Blue spinel crystals in the MgAl\textsubscript{2}O\textsubscript{4}-CoAl\textsubscript{2}O\textsubscript{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 (Mg\textsubscript{1-x}Co\textsubscript{x})Al\textsubscript{2}O\textsubscript{4} solid solution (x = 0.07–1.00). The site distributions of Mg, Co\textsuperscript{2+}, and Al show that the tetrahedrally coordinated site (T) is mainly populated by Mg and Co\textsuperscript{2+}, with a marked preference of Co\textsuperscript{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\textsuperscript{2+} content.

Short-range information based on the crystal field splitting parameter \(D_Q\) derived from single-crystal optical spectra suggests that the local Co\textsuperscript{2+}-O bond length at the T-site may increase marginally at increasing Co\textsuperscript{2+} content. An almost constant value for the Racah B-parameter, also derived from optical spectra, for tetrahedrally coordinated Co\textsuperscript{2+} suggests that any influence of substitutional second nearest neighbor cations on the ionicity of Co\textsuperscript{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\textsuperscript{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\textsubscript{2}O\textsubscript{4}-CoAl\textsubscript{2}O\textsubscript{4} solid-solution series.

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

**Introduction**

Many substances crystallize in the spinel type structure, most of which are oxides, in addition to sulfides (e.g., ZnAl\textsubscript{2}S\textsubscript{4}), selenides (e.g., CuCr\textsubscript{2}Se\textsubscript{4}), halides (e.g., Li\textsubscript{2}NiF\textsubscript{4}), and pseudohalides [e.g., ZnK(CN)\textsubscript{4}]. In spinel oxides, steric factors are important for the cation distribution among the structural sites, as exemplified by, e.g., FeAl\textsubscript{2}O\textsubscript{4}, CuAl\textsubscript{2}O\textsubscript{4}, and CoAl\textsubscript{2}O\textsubscript{4} spinels (Harrison et al. 1998; O’Neill 1994; O’Neill et al. 2005), in which the small Al\textsuperscript{3+} cation prefers the octahedrally coordinated (M) sites to the tetrahedrally coordinated (T) ones. In these spinels, cation size and crystal field stabilization energy suggest that Fe\textsuperscript{2+}, Cu\textsuperscript{2+}, and Co\textsuperscript{2+} should prefer the octahedra, but the presence of Al obviously counters this behavior. They are in fact (almost) normal spinels with the divalent cations ordered at T and Al\textsuperscript{3+} cations ordered at the M sites in the slightly distorted cubic close-packed array of oxygen atoms. Moreover, it has been shown on a limited number of spinel solid-solution series that the average structure determined from diffraction data often differs from the local structure retrieved by spectroscopic methods; this means that Vegard’s rule is not obeyed at the atomic scale due to lattice relaxation during atomic substitution (Galoisy 1996; Hålenius et al. 2010, 2011).

As comprehensively described in the part I of the present study (D’Ippolito et al. 2012, this issue), CoAl\textsubscript{2}O\textsubscript{4} oxide is rarely found as a mineral but is widely used, since the discovery of its industrial synthesis route, as a pigment for the coloration of a large range of materials (e.g., ceramics, and many others). This is due to its peculiar and highly efficient optical absorption in the red-yellow region, which gives the typical, highly saturated blue color in daylight and violet in tungsten light (Dharmaratne 1993). In addition to that, Co-bearing materials with spinel structure exhibit many other remarkable properties (e.g., catalytic activity, Fierro et al. 2005 and references therein) and are extensively investigated because of that. However, in spite of the interest due to physical properties, very little information is available in the literature on CoAl\textsubscript{2}O\textsubscript{4} (and Co-bearing materials) crystal chemistry, and many aspects regarding electronic structure and cation distribution are not well understood or even unknown. Previous studies on CoAl\textsubscript{2}O\textsubscript{4} include investigations of electron density (Toriumi et al. 1978), crystal field transitions (e.g., Kuleshov et al. 1993) and cation distribution as a function of temperature (O’Neill 1994; Nakatsuoka et al. 2003). In particular, the latter authors highlighted that at high temperatures, limited fractions of the Co\textsuperscript{2+} and Al\textsuperscript{3+} ions may interchange their structural positions. Nevertheless, systematic investigation of the structural variations all along the entire (Mg\textsubscript{1-x}Co\textsubscript{x})Al\textsubscript{2}O\textsubscript{4} solid-solution series is missing.