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SOLID STATE SYNTHESIS AND CHARACTERIZATION OF Co, Mn-DOPED KARROOITE PIGMENTS FOR THE CERAMIC INDUSTRY

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Introduction

A huge amount of toxic organic dye wastewaters are produced by numerous industries, including the ceramic industry. The majority of synthetic dyes consists in aromatic structures that cannot be effectively degraded, leading to ocean pollution when they are released.
Recently, the traditional ceramic industry showed an increased interest on research of new ceramic pigments, so they could be able to replace the organic dyes. These pigments are presented as fine powders and are used for the coloration of glazes, ceramic bodies, and porcelain enamels. These ceramic pigments must have some characteristics, including: high thermal stability, high chemical resistance, low toxicity level and must be inert to the action of molten glass. Karrooite, $MgTi_2O_5$, can be considered a potential ceramic pigment due to its refractoriness and high refractive indices. Moreover, it is possible to develop different colors and shades because karrooite can be a host lattice for several transition metal ions.

Materials and methods

The ceramic pigments were obtained by the classical ceramic route.
Firstly, there were obtained the oxide precursors MgO and Co_3O_4. MgO was obtained by sol-gel route using $Mg(NO_3)_2.6H_2O$ and NaOH. Co_3O_4 was obtained via a mecanochemical synthesis using $Co(NO_3)_2.6H_2O$ and NH_4HCO_3, molar ratio of 2:5.
All the oxide precursors (TiO_2, MgO, Co_3O_4 and MnO_2) where then mixed together (according to the stoichiometry) and wet homogenized. After the homogenization, the mixture was dried and calcinated at 1200°C. The obtained pigments were then characterized and tasted in a ceramic glaze.

Results and conclusions

The pigments color range from light green to a darker shade once the Co^{2+} content increase, and turn brown when MnO_2 is added.

The XRD spectra of the Co-doped karrooite samples are represented in Figures 1 and 2. The diffraction interferences confirmed the effective formation and relative stabilization of karrooite solid solutions in all samples, although with decreasing quantities of residual TiO_2 (rutile) and $MgTiO_3$ (geikielite) the higher the Co content.

The spectra obtained via Fourier transform infrared spectroscopy are specific to the karrooite. The set of bands from 615 cm^{-1} to 350 cm^{-1} are characteristics of the bending modes of O-Ti-O-Mg-O.

The color characterization revealed that the resulted colors are more saturated or darker (lower L values) the higher the cobalt and manganese content, and that the Co-doped samples are less yellow (lower b values) than the Co, Mn-codoped samples.

In conclusion, the complex characterization confirmed the formation of karrooite solid solutions. The color characterization revealed that the resulted colors are more saturated or darker (lower L values) the higher the cobalt and manganese content, and that the Co-doped samples are less yellow (lower b values) than the Co, Mn-codoped samples.

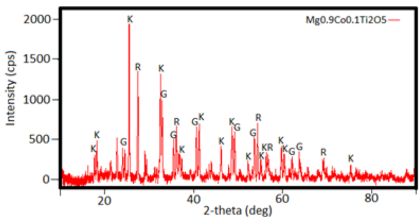

Fig. 1. XRD spectrum of karrooite solide solution ($Mg_{1-x}Co_xTi_2O_5$ with x = 0.1)

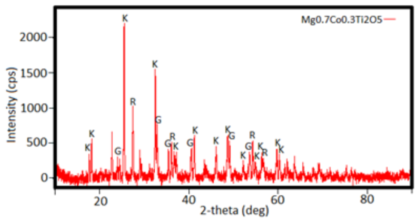

Fig. 2. XRD spectrum of karrooite solide solution ($Mg_{1-x}Co_xTi_2O_5$ with x = 0.3)

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