KARROOITE PIGMENTS DOPED WITH Co $(Mg,Co)Ti_2O_5$: EFFECT OF THE GLAZE, Co-DOPING WITH Zn, AND SYNTHESIS ROUTE

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Research is being conducted into Mg-Ti pseudobrookite (karrooite $MgTi_2O_5$, spatial group *CmCm*) as structure host for the development of ceramic pigments, forming solid solutions with different chromophore ions (Co^{2+}, Cr^{4+}, Fe^{3+}, Mn^{2+}/Mn^{3+}, Ni^{2+}, and V^{4+}) [1–3]. In a recent study [2] Co-$MgTi_2O_5$ pigments developed green colorations, which were stable in glassy coatings or ceramic glazes fired at low temperature (< 1050ºC). In contrast, their stability decreased steadily in ceramic glazes fired at increasing peak temperatures (from 1050 to 1250ºC), giving rise to increasingly bluish colorations. This study analyses the effect of co-doping with Zn and the synthesis route (comparing the ceramic route with the citrate or MOD routes) on the coloration and stabilisation in different ceramic glazes of Co pigments in karrooite. To do so, solid solutions of Co^{2+} in karrooite (compositions ***KAR***, $Mg_{1-x}Co_xTi_2O_5$, x= 0-0.4) were initially prepared by the ***ceramic route*** **(CER)**, in addition to compositions co-doped with Zn using low Zn/Mg ratios (***KAR-Zn1***, $Mg_{0.8-x}Zn_{0.2}Co_xTi_2O_5$, x=0-0.2) and high Zn/Mg ratios (***KAR-Zn2***, $(Mg_{0.5}Zn_{0.5})_{1-x}Co_xTi_2O_5$, x=0-0.2). After calcination at **1200ºC/3h** of mixtures of Co_3O_4, ZnO, TiO_2 (anatase) and Mg hydroxycarbonate, XRD analysis confirmed effective formation of the karrooite (K) phase, albeit with increasing quantities of residual ilmenite (I) on increasing the doping with Co in the systems *KAR* (without Zn) (**Fig. 1a**) and *KAR-Zn1* (low co-doping of Zn). It may be noted that high co-doping of Zn (*KAR-Zn2*) allowed solid solutions of $(Co,Zn,Mg)Ti_2O_5$ to stabilize as sole phase (x=0.05-0.2).

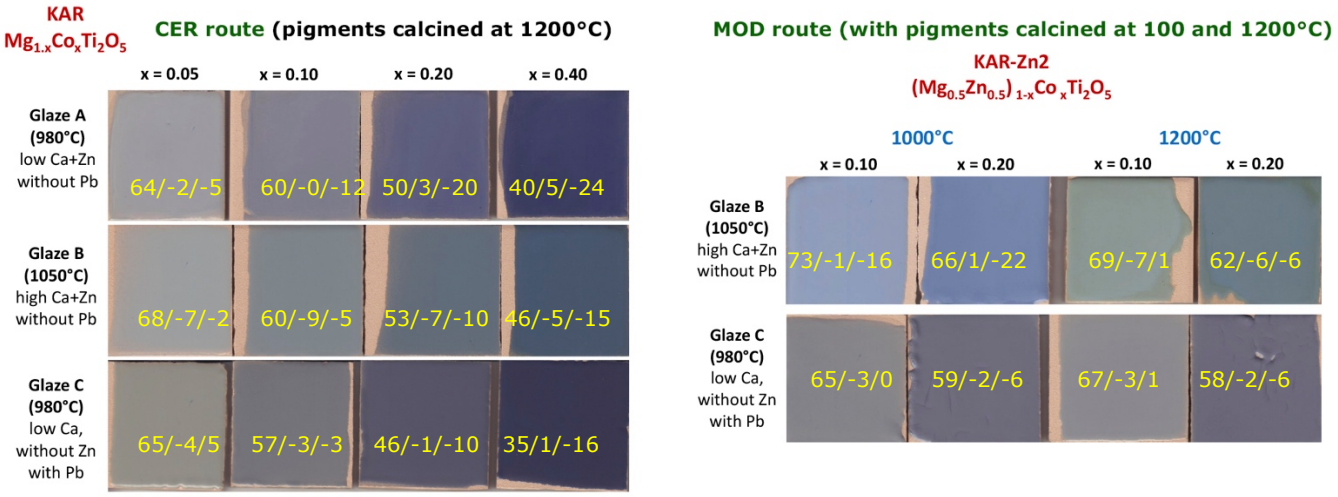

Figure 3. *Visual appearance and colorimetric parameters (L*/a*/b*) of the glazed compositions:* ***KAR CER*** *route (left) and* ***KAR-Zn2 MOD*** *route (right).*

On the other hand, the use of the ***metal-organic decomposition route (MOD)*** of citrate gels [1,3] led to a notable increase in reactivity (sole Co-karrooite phase already at 1000ºC for x=0.2 in the *KAR* system). It may be noted that the powders in the system ***KAR-Zn2*** (high Zn co-doping) gave rise to sky-blue colours at 1000ºC ($b^*<0$, **Fig. 2** (right)), associated with octahedral Co^{2+} in ilmenite and rutile phases, which became green-greyish at 1200ºC with the stabilisation of Co-karrooite (XRD in **Fig. 1b**). These colours were more stable in glaze B (1050ºC) than in glaze A (980ºC) (**Fig. 3** (right)), just as in the pigments obtained by the ceramic route.

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