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Karrooite green pigments doped with Co and Zn: Synthesis, color properties and stability in ceramic glazes

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ABSTRACT

The solid-state synthesis and stabilization of Co doped ($Mg_{1-x}Co_xTi_2O_5$), Zn doped ($Mg_{1-x}Zn_xTi_2O_5$) and Co- and Zn-codoped karrooite solid solutions ($Mg_{0.8-x}Zn_{0.2}Co_xTi_2O_5$ and ($Mg_{0.5}Zn_{0.5})_{1-x}Co_xTi_2O_5$) were investigated. In addition, the optical spectra, color properties and technological performance of (Co,Zn)-karrooite compositions as new green ceramic pigments were also analyzed. XRD characterization revealed for the first time the high solid solubility of Zn^{2+} in $MgTi_2O_5$ karrooite at 1200 °C (between 60 and 80 mol% per Mg or karrooite formula unit). In contrast, the reactivity and stabilization of karrooite phase decreased in the case of Co^{2+} doping. Interestingly, codoping with Zn^{2+} ions at high molar ratios (Zn:Mg ratio equal to 1:1) enhanced the reactivity and enabled the stabilization of (Co,Zn)-$MgTi_2O_5$ karrooite solid solutions, even with high Co^{2+} loadings (20 mol% per karrooite formula unit). The (Co,Zn)-$MgTi_2O_5$ pigments exhibited yellowish-green colors associated to Co^{2+} ions allocated in octahedral M1 and M2 sites of karrooite lattice, and becoming more intense and less yellow the higher the Co content. However, Zn^{2+} codoping produced less saturated green colors with similar green but lower yellowish hues. The obtained pigments were not stable enough within the tested ceramic glazes, giving rise to turquoise colorations due to cobalt leaching and incorporation into tetrahedral sites of the glassy phase. The stability of Co-karrooite green pigments was higher in a Ca- and Zn-enriched ceramic glaze (B) fired at a higher temperature (1050 °C).

1. Introduction

Karrooite is the non-official name provided for synthetic magnesium-titanium pseudobrookite ($MgTi_2O_5$), which crystallizes in orthorhombic symmetry and *Cmcm* (63) space group [1]. In the last years, karrooite has been investigated as potential host lattice for the preparation of ceramic pigments. For instance, karrooite solid solutions doped with different transition metal chromophore ions ($Mg_{1-x}M_{2x}Ti_{2-x}O_5$, x=0.02 and 0.05, M=$Co^{2+}$, Cr^{4+}, Fe^{3+}, Mn^{2+}/Mn^{3+}, Ni^{2+} and V^{4+}) were prepared by the classical ceramic route from mixtures of oxide precursors (fired at 1300 °C) and analyzed as alternative ceramic pigments [2]. The obtained colors were found stable in low-temperature (< 1050 °C) ceramic glazes and glassy coatings, although they were rather unstable in highly opacified glazes containing large amounts of CaO and ZnO. In the case of Ni^{2+}-doping, the whole range of Ni: $MgTi_2O_5$ solid solutions ($Mg_{1-x}Ni_{2x}Ti_{2-x}O_5$) has been also recently investigated [3], giving rise to intense yellowish orange pigments with increased chromaticity and saturation the higher the Ni content (up to x=0.4–0.5).

In regard to Co^{2+}-doped karrooite pigments, Matteucci et al. on [2] investigated the effect of relatively low Co loadings (4 and 10 mol% with respect to karrooite). Interestingly, the obtained Co^{2+}-doped karrooite powders were green-colored, which is less common for Co^{2+}-based pigments. Indeed, the color of Co^{2+} pigments can range from blue, green to violet or pink depending on the host lattice and coordination environment, although pink is the usual color when cobalt is accommodated in octahedral sites, and much more intense or deep blue colors are generally associated to cobalt in tetrahedral coordination [4–6]. Today a common source of green color for the ceramic industry is a mixture of Pr-zircon yellow and V-zircon blue pigments, since other alternative green pigments contain large amounts of toxic and pollutant elements such as Cr, Co or Ni ("green of Sèvres" based on Cr_2O_3; Uvarovite green garnet, $Ca_3Cr_2Si_3O_{12}$, with CPMA number 04-07-3 [7]; cobalt chromite green spinel, $CoCr_2O_4$, with CPMA number 13–30-3; cobalt titanate green spinel, Co_2TiO_4,with CPMA number 13-31-3; and nickel silicate green olivine, Ni_2SiO_4, with CPMA number 05-45-3). In this respect, the employment of allochromatic solid solutions doped with a low or minimized amount of Co (Ni or Cr) may be an interesting, less-pollutant and less-expensive alternative for green ceramic pigments [8–11], instead of idiochromatic (non-substituted)

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pigments of $CoCr_2O_4$, Co_2TiO_4 and Ni_2SiO_4.

