

NEW PEROVSKITE PIGMENTS CaMO_3 , $\text{M}=\text{Ti}, \text{Zr}$, DOPED WITH TRANSITION METALS

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1. INTRODUCTION

Perovskite is a crystalline structure that should be added to the DCMA classification of ceramic pigments [1] because its use has been well known since R.A. Eppler [2] developed black pigments based on perovskite $(\text{Sr,Ca})\text{MnO}_3$ from oxides and carbonates mixed with conventional mineralisers, calcined at 730°C for 3 hours. Other perovskites have subsequently been proposed, such as neodymiates and titanates, as ceramic pigments [3]. The ABO_3 perovskite is ideally a cubic phase, but it exhibits an orthorhombic distortion (Spatial Group: Pnma). The A cation (Ca^{2+} , Sr^{2+} , Cd^{2+} , Ba^{2+} , Ni^{2+} , Co^{2+}) ideally occupies the vertex of the cube and the B cation (Ti^{4+} , Zr^{4+} , Sn^{4+}) the centre, while oxygens occupy the centre of the faces.

In this study, new perovskite pigments CaMO_3 , $\text{M}=\text{Ti,Zr}$ doped with transition metals, such as iron or chromium, which act as chromophore agents in the presence of mineralisers, were studied. The materials were obtained by the ceramic route and by alkaline coprecipitation.

2. EXPERIMENTAL AND DISCUSSION OF RESULTS

Compositions were prepared of CaMO_3 $\text{M}=\text{Ti, Zr}$, modified by introducing Fe and Cr transition metals replacing M, using NH_4Cl in a molar quantity of 0,5 mol by formula weight as mineraliser. The traditional ceramic method (CE) from carbonates and oxides was used, as well as a non-conventional alkaline coprecipitation method (COP) starting with a nitrate solution, to which titanium isopropoxide or zirconium acetate was added dropwise and alkalised to pH 8 with ammonia. The dry materials were successively calcined at 1000 and 1200°C with a 3 hour soak. The powders were characterised by X-ray diffraction, UV-Vis-NIR spectroscopy and micrography with a binocular magnifying glass (40x). Conventional monoporous tiles glazed with 5% of the calcined materials were colorimetrically evaluated by the $\text{CIEL}^*\text{a}^*\text{b}^*$ method.

In the introduction of iron into CaTiO_3 the crystallisation of the perovskite CaTiO_3 was observed together with the pseudobrookite Fe_2TiO_5 and rutile. When the quantity of iron increased, the pseudobrookite peaks increased, indicating that a Fe solid solution did not occur in the perovskite (Fig. 2). Yellow colorations were obtained ($\text{L}^*\text{a}^*\text{b}^*=65/16/17$ in the COP sample with 0,2 mol Fe by formula weight) and pink colorations ($\text{L}^*\text{a}^*\text{b}^*=59/11/13$ for COP with 1 mol iron by formula weight) (Fig. 1). The substitution of Cr for Ti in CaTiO_3 produced red-pink colorations with a little Cr ($\text{L}^*\text{a}^*\text{b}^*=46/14/2$ in the COP sample with 0,025 mol chromium by formula weight) and bluish colorations with a high quantity of Cr ($\text{L}^*\text{a}^*\text{b}^*=45/3/-3$ in the COP sample with 0,2 mol chromium by formula weight at 1200°C) (Fig. 1). However, in both cases the powder diffraction only exhibited perovskite peaks, indicating complete solubility of chromium (band at 600 nm of Cr(IV) in the UV-Vis-NIR spectrum of Fig. 2).

