

STABILISATION OF MAGNÉLI PHASES IN THE SYNTHESIS OF ILMENITE $M\text{TiO}_3$ ($M=\text{Cr,Fe,Co,Ni}$) CERAMIC PIGMENTS

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1. INTRODUCTION

Ilmenites are isostructural with corundum whose cations are substituted in accordance with the mechanism: $2\text{Al}^{3+} \rightarrow (\text{Fe}^{2+}, \text{Mg}^{2+}) + \text{Ti}^{4+}$. These cations arrange themselves in an orderly manner, so that the octahedrons of one layer are duly occupied by the divalent cations Mg or Fe and the successive layer by Ti. Consequently, two contiguous octahedrons pertaining to two adjacent layers are occupied by a divalent cation and the other by Ti^{4+} resulting in an intermediate valency of +3, similar to that of corundum. Related to this system, the Mg_2TiO_4 compounds with spinel structure and MgTi_2O_5 with pseudobrookite structure are considered in the literature to be entropy-stabilised structures: their relatively high entropy is associated with the mixing in specific crystallographic positions of different cations (1).

2. EXPERIMENTAL AND RESULTS

This study describes the possible ceramic pigments based on the ilmenite lattice. $MTiO_3$ compositions were prepared with $M=Cr, Fe, Co, Ni$. The samples were characterised by X-ray diffraction, UV-Vis-NIR spectrophotometry by diffuse reflectance, CIEL*a*b* colorimetry, and they were tested in matrices with through-body colouring in sodium calcium glass powder at 5% (800°C) and in a double-firing frit (1050°C). The results indicate the formation of $CoTiO_3$ and $NiTiO_3$ ilmenites with green dark and yellow colorations, respectively. In the case of $M=Fe$, pseudobrookite Fe_2TiO_5 stabilised, rutile remaining as residual phase, as usual. The colorations in the glass and the double-firing frit provided intense green colours in the frit and brown in the glass (Cr), brown (Fe), blue-greenish (Co), and yellow-greenish (Ni), respectively, associated with the trivalent ions in VI coordination, except in the case of chromium, where the chemistry was more complex.

In the pigment synthesis based on solid solutions of transition metals in ilmenites, pseudobrookites or titanium-based spinels, anatase is usually used as titanium precursor. In firing, the anatase is usually converted into rutile. The subsequent transition to sub-stoichiometric phases of titanium oxide Ti_nO_{2n-1} called Magnéli phases, of high interest as thermo-electronic materials, require using sol-gel methods and inert or reducing atmospheres, given the need to partially reduce Ti(IV) to Ti(III) with the ensuing generation of oxygen vacancies (2). The stabilisation of oxidised phases of chromium in firing and their eventual reduction to eskolaite in the final stretch would explain the stabilisation in the sample $M=Cr$ of the Magnéli phase Ti_8O_{15} (M) detected by X-ray diffraction.

3. CONCLUSIONS

Ceramic pigments based on the ilmenite $MTiO_3$ stoichiometry with $M=Cr, Fe, Co, Ni$ were obtained. In the case of Co and Ni, the cobalt and nickel ilmenites were obtained that produced intense colorations in the sodium calcium glass and a double-firing frit (blue-greenish with Co and yellow-greenish with Ni). In the case of iron, pseudobrookite Fe_2TiO_5 was obtained (with rutile as residual phase), which provided brown colorations. Finally, chromium produced green colours in the frit and brown in the glass (Cr); however, the residual phase was not rutile but a sub-stoichiometric phase of titanium oxide Ti_8O_{15} belonging to the so-called Magnéli phases.

