

Structural refinement and crystal chemistry of Mn-doped spinel: A case for tetrahedrally coordinated Mn³⁺ in an oxygen-based structure

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ABSTRACT

Spinel single crystals of four compositions along the MgAl₂O₄–MgMn₂O₄ join, with Mn³⁺ up to 0.25 apfu, were synthesized by use of a flux-growth method. The crystals were analyzed by electron microprobe, X-ray single-crystal diffraction, and optical absorption spectroscopy. Results revealed that Mg contents vary from 0.90 to 0.99 apfu, Mn²⁺ ≤ 0.11 apfu, Mn³⁺ varies from zero to 0.25 apfu, and Al-contents from 1.75 to 1.99 apfu. The unit-cell parameter increases linearly from 8.0883(3) to 8.1413(4) Å with increasing Mn³⁺ content. The crystals show moderately disordered cation distributions, with $i = 0.23(1)$, and different distribution trends have been observed: the Mg content is constant at the T site and is replaced by Mn²⁺ at the M-site; Al decreases while Mn³⁺ increases in T- and M-sites. Mn³⁺ shows a preference for the T site, and a specific bond distance was refined, ¹⁹Mn³⁺-O = 1.88(1) Å. Unpolarized room-temperature single-crystal spectra reveal two relatively broad absorption features at ca. 23 000 and 10 800 cm⁻¹, which are assigned to spin-allowed d-d transitions in Mn³⁺ located at octahedral and tetrahedral sites, respectively. The bond valence approach shows that the bonds are strained in the tetrahedron indicating underbonding in T, whereas the bonds are unstrained in the octahedron. To reduce the M-M repulsion, the steric effect is driven by the movement of the oxygen atoms, which improves the shielding effect around the M-site, thus increasing the distortion of the structure relative to the CCP. As a result the tetrahedron undergoes an isotropic expansion, which constrains the structure to incorporate larger cations such as Mn³⁺ rather than smaller cations like Al at the T-site. This behavior, which is in disagreement with predictions based on crystal field energy considerations, illustrates the greater importance of steric factors on the cation distribution in spinels.

Keywords: Chemical analysis (mineral), spinel, crystal structure, optical spectroscopy, Mn³⁺ in spinel, order-disorder, XRD data