

Blue spinel crystals in the MgAl_2O_4 - CoAl_2O_4 series: Part II. Cation ordering over short-range and long-range scales

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ABSTRACT

Optical absorption spectroscopy and X-ray structural refinements were used to characterize short-range and long-range structures of 10 gem-quality, blue spinel single crystals synthesized on the $(\text{Mg}_{1-x}\text{Co}_x)\text{Al}_2\text{O}_4$ solid solution ($x = 0.07$ – 1.00). The site distributions of Mg, Co^{2+} , and Al show that the tetrahedrally coordinated site (T) is mainly populated by Mg and Co^{2+} , with a marked preference of Co^{2+} for tetrahedral coordination with respect to Mg, while the octahedrally coordinated site (M) is dominated by Al. Crystals also show a certain degree of inversion, i.e., occurrence of Al at T counterbalanced by the occurrence of divalent cations at M, which decreases from 0.24 to 0.13 with increasing Co^{2+} content.

Short-range information based on the crystal field splitting parameter Dq derived from single-crystal optical spectra suggests that the local Co^{2+} -O bond length at the T-site may increase marginally at increasing Co^{2+} content. An almost constant value for the Racah B -parameter, also derived from optical spectra, for tetrahedrally coordinated Co^{2+} suggests that any influence of substitutional second nearest neighbor cations on the ionicity of Co^{2+} -O bonds at the T-site is very small. Long-range information shows that variations in the unit-cell parameter from 8.084 to 8.105 Å along the solid-solution series are mainly related to the ordering of Al at the M site as a result of the replacement of Mg by Co^{2+} . Therefore, the spinel structure responds to the chemical variation by ordering of Al in such a manner that M-O remains almost constant and T-O increases. In this way, the lengths of shared octahedral edges are reduced and the destabilization effect due to the increased octahedral cation-cation repulsion is minimized. In line with other studies, the importance of steric factors for controlling the cation distributions in the spinel structure has also been shown to be valid in the MgAl_2O_4 - CoAl_2O_4 solid-solution series.

Keywords: Cobalt spinel, optical absorption spectroscopy, X-ray diffraction, cation ordering, ionic potential