CERAMIC PIGMENTS BASED ON SOLID SOLUTIONS OF CHROMIUM IN GEIKIELITE $MgTiO_3$ AND/OR KARROOITE $MgTi_2O_5$

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1. INTRODUCTION

Geikielite ($MgTiO_3$) belongs to the ilmenite ($FeTiO_3$) group (trigonal, Point Group 3, Spatial Group R3). Many studies have reported the stability and crystallisation of the Co–ilmenite phase ($CoTiO_3$) as a ceramic pigment. Geikielite forms solid solutions with ilmenite ($FeTiO_3$) and with pyrophanite ($MnTiO_3$), which are the end members of the solid solutions by replacement of iron (II) and manganese (II) with magnesium (1). Related to this system, the Mg_2TiO_4 compound with a spinel structure and $MgTi_2O_5$ with a 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 (2). 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.

2. EXPERIMENTAL AND RESULTS

This study describes the possible ceramic pigments based on the solid solution of chromium ions in the geikielite lattice. Compositions were prepared of $(Mg_{1-x}Cr_x)TiO_3$ with x=0,02, 0,1, and 0,5 from oxides that were successively calcined at 800, 1000, and 1200ºC/3h. The samples were characterized by X-ray diffraction and UV-Vis-NIR spectrophotometry by diffuse reflectance (Fig. 1) and CIEL*a*b* colorimetry (Fig. 2). They were tested in through-body coloured matrices in sodium calcium glass powder at 5% (800ºC) and in a double-firing frit (1050º C) (Fig. 2). The results indicate that geikielite stabilised as major phase in samples x=0,02, karrooite $MgTi_2O_5$ predominated in x=0,1 and the spinel $MgCr_2O_4$ formed together with karrooite and free rutile in x=0,5. With x=1 eskolaite, Cr_2O_3 was detected in addition to a Magnéli phase and the colour evolved to green. The results indicate yellow–orange tones associated with Cr^{4+} (manifested by the band at 500 nm in the UV-Vis-NIR spectrum of x=0,02 and 0,1) and Cr^{3+} in various octahedral positions (bands around 450 nm, $^4A_2(^4F)\rightarrow {}^4T_1(^4F)$, and 600 nm, $^4A_2(^4F)\rightarrow {}^4T_2(^4F)$ depending on the crystalline field strength on Cr^{3+}) (2). The yellow tone diminished with x, and a decrease in geikielite and appearance of karrooite and spinel were detected in all cases, as well as an increase in colour intensity (decrease in L*), with the increase in x.

3. CONCLUSIONS

Yellow–orange pigments were obtained by doping geikielite with chromium $(Mg_{1-x}Cr_x)TiO_3$ with x=0,02 and 0,1 associated with the entry of Cr^{4+} substituting Ti^{4+}. When the chromium concentration increased, crystallisation was detected first of karrooite $MgTi_2O_5$ in x=0,1 and the formation of the spinel $MgCr_2O_4$ together with karrooite and free rutile in x=0,5; with x=1, eskolaite was detected and a Magnéli phase and the colour evolved to green.

