy of enamelled samples, collected using a Lambda 2000 spectrometer supplied by Perkin Elmer through diffuse reflectance technique, show bands associated to Cr^{4+} along with Cr^{3+} both in octahedral coordination but Cr^{4+} ion acts as red chromophore agent associated with 520 nm absorption band (Figure 2) (10,11). The general absorption feature of samples shown in Fig. 2 indicates that temperature and chromium amount increase slightly the intensity of absorption but not the bands position.

The optimal pigmenting sample $x=0.015$ were modified by addition of 5%w of three different flux agents: $NaNO_3$ (m.p. 308°C, b.p 380°C, decomposes), NH_4Cl (m.p.338°C, decomposes) and NaF (m.p. 993°C). The $CIEL^*a^*b^*$ valours measured in 5%w. glazed samples fired at 1100°C were 73.4/9.3/14.7 ($NaNO_3$), 55.6/13.9/9.6 (NaF) and 45.2/15.3/5.3 (NH_4Cl) respectively, indicating that NH_4Cl mineralizer increase significantly the red shade ($b^*=15,3$) and also the colour intensity ($L^*=45.2$)

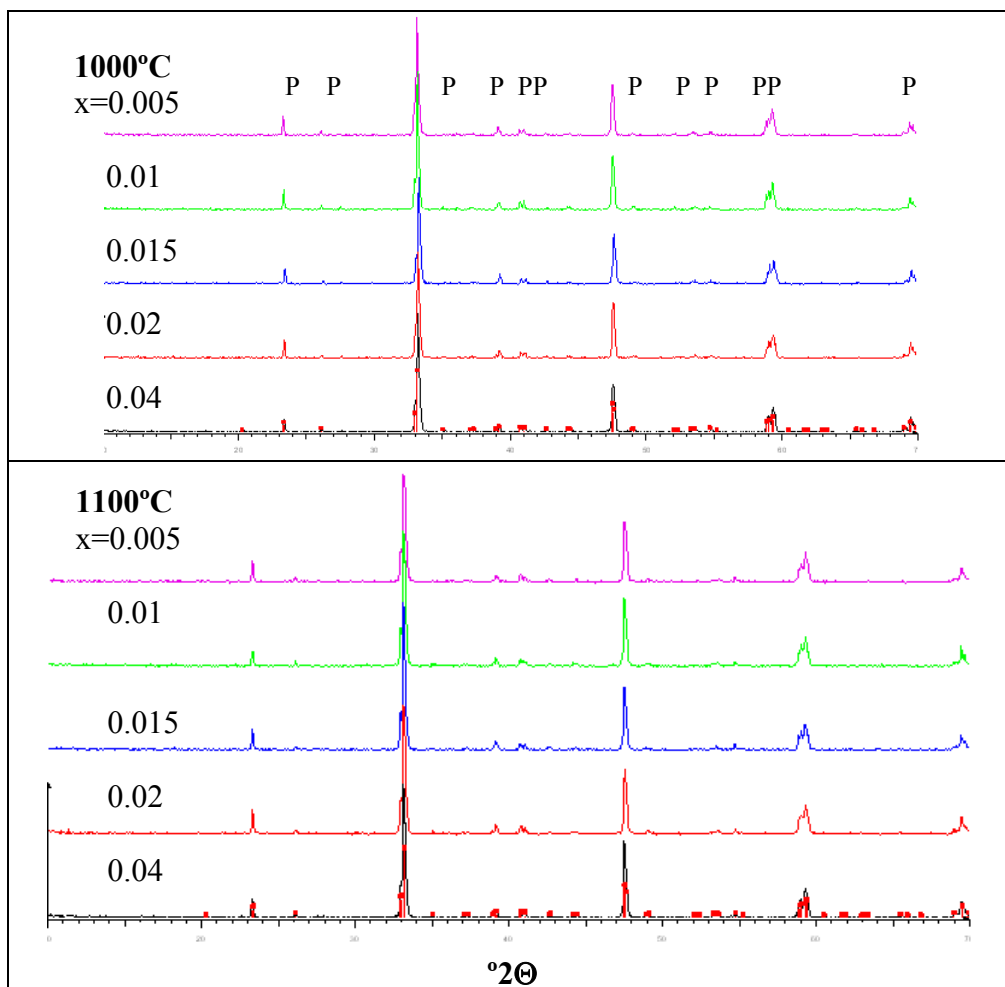


Figure 1. XRD of $(Cr_xCa_{1-x})TiO_3$ samples fired a 1000 and 1100°C (P=Perovskite $CaTiO_3$).