With the above precedents, in the present investigation we scrutinized the formation by ceramic route of $MgTi_2O_5$-$CoTi_2O_5$ greenish solid solutions ($Mg_{1-x}Co_xTi_2O_5$) in a more extended compositional range (up to 40 mol% of Co per karrooite unit formula, due to the environmental concerns previously mentioned). $CoTi_2O_5$ crystallizes in the same pseudobrookite structure as $MgTi_2O_5$ karrooite, and it is also an entropy-stabilized phase [12–14]; it becomes more stable the higher the temperature, and below 1142 °C it decomposes in a mixture of the more stable $CoTiO_3$ ilmenite and TiO_2 rutile phases [15–17]. Given the isomorphism between Co-Ti and Mg-Ti pseudobrookites as well as the quite similar effective ionic radii for Co^{2+}(74.5 pm) and Mg^{2+}(72 pm) ions in octahedral coordination [18], we could expect a whole range of solid solubility of Co ions in $MgTi_2O_5$ karrooite.

Moreover, we also investigated the effect of Zn^{2+} codoping on the stabilization of Co-doped karrooite solid solutions ($Mg_{1-x-y}Co_xZn_yTi_2O_5$), the color and optical properties of the resulting pigments, and its industrial performance either as ceramic pigments or dyes within ceramic glazes [19–23]. In spite of the existence of some precedent investigations analyzing the effect of Co- and Zn-codoping on related $MgTiO_3$ ilmenites (in order to improve its dielectric properties) [24,25], as far as we know there are not preliminary reports in the literature concerning Co- and Zn-codoped $MgTi_2O_5$ karrooite. In addition, there is also no experimental evidence of the synthesis of $ZnTi_2O_5$ with a parent structure to $MgTi_2O_5$ and $CoTi_2O_5$ pseudobrookites. Indeed, although some TiO_2·xZnO compositions including $ZnTi_2O_5$ stoichiometry have been prepared as high frequency dielectric materials [26] or as photoactive $ZnTi_2O_5$ thin films for solar cells [27], the supposed crystallization of $ZnTi_2O_5$ was not demonstrated.

In this respect, different ternary compounds with interesting technological applications are already known as stable phases in the Zn-Ti-O ternary system [28–31], such as Zn_2TiO_4 inverse cubic spinel, $ZnTiO_3$ rhombohedral ilmenite and $Zn_2Ti_3O_8$ cubic defect spinel. Interestingly, other unreported or missing phases in this system have been very recently predicted to be borderline stable, such as $ZnTi_2O_4$ normal spinel, $ZnTi_2O_5$ pseudobrookite (chemically similar or equivalent to $MgTi_2O_5$ karrooite), and $ZnTi_5O_{10}$ in the high-symmetry Ti_3O_5 pseudobrookite structure [32]. As experimental evidence, the related $Zn_xTi_{3-x}O_5$ phase (with x≈0.6) was successfully synthesized in this recent study, adopting essentially the same structure as $ZnTi_5O_{10}$. This compound was found as much stable as the other unreported ternary Zn-Ti-O phases, highlighting the interest to perform further explorative investigations on these missing materials of the Zn-Ti-O system, including $ZnTi_2O_5$ pseudobrookite.

Accordingly, in addition to the use of Zn as codoping agent in Co-$MgTi_2O_5$ pigments, in this study we firstly investigated the $MgTi_2O_5$:$ZnTi_2O_5$ system to elucidate the solid solubility limit of Zn^{2+} ions in karrooite lattice. In the case of Co-karrooite pigments, the addition of Zn^{2+} as codoping agent or structure modifier could induce a considerable color change due to modification of Co^{2+} octahedral crystal field [33] and the covalent character of Co-O bonds [34] in karrooite lattice. On the other hand, the choice of Zn^{2+} ions could also serve to improve the stability of Co-karrooite compounds as true ceramic pigments within Zn-Ca-borosilicate ceramic glazes, as it has been recently found in other Zn-containing pigments such as Co-doped $Ca_2(Zn,Co)Si_2O_7$ hardystonite [35].

