MODULATION OF COLOUR AND SOLAR REFLECTIVITY IN QANDILITE PIGMENTS DOPED WITH Co AND Zn, (Mg, Zn, Co)$_2$TiO$_4$

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Optical properties of ceramic pigments (colour, absorbance, reflectivity, etc.) may be modulated by adequate control of key crystallochemical parameters, such as coordination environments, cationic disorder, covalence, etc. For example, the different octahedral positions in the mixed oxides of Mg and Ti with pseudobrookite structures (karrooite $MgTi_2O_5$), ilmenite (geikielite $MgTiO_3$) or spinel (qandilite Mg_2TiO_4) enable development of orange, yellow or green pigments, respectively, using Ni^{2+} as chromophore [1]. Recently, it has been shown that using Co^{2+} as a chromophore also produces an interesting change from greenish-yellow in karrooite to intense blue in geikielite [2,3] to intense blue in geikielite (with Co^{2+} ions in octahedral positions in both structures). On the other hand, in the qandilite spinel, the preferential entry of Co^{2+} in tetrahedral positions and the greater intensity of the octahedral crystalline field give rise to very intense turquoise (green-blue) colourations [4].

In this study, the effect of co-doping with Zn on reactivity, stabilization and optical properties of solid solutions of Qandilite doped with Co ($Mg_{1.8-x}Zn_xCo_{0.2}TiO_4$, x = 0, 0.2, 0.9, 1.6 and 1.8) is investigated. Its performance is also analysed as pigments or ceramic dyes (5%) applied in conventional double-fired (1050°C) and porcelain (1190°C) glazes, and also as dispersions (20%) in diethylene glycol (DEG) used for ceramics and firing of porcelain cycle. Solar reflective indexes have also been obtained, with the aim of developing new cooling pigments ("cool pigments") for façades or roofs that contribute to improving energy efficiency of buildings [5]. The pigments were prepared by decomposition (500°C/1 h) and calcination (1000 and 1200°C/3 h) of citrate gels.

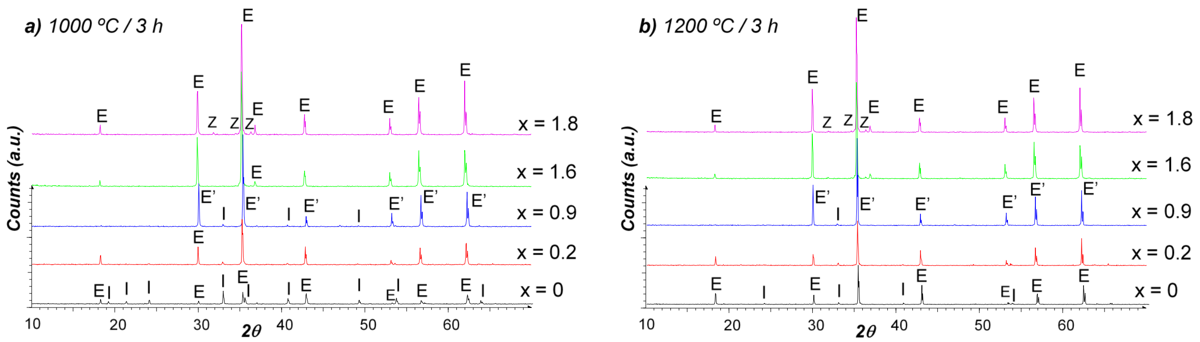

Figure 1. *Pigment DRX $Mg_{1.8-x}Zn_xCo_{0.2}TiO_4$ calcinados a 1000 (a) y 1200 ºC (b); Crystalline phases: **E**=spinel (Mg, Zn, Co)$_2$TiO$_4$; **E'**=spinel (Mg, Zn, Co)$_2$Ti$_3$O$_8$; **I**=ilmenite (Mg, Zn, Co)TiO$_3$); **Z**=ZnO (hexagonal).*

XRD analysis confirms a significant increase in reactivity through doping with Zn (*Fig.1*): although at 1000ºC and for x = 0 there is still enough secondary phase of ilmenite, the spinel stabilizes (*Fd-3m*) and practically as a single phase for x≥0.2, improving its crystallization through doping with Zn or calcining at a higher temperature (1200ºC). Likewise, for intermediate contents of Zn (x = 0.9), a defective spinel with structure type $Zn_2Ti_3O_8$ and primitive cubic cell (*$P4_332$*) seems to stabilize. As a very important aspect, increasing doping with Zn^{2+} produces an interesting colour change (*Fig.2a-I*) of turquoise (x = 0, $Mg_{1.8}Co_{0,2}TiO_4$, L * / a * / b * = 44 / -27 / -10 to 1200ºC) to greenish-yellow (x = 0.9, $Mg_{0.9}$ $Zn_{0.9}Co_{0,2}TiO_4$, L * / a * / b * = 46 / -17 / 11), and even yellowish brown (x = 1.8, $Zn_{1.8}Co_{0,2}TiO_4$, L * / a * / b * = 55/7 / 32).