Table 1, CIEL*a*b* colourimetric parameters of glazed samples.

	x=0.005	0.01	0.015	0.02	0.04
1000°C	69.2/12.3/13	63.4/13/12.1	60.7/12.5/12.3	60/12.2/12.5	53.3/11.1/10
1100°C	68.1/12.4/10.6	61.2/12.7/9.2	59.3/12.5/9.5	60.7/11.8/9.4	54.3/11.3/8.4

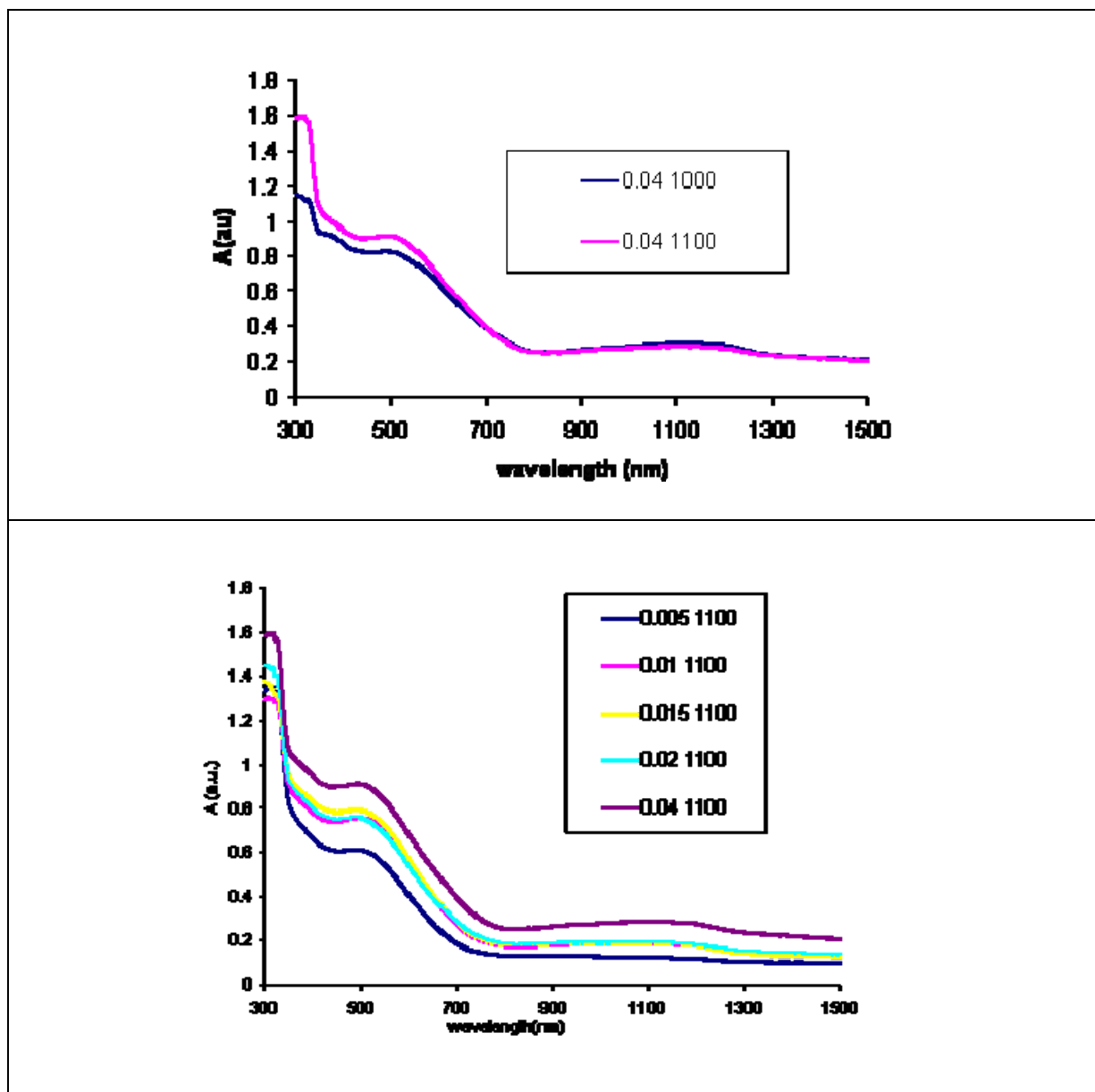


Figure 2. UV-Vis-NIR spectra of glazed samples.

Summary.

A new red ceramic pigment based on the solid solution of chromium (IV) in calcium ($\text{Cr}_x\text{Ca}_{1-x}\text{TiO}_3$) has been obtained and characterized by 5%w. addition to a CaO-ZnO-SiO_2 transparent glaze used for ceramic tiles. XRD, UV-Vis-NIR spectroscopy and CIE- $L^*a^*b^*$ techniques of characterization have been employed. The $L^*a^*b^*$ valour of the optimal pigment with 0,015 mol/mol of chromium fired at 1100°C with a soaking time of 3 hours and 5% weight added to the transparent glaze is 59.3/12.5/9.5. Likewise, 5%w addition of NH_4Cl used as flux agent increase b^* and decrease L^* valor ($L^*a^*b^*=45.2/15.3/5.3$).

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