CHROMIUM-DOPED $BiVO_4$ PIGMENTS WITH PHOTOCATALYTIC ACTIVITY AND HIGH NIR REFLECTANCE OBTAINED BY COLLOIDAL METHODS

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1. INTRODUCTION

$BiVO_4$ is a broadband semiconductor that has displayed promising behaviour as a photoelectrochemical (PEC) anode for photoelectrochemical decomposition of water and production of so-called green H_2, while also being studied as a photocatalyst in solar photocatalytic applications [1]. $BiVO_4$ is found in four polymorphs: orthorhombic, zircon–tetragonal structure, monoclinic, and tetragonal. Although the orthorhombic polymorph is the most common phase in the nature, (pucherite mineral), it has not been synthesised in the laboratory. Low-temperature synthesis of $BiVO_4$ produces the zircon–tetragonal phase with a bandgap at 2.9 eV that, at 528 K, transforms into the monoclinic phase, reversible to tetragonal on adjusting temperature. In these crystal structures, V is coordinated by four O atoms in tetrahedral coordination and each Bi is coordinated with eight O atoms from eight different tetrahedral units of VO_4. The only difference between t-$BiVO_4$ and m-$BiVO_4$ is that the VO_4 and BiO_8 polyhedrons in t-$BiVO_4$ are symmetrical, whereas those of m-$BiVO_4$ are not, both being indirect semiconductors with a bandgap between 2.3 and 2.4 eV [2]. This study examined the synthesis and characterisation of chromium-doped bismuth vanadate pigments using different colloidal coprecipitation methods and metal-organic decomposition or carboxylate route and it is compared with the ceramic route [3].

2. EXPERIMENTAL

Using aqueous route methods, CO (colloidal sol-gel) and MOD (metal-organic colloid with polycarboxylate acids) were prepared of compositions $Cr_{0,4}Bi_{0,6}V_4O_4$ from nitrates of the cations present dissolved in water and peptised with ammoniacal solution in the case of the CO samples; in the MOD method, at the same nitrate dilution, x=0.25, 1, 1.5, 2 mol carboxyl acid/mol $BiVO_4$ were added prior to the ammoniacal peptisation. The results and characterisations obtained by the indicated deposition and glazing are shown in Figure 1.

3. RESULTS AND CONCLUSIONS

Doping with chromium crystallises Cr solid solutions in the monoclinic lattice of $BiVO_4$ (*I2/b*), producing grey colorations in the direct screen print application of colloidal inks on the unfired monoporosa vitreous sample. The powders calcined at 600ºC/3h produced turquoise colorations in applications with twice-fire vitreous samples that became dark in single-fire vitreous samples, producing almost black, grey shades in high proportions of citrates. The powders exhibited photocatalytic activity in relation to Orange II with better results in the ceramic micrometre-sized aggregates (1-2 μm) than with the colloidal nanometre-sized ones ($t_{1/2}$=85 min compared to 150 min of the colloids).

These materials were studied by transmission electron microscopy (TEM) and selected area electron diffraction (SADP) (nanoparticles of 10–80 nm being observed). All the coloured (turquoise and grey) vitreous samples exhibited high NIR reflectance (R_{vis}/R_{NIR}/R=6/24/15 (CE) 6/26/16 (CO) and 6/25/15 (MOD x=1.5 citrates).