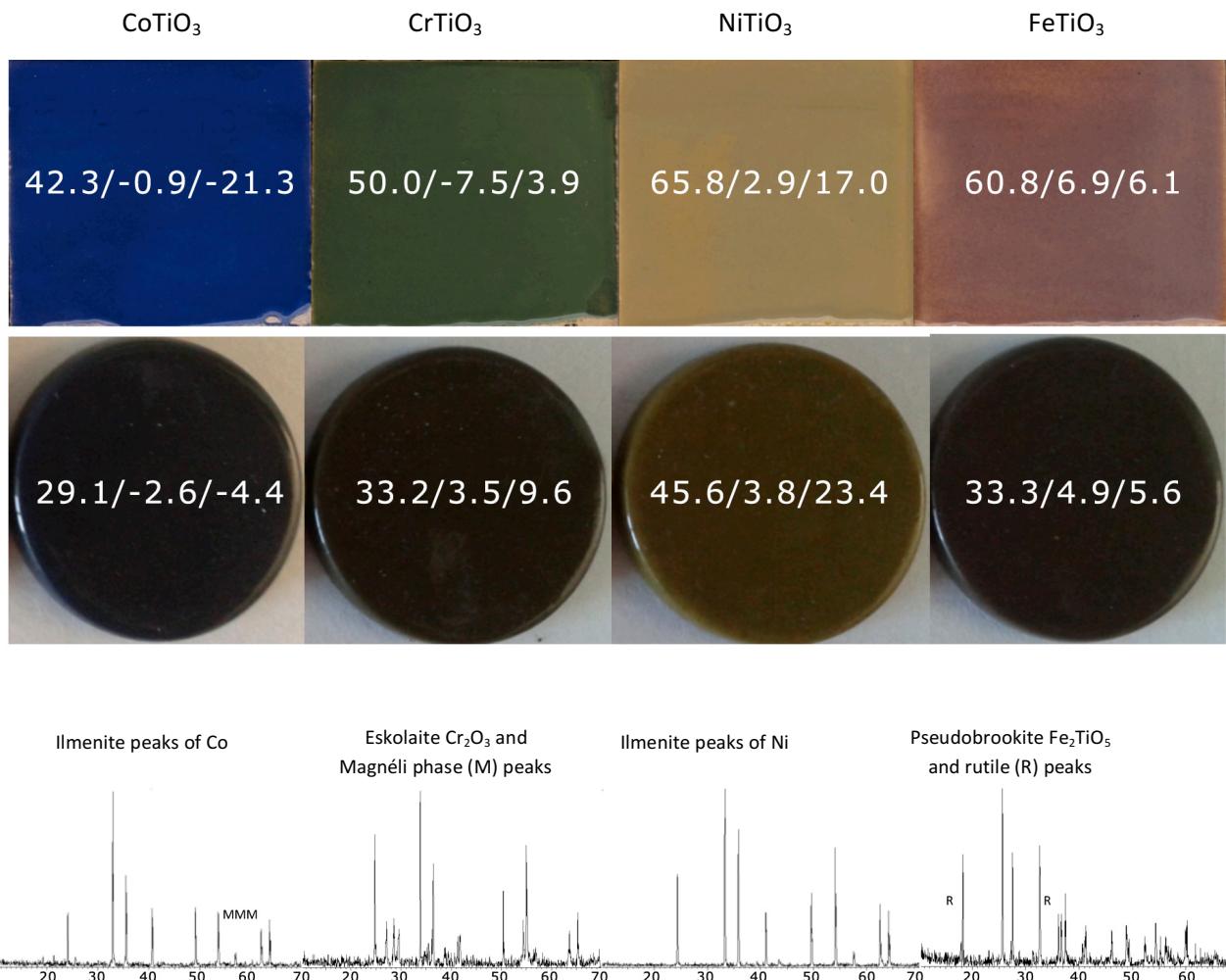


Figure 1. Photograph of the $MTiO_3$ powders fired at $1200^\circ C/3h$ glazed in a double-firing frit ($1050^\circ C$) and in sodium calcium glass powder ($800^\circ C$) at 5% by weight. The $CIEL *a*b*$ value of the pieces (illuminant D65, observer 10°) is indicated. The bottom part shows the X-ray powder diffractograms with the detected crystalline phases.

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