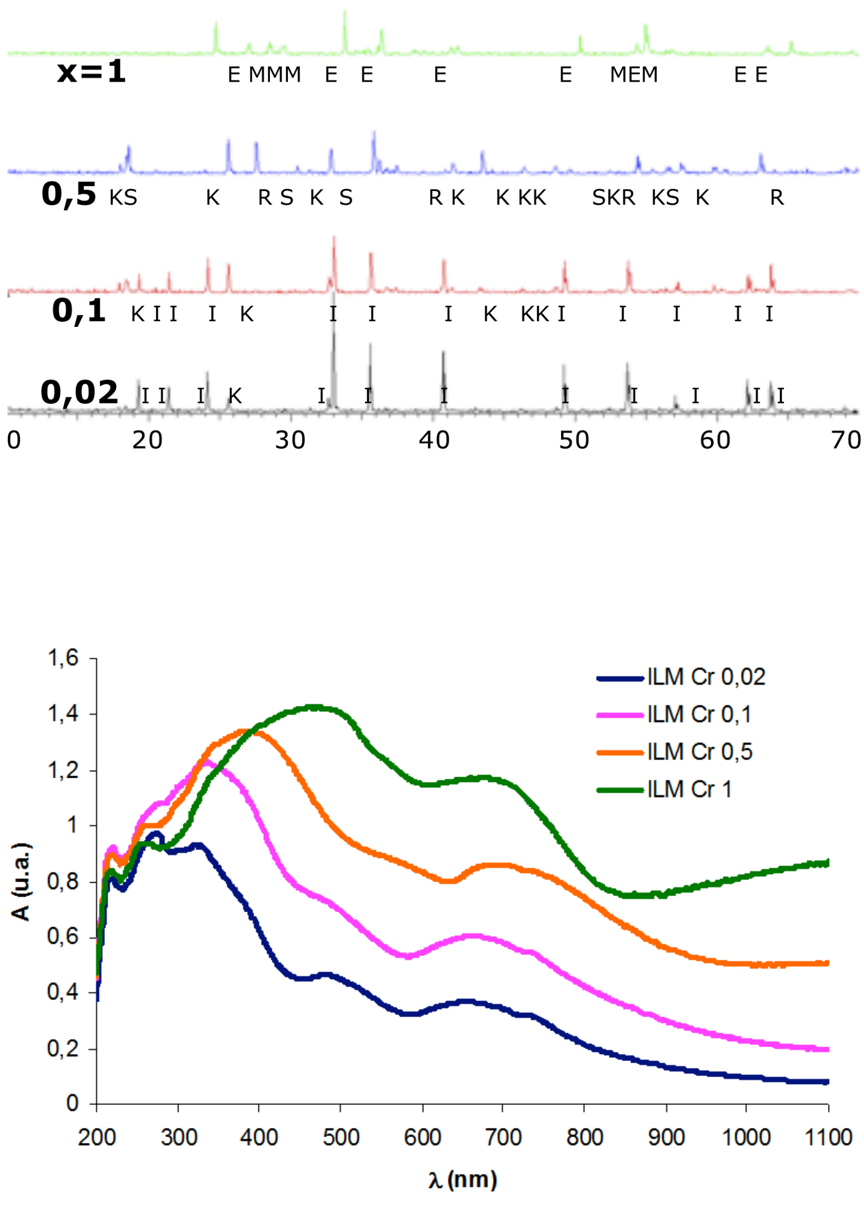
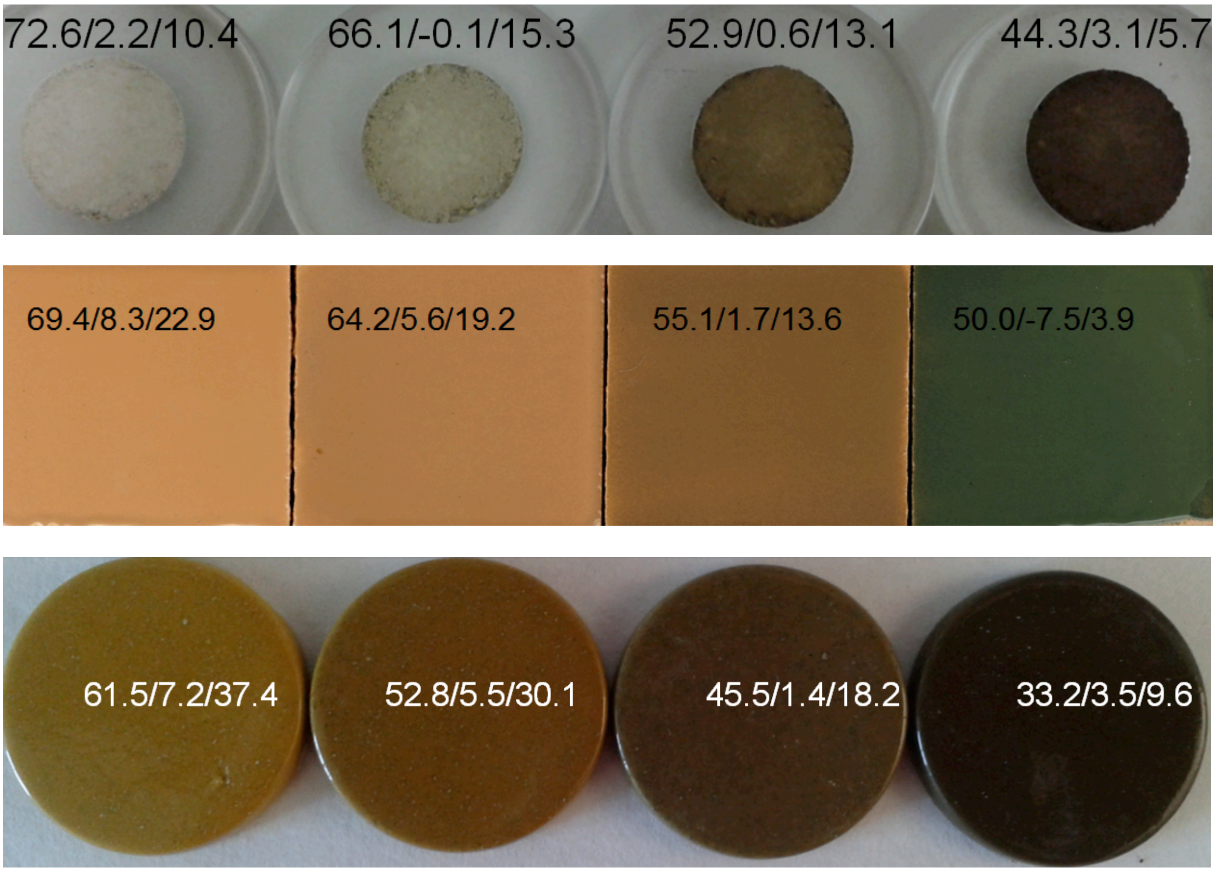


Figure 1. *X-ray diffractograms of the powders ($Mg_{1-x}Cr_x$)TiO_3 calcined at 1200ºC/3h with the detected crystalline phases and UV-Vis-NIR spectra. CRYSTALLINE PHASES: E (Eskolaite Cr_2O_3, M (Magnéli phase Ti_8O_{15}), K (Karrooite $MgT_{i2}O_5$), S (Spinel $MgCr_2O_4$), I (Geikielite $MgTiO_3$)*



X=0,02 **0,1** **0,5** **1**

Figure 2. *Photograph of the powders* $(Mg_{1-x}Cr_x)TiO_3$*, glazed at 5% in double-firing frit (1050ºC) and in sodium calcium glass powder (800ºC) with the CIEL*a*b* colorimetric parameters (illuminant D65, observer 10º)*

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