In the substitution of Fe for Zr in CaZrO_3 , in addition to the perovskite, diffraction peaks appeared associated with monoclinic zirconia and metastable cubic zirconia polymorphs (in a greater proportion in the COP samples). Although the powders were pink (more intense in the COP samples, $L^*a^*b^*=50/7/15$ in the COP sample with 0,2 mol Fe by formula weight at 1200°C), they did not produce colour in the monoporosa glaze or produced soft yellow colours, evidencing the dissolution of iron in the glaze. In the case of the substitution of Cr for Zr in CaZrO_3 , perovskite crystallised together with monoclinic and cubic zirconia (in greater proportion in the COP samples). Similarly, the powders exhibited red–pink colorations in the CE and the COP samples ($L^*a^*b^*=40/10/9$ and $L^*a^*b^*=41/9/10$ for the CE and COP samples, respectively, calcined at 1200°C) (Fig. 1), indicating the obtainment of the chromium solid solution in the perovskite lattice (band at 600 nm of Cr(IV) in the UV-Vis-NIR spectrum of Fig 2); however, in the glaze the green colour was associated with dissolved chromium.

3. CONCLUSIONS

New perovskite pigments CaMO_3 , $M=\text{Ti,Zr}$ doped with transition metals, such as iron or chromium, which acted as chromophore agents in the presence of NH_4Cl as mineraliser, were studied. The materials were obtained by the ceramic route as well as by alkaline coprecipitation. In the case of the titanates, depending on the chromophore and its concentration, yellow, brown–red, and bluish pigments were obtained in monoporosa glazes. In the case of the zirconates, the stability was lower and though the coloration of the powder was similar to that of the titanate counterparts, the coloration in the glazes only allowed gentle yellows and low-intensity greens, associated with iron and chromium dissolved respectively in the glaze, to be obtained.

Fe-CaTiO₃ COP 0,2molFe/formula $L^*a^*b^*=62/9/18$	Cr-CaTiO₃ COP 0,025molCr/formula $L^*a^*b^*=41,574,3/2,3$	Cr-CaTiO₃ CE 0,2molCr/formula $L^*a^*b^*=50,0/11,2/11,4$	Fe-ZrTiO₃ COP 1 molFe/formula $L^*a^*b^*=43,5/2,8/0,2$	Cr-CaZrO₃ COP 0,5molCr/formula $L^*a^*b^*=43,5/2,8/0,2$
$L^*a^*b^*=65/16/17$	$L^*a^*b^*=46/14/2$	$L^*a^*b^*=49,4/2,9/-2,2$	$L^*a^*b^*=56,6/9,8/18,8$	$L^*a^*b^*=71,3/-2,5/14,4$

Figure 1. Photographs under a binocular magnifying glass (40x) of the powders and glazed tiles with the pigments indicated, calcined at $1200^\circ\text{C}/3\text{h}$, showing the $L^*a^*b^*$ values.

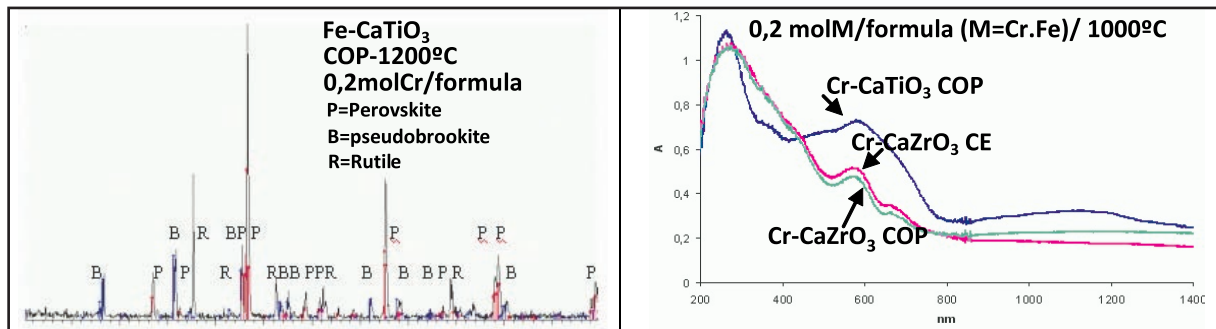


Figure 2. X-ray diffraction and UV-Vis-NIR spectra of the samples indicated.

ACKNOWLEDGEMENTS

The authors thank Fundación Bancaja-UJI (Project P1-1B2010-09) and the Ministry of Education (Project MEC 05I403) for the funding received.

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