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Cation ordering over short-range and long-range scales in the $MgAl_2O_4$-$CuAl_2O_4$ series

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ABSTRACT

A multi-analytical approach using electron microprobe analysis, X-ray structural refinement, and optical absorption spectroscopy was applied to characterize short-range and long-range structures of synthetic spinel single crystals along the $MgAl_2O_4$-$CuAl_2O_4$ solid-solution series. Site populations, derived from the results of site-scattering refinement and stereochemical analysis, show that the tetrahedrally coordinated site (T) is mainly populated by Mg and Cu^{2+}, while the octahedrally coordinated site (M) is dominated by Al. Crystals also show a significant degree of inversion, i.e., occurrence of Al at T counterbalanced by occurrence of divalent cations at M, which increases slightly from 0.24 to 0.29 for the highest Cu^{2+} contents.

Short-range information derived from optical spectra suggests that the local $^{T}Cu^{2+}$-O distances remain constant at increasing Cu^{2+} content, whereas local $^{M}Cu^{2+}$-O distances are ca. 0.02 Å shorter in Cu-poor $MgAl_2O_4$ spinels as compared to $^{M}Cu^{2+}$-O distances in end-member $CuAl_2O_4$. The observed splitting of an absorption band, at ca. 7000 cm^{-1}, caused by electron transitions in $^{T}Cu^{2+}$ as well as the anomalous broadness of an absorption band, at ca. 13 500 cm^{-1}, caused by electron transitions in $^{M}Cu^{2+}$ indicates the occurrence of local Jahn-Teller distortions at T and M. Long-range information, however, shows no violation of $Fd\overline{3}m$ symmetry. From refinements of our single-crystal XRD data we could for the first time derive for a cubic spinel phase a $^{M}Cu^{2+}$-O distance of 2.080 Å and a $^{T}Cu^{2+}$-O of 1.960 Å. The very limited variations in the unit-cell parameter *a* from 8.079 to 8.087 Å are mainly related to the disordering of Al. Because of the very similar size of Cu^{2+} and Mg at the T and M sites, the spinel structure responds to the $Cu^{2+} \rightarrow$ Mg substitution by increasing cation disordering in such a manner that mean M-O distances remain constant and the mean T-O distances decrease slightly. This results in increasing length of shared octahedral edges and thereby increase of the octahedral cation-cation repulsion. In line with other studies, the importance of steric factors for controlling the cation distributions in the spinel structure is demonstrated to be valid also in the $MgAl_2O_4$-$CuAl_2O_4$ solid-solution series.

Keywords: Copper spinel, electron microprobe, optical absorption spectroscopy, X-ray diffraction, cation ordering, ionic potential