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A first record of strong structural relaxation of TO_4 tetrahedra in a spinel solid solution

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Abstract

Optical absorption spectroscopy and X-ray structural refinements of seven different spinel single crystals on the $(Mg_{1-x}Mn_x)Al_2O_4$ solid solution (x = 0.02–1.00) evidences exceptionally strong relaxation (ε = 0.83) of $^{IV}Mn^{2+}$-O bonds. Our single-crystal structure refinements demonstrate that the ideal $^{IV}Mn^{2+}$-O bond distance in fully ordered galaxite ($MnAl_2O_4$) should be 2.050 Å, which is 0.014 Å longer than previously suggested, and that structural parameters are mainly affected by the variations occurring at the TO_4 tetrahedron. The very strong structural relaxation observed around the T site may be explained by the fact that the TO_4 polyhedra of the spinel structure share only corners with neighboring MO_6 octahedra and are fully isolated from neighboring TO_4 tetrahedra. This provides structural flexibility around the T site and allows for considerable local T-O bond distance variations.

Keywords: Spinel, galaxite, electronic spectra, structure refinement, microprobe analysis, synthesis