2. Materials and methods

2.1. Samples preparation (Ceramic route)

A set of four different $(Mg_{1-x-y}Co_xZn_y)Ti_2O_5$ karrooite-based solid solutions (series) were prepared by the conventional ceramic route, using $Mg_5(CO_3)_4(OH)_2.xH_2O$ (42% as Mg, Aldrich), Co_3O_4 (70% as Co, Panreac), ZnO (98%, Panreac) and TiO_2 (anatase, 99–100.5%, Panreac) as precursors. The location of the four series compositions on a ternary Mg-Zn-Co diagram is shown in Fig. 1. First of all, a whole series of Zn: karrooite solid solutions (***Kar-Zn*** series: $\boldsymbol{Mg_{1-x}Zn_xTi_2O_5}$, with x=0, 0.1, 0.2, 0.4, 0.5, 0.6, 0.8 and 1.0) was prepared for the previous investigation on the $MgTi_2O_5$–$ZnTi_2O_5$ system. In regard to Co-doped samples, the ***Kar-Co*** series ($\boldsymbol{Mg_{1-x}Co_xTi_2O_5}$; x=0.05, 0.1, 0.2 and 0.4) corresponds to Zn-free Co-karrooite compositions ($MgTi_2O_5$–$CoTi_2O_5$ system). Then, the ***Kar-CoZnL*** series ($\boldsymbol{Mg_{0.8-x}Zn_{0.2}Co_xTi_2O_5}$, with x=0.05, 0.1 and 0.2) contains a relatively low and fixed amount of Zn (0.2 mol) per MTi_2O_5 karrooite formula unit, with Co only replacing Mg ions and having a variable Mg:Zn ratio. Finally, the ***Kar-CoZnH*** series ($\boldsymbol{(Mg_{0.5}Zn_{0.5})_{1-x}\ Co_xTi_2O_5}$, with x=0.05, 0.1 and 0.2) was prepared with a considerably higher Zn doping level (0.4–0.475 mol of Zn^{2+} per karrooite formula unit), and using this time a fixed Mg:Zn ratio equal to 1:1 (note that in this series Co ions are equally replacing both Mg and Zn ions).

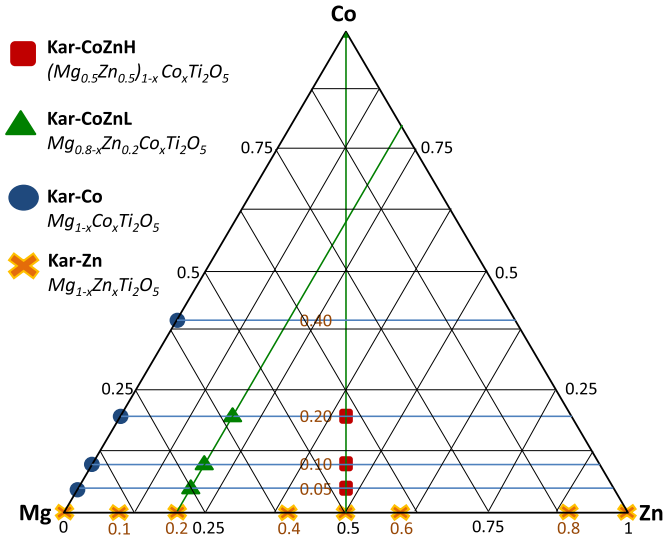

Fig. 1. Ternary Mg-Zn-Co diagram showing the location of the prepared compositions for the four *(Co,Zn)-Karrooite* solid solution series: ***a) Kar-Zn***, $Mg_{1-x}Zn_xTi_2O_5$; ***b) Kar-Co***, $Mg_{1-x}Co_xTi_2O_5$; ***c) Kar-CoZnL***, $Mg_{0.8-x}Zn_{0.2}Co_xTi_2O_5$; and ***d) Kar-CoZnH***, $(Mg_{0.5}Zn_{0.5})_{1-x}Co_xTi_2O_5$.

In a typical sample preparation, the corresponding stoichiometric mixture of precursors was homogenized in planetary mills (20 min) using acetone as dispersant. The dried powders were then directly calcined in an electrical furnace up to 1200 ºC with heating rate of 5ºC/min, a soaking time of 3 h and with free cooling to room temperature. *Kar-Zn* samples were also subsequently fired at 1400 ºC (after due homogenization and micronization of previously fired compositions). After the firing treatment, all the fired powders were homogenized and micronized (mortar and pestle) and sieved below 63 μm before further characterization (Section 2.2).

2.2. Samples characterization

Crystal chemical characterization of karrooite-based (Mg,Zn,Co) Ti_2O_5 calcined samples was performed by X-ray powder diffraction (XRD) in a D4 Endeavor (Bruker-AXS) powder diffractometer with Cu-K_α radiation (from 10 to 70º 2θ, with steps of 0.05º 2θ and a counting time of 2 s per step). The diffractometer was equipped with a graphite secondary monochromator to eliminate K_β and fluorescence signals. The cell parameters were also determined by indexing and least-squares refinement of XRD patterns of selected powder compositions mixed (50 wt%) with Al_2O_3 corundum as internal standard and measured under slower conditions (steps of 0.02º 2θ and a counting time of 4 s per step), using the POWCAL and LSQC programs (Department of Chemistry, University of Aberdeen, UK).

On the other hand, the microstructure and morphology of