MS15 Mineralogical and inorganic crystallography

MS15-01

Structural characterization of pink $MgCo_xNi_{1-x}SiO_4$ ($0 \le x \le 1$) solid solutions with olivine structure

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Abstract

Yellow-green Ni_2SiO_4 olivine and blue Co_2SiO_4 olivine are in the DCMA Classification of the Mixed Metal Oxide Inorganic Colored Pigments (DCMA-5-45-3 and DCMA-5-08-2) [1]. These compounds can be used as ceramic dyes when they are dissolved in glazes. Formation of solid solutions with Mg(II) decreases the high content of nickel or cobalt in them and makes these materials less hazardous. White Mg_2SiO_4 also crystallizes in this structure. M(II) ions are in two octahedral positions in olivine. M1 is a 4a site and M2 4c. The transition metal ions prefer the M2 site and Mg^{2+} ions (without electrons in d orbitals) the more ionic M2 site [2, 3].

In this study $MgCo_xNi_{1-x}SiO4$ ($0.0 \le x \le 1.0$) solid solutions with olivine structure have been synthetized via the chemical coprecipitation method obtaining materials with a smaller M(II) (M = Co, Ni) amount. Increasing the unit cell parameters with x is consistent with the replacement of Ni(II) by the larger Co(II) ion, confirming the formation of olivine solid solutions. At 1200 °C, the unit cell parameters increase linearly with x according to the Vegard's law. Thus, the Co(II) and Ni(II) are randomly distributed in the $MgCo_xNi_{1-x}SiO_4$ ($0.0 \le x \le 1.0$) solid solutions with the olivine structure. The different scattering factor of Mg(II) ion allows to refine occupations considering the occupation of (Ni(II)/Co(II)) + Mg(II) as 1.0. The occupation of Co(II) ions in M1(4a) was found higher than in M2(4c) sites.

At 1000 and 1200 °C, only small amounts of minor crystalline phases are detected with olivine. The composition without cobalt ($x = 0.0$) is green and pink samples are obtained with cobalt ($x > 0.0$) at these temperatures. The pink colour of samples with $x > 0.0$ is due to the absorbance between 440 and 630 nm, assigned to third transition band in octahedral Co(II), $^4T_1 \rightarrow {}^4T_1(P)$. The absorbance increases with x (cobalt amount), the a* colour parameter (+, red amount) increases with x and the b* colour parameter (yellow amount (+) to blue amount (-)) decreases with x.

Colour and distances in the coordination of Co(II) in these materials will be compared with other Co(II) compounds to explain the reason for the pink $MgCo_xNi_{1-x}SiO_4$ ($0.25 \le x \le 1.0$) solid solutions and the blue or violet in Co_2SiO_4.

Fig. 1. The diffraction profile refinement by Rietveld's method from pink $MgCoSiO_4$ composition fired at 1200 °C (The CIEL*a*b* colour parameters: 66.67, +12.55, -5.61; L* is the lightness axis (black (0)→white (100)), a* is the green (-)→red (+) axis, and b* is the blue (-)→yellow (+) axis [4]).

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References

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Pink MgCoSiO4 composition fired at 1200 ºC