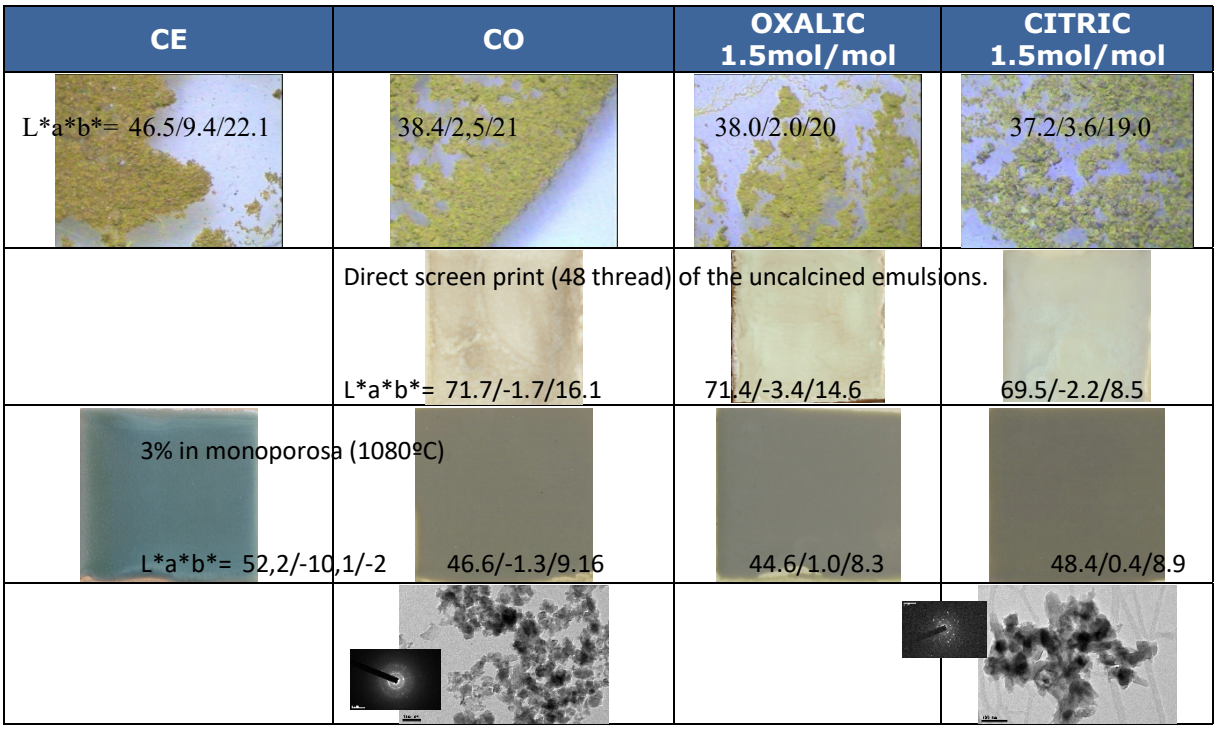
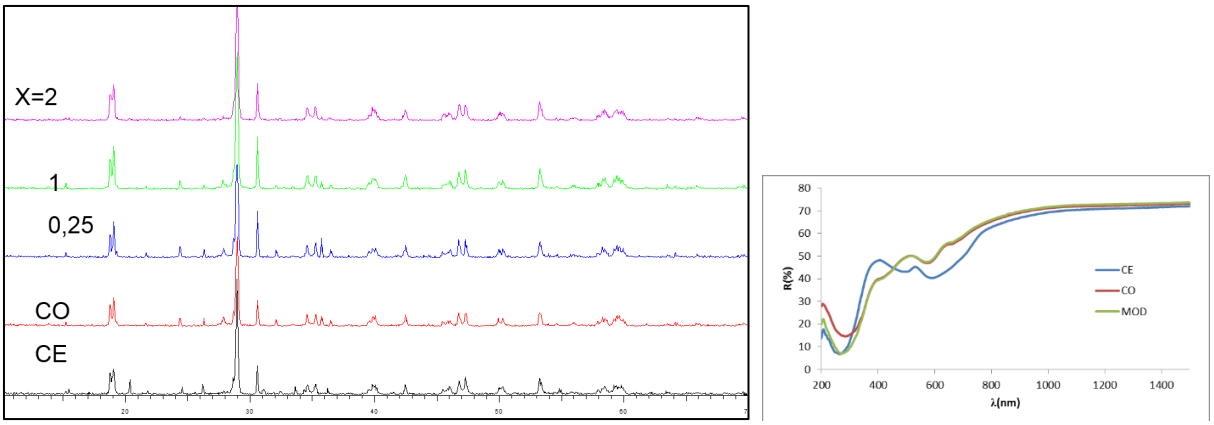


***Figure 1**. Results and characterisations obtained by the indicated deposition and glazing of the powders calcined at 600ºC/3h.*

Figure 2. (a) XRD for samples CE, CO, and OXALIC (as a function of x). CRYSTALLINE PHASES: m (m-$BiVO_4$), V(V_2O_5), C($CrVO_4$), B($(BiO)_2CrO_4$), (b) UV-Vis-NIR spectra.



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