Structural characterization and colour of $CaMg_{0.5}Co_xNi_{0.5-x}P_2O_7$ ($0.0 \leq x \leq 0.5$) compositions

M. A. Tena[1], Mohammed S. M. Abdelbaky[2,3], Camino Trobajo[3], Santiago Garcia-Granda[3,*]

[1] University of Jaume I - Castellon de la Plana (Spain), [2] University of Salamanca - Salamanca (Spain), [3] University of Oviedo – CINN(CSIC), Oviedo (Spain).

**s.garciagranda@cinn.es*

In our pursuit of developing more sustainable and environmentally friendly materials, we have created new color palettes through solid solutions. This study focuses on the structural characterization of $CaMg_{0.5}Co_xNi_{0.5-x}P_2O_7$ (where $0.0 \leq x \leq 0.5$) compositions, prepared using the chemical co-precipitation method. To reduce the toxic and costly amounts of cobalt and nickel, we substituted half of the Ni(II) and/or Co(II) ions in $CaMP_2O_7$ (M = Ni, Co) with Mg(II) ions. We observed the formation of the $CaNi_3(P_2O_7)_2$ compound when $0.0 \leq x \leq 0.1$; however, this structure was not present for $x > 0.1$, despite the existence of $CaCo_3(P_2O_7)_2$ reported in the literature [2]. In these structures, Co(II) and Ni(II) ions occupy octahedral sites. The presence of $CaNi_3(P_2O_7)_2$ was also confirmed during the crystallization of $CaNiP_2O_4$ from a melt of $Ca_2P_2O_4$ and $Ni_2P_2O_4$ in a 1:1 molar ratio [1]. The coloration in these compositions primarily arises from the presence of Co(II) and/or Ni(II) ions within the $CaMP_2O_7$ structure [1, 2]. Modified by the $CaNi_3(P_2O_7)_2$ when $0.0 \leq x \leq 0.1$ and by the diphosphate phase, α-$M_2P_2O_7$ (M = Mg, Ni, Co) present in all compositions in smaller amounts. The coordination numbers for M are 5 and 6 in this last structure.

The variation in unit cell parameters, as determined by diffraction profile refinement (Figure 1), indicates the formation of solid solutions with the triclinic structure of $CaMP_2O_7$ (M = Mg, Ni, Co) and with the monoclinic structure of $M_2P_2O_7$ (M = Mg, Ni, Co).

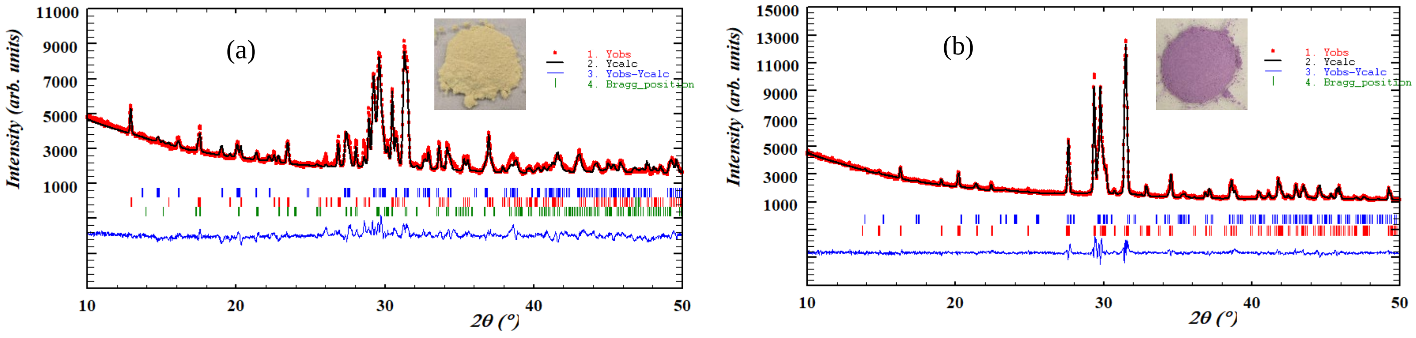

Figure 1. The diffraction profile refinement of $CaMg_{0.5}Co_xNi_{0.5-x}P_2O_7$ ($0.0 \leq x \leq 0.5$) compositions with x = 0.0 (a) and x = 0.5 (b) fired at 1000 °C by Rietveld. The image of coloured material is shown in inset.

The Co–O bond distances in $CaCoP_2O_7$ range from 2.11 to 2.22 Å, while in $CaCoSi_2O_7$, they are between 1.83 and 1.87 Å. These variations influence the electronic transitions of octahedral Co(II) ions, leading to absorption bands at longer wavelengths (lower energies) in the UV-Vis spectra of $CaCoP_2O_7$, which corresponds to the violet color observed in the samples. In contrast, similar compositions in the diopside structure exhibit pink hues [4]. Transition bands of pentacoordinated Co(II) from diphosphate structure is also detected.

When incorporated into ceramic glazes, these compositions serve as ceramic dyes, with the resulting color in enamelled samples depending on the value of x. Intense green and blue colorations are achieved when these pigments are dissolved in commercial glazes, both in $CaMg_{0.5}CoxNi_{0.5-x}P_2O_7$ ($0.0 \leq x \leq 0.5$) and $CaMg_{0.5}CoxNi_{0.5-x}Si_2O_6$ ($0.0 \leq x \leq 0.5$) compositions.

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