According to the *UV-vis-NIR* absorbance spectra (*Fig.2b*), this colour change with doping follows a notable and progressive increase of Co^{2+} investment in the spinel (higher proportion of Co^{2+} in octahedral positions), predominantly the octahedral Co^{2+} for high content of Zn (x = 1.6 and 1.8). This greater investment of Co^{2+}, responsible for the colour change, also produces a large increase in reflectance in the *NIR* (*Fig.2c*) and the solar reflection index of the powders (*SRI*= 32, 41 and 60 for x = 0, 0.9 and 1.8).The pigments were not stable in the ceramic glazes tested, developing the typical blue-purple colourations due to Co^{2+} leaching in the vitreous matrix (*Fig.2a-IV*). However, the turquoise pigment (x = 0) dispersed in diethylene glycol and applied on ceramic medium (*Fig.2a-II*) is stable and with high SRI (53) after firing with a porcelain cycle at 1190°C (*Fig.2a-III*), obscuring the rest.

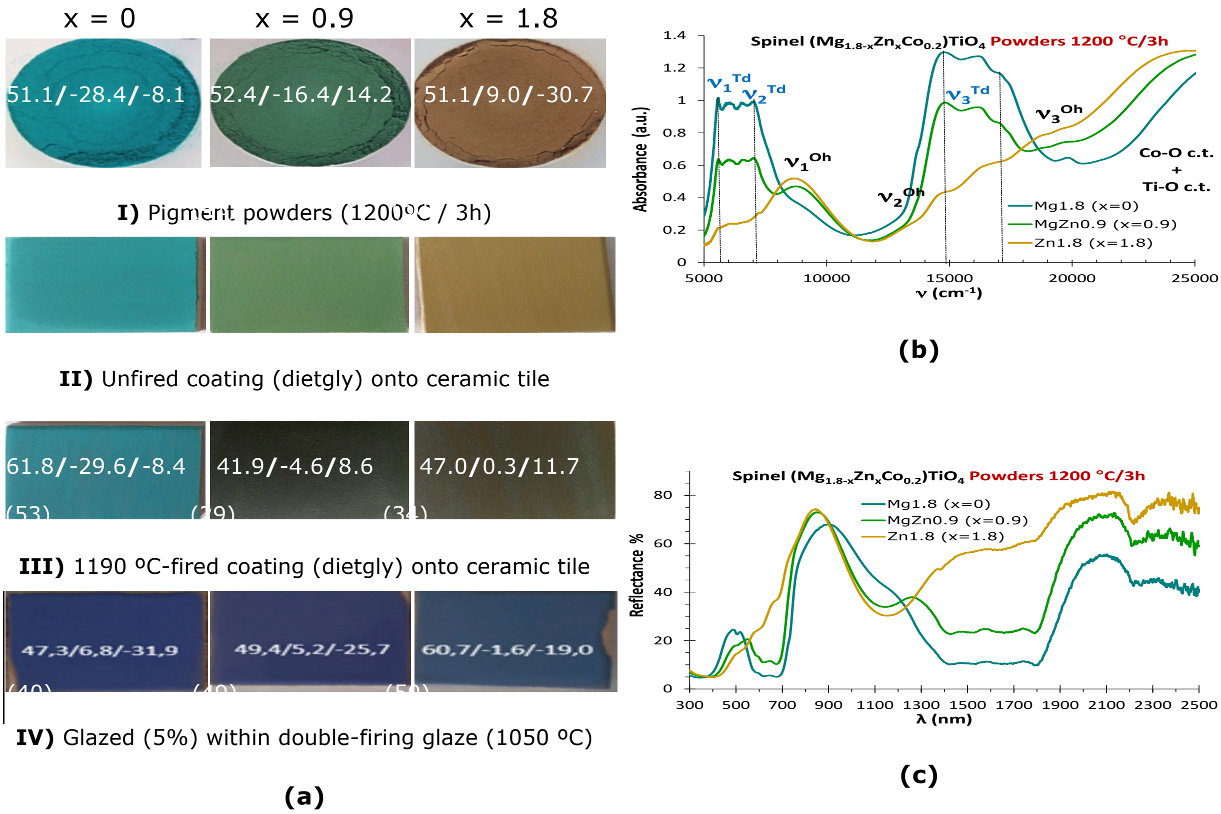

Figure 2. (a) *Visual appearance, colorimetric parameters (L*/a*/b*) and solar reflection index (SRI) of pigments (x = 0, 0.9 and 1.8) in powder and in different applications;* ***(b)*** *UV-vis-NIR absorbance spectra (powders), and* ***(c)*** *reflectance spectra.*

7. ACKNOWLEDGMENTS

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1. REFERENCES

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