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SPINELS RENAISSANCE: THE PAST, PRESENT, AND FUTURE OF THOSE UBIQUITOUS MINERALS AND MATERIALS

Chromium influence on Mg-Al intracrystalline exchange in spinels and geothermometric implications

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Abstract

Flux-grown spinel crystals belonging to the $MgAl_2O_4$-$MgCr_2O_4$ spinel series were investigated to reveal the effects of Cr substituting for Al on cation distribution and their influence on Mg-Al intracrystalline exchange. Samples were structurally and chemically characterized by single-crystal X-ray diffraction and electron microprobe, and cation distribution was obtained with a tested optimization model for site populations. The results evidenced that the contribution of the tetrahedral bond distance to the unit-cell parameter is smaller than that of the octahedral bond distance, which is driven by the substitution of Cr for Al. Moreover, the influence that Cr exerts on Mg-Al order-disorder intersite exchange is non-linear along the whole series.

The comparison between the cation distributions derived from crystal-chemical data and the O'Neill-Navrotsky thermodynamic model (with $\alpha_{Mg\text{-}Al}$ = 23 kJ/mol and $\beta_{Mg\text{-}Al}$ = 13 kJ/mol) shows large discrepancies, which can be reconciled assuming $\alpha_{Mg\text{-}Al}$ values variable from 23 to 100 kJ/mol as a function of Cr. This suggests that, irrespective of temperature, the Al ordering at the octahedrally coordinated site increases with increasing Cr substitution for Al. The geothermometric implications of the present study point out that closure temperatures, calculated from a well-tested intersite geothermometer, are reliable for spinels with magnesiochromite component smaller than 85%, i.e., Cr/(Cr+Al) < 0.85, whereas spinels with larger magnesiochromite component yield unreliable closure temperature.

Keywords: Electron microprobe, crystal synthesis, X-ray diffraction, spinel, magnesiochromite, geothermometer