

Raman spectroscopic study of structural relaxation and cation occupancies in a spinel solid solution

Peter Lazor¹, Ulf Hålenius², Henrik Skogby², Ferdinando Bosi³

¹Uppsala University, Department of Earth Sciences, Uppsala, Sweden

²Department of Mineralogy, Swedish Museum of Natural History, Stockholm, Sweden

³Dipartimento di Scienze della Terra, Sapienza Università di Roma, Rome, Italy

Spinelns represent a large and important class of oxides of geological and technological interests. Even though crystal-chemical aspects of cation substitutions, order-disorder behavior and occupancies over the tetrahedral and octahedral sites have been widely studied, major gaps still remain in understanding the salient features of these phenomena. Application of multiple analytical methods on the same samples represents a powerful approach, yielding a detailed and more profound interpretation.

Raman spectroscopic study on spinel single crystals have been carried out for the solid solution series $(\text{Mg}_{1-x}\text{Mn}_x)\text{Al}_2\text{O}_4$, $x = 0.02-1.00$. The results of this study complement and corroborate earlier investigation of the same s.s. series by techniques of optical absorption spectroscopy and x-ray diffraction (Hålenius et al., 2011). The Raman setup consisted of a single-stage imaging spectrometer equipped with two notch filters, holographic transmission grating and thermoelectrically cooled CCD detector. Polarized spectra were obtained from octahedrally-shaped crystals in the back-scattering geometry using argon ion laser as the excitation source (514.5 nm) at a resolution of about 3 cm^{-1} . The acquisition time lasted typically few minutes.

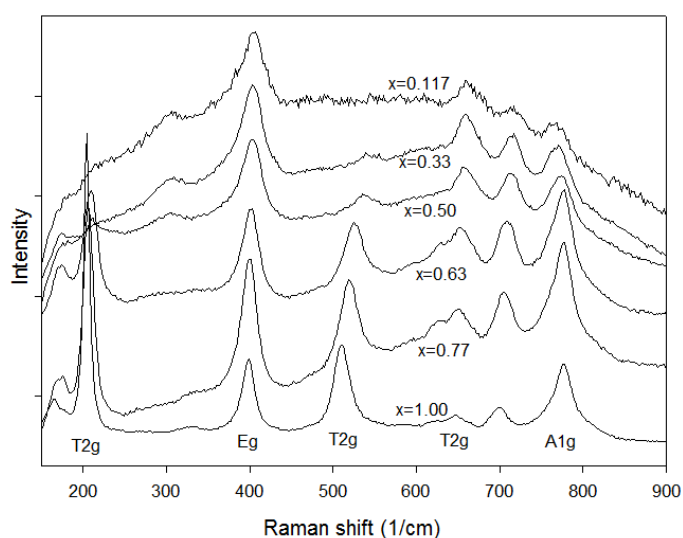


Fig. 1. Raman spectra of spinel solid solution series $(\text{Mg}_{1-x}\text{Mn}_x)\text{Al}_2\text{O}_4$

A_{1g} , E_g and T_{2g} modes, characteristic of spinel structures, were identified in the spectra, representing vibrations of coordination tetrahedra (Fig. 1.). Upon the Mn^{2+} to Mg^{2+} cation substitutions, intensities and positions of Raman bands exhibit distinct changes, the origin of which have been analyzed in terms of cation occupancies and structural relaxation of TO_4 tetrahedra, utilizing methodologies of spectroscopic and chemical Grueneisen parameters, and comparative crystal chemistry of spinels.

References:

Hålenius U., Bosi F., Skogby H. (2011), *American Mineralogist*, 96, 617-622.