Supplementary Material for

Si-disordering in $MgAl_2O_4$-spinel at high *P-T* conditions, with implication to Si-Mg disorder in Mg_2SiO_4-ringwoodite

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One fragment of the red, Si-free $MgAl_2O_4$-Sp crystal (N-Sp) with an octahedral shape from Mogok (Burma), 100*80*50 μm^3, was analyzed by the single-crystal X-ray diffraction method at ambient condition. Data were collected by an Agilent Technologies Rigaku micro-focused four-circle diffractometer using Mo Kα radiation (λ = 0.71073 nm), with the theta range from 4.37 to 28.30 °.

An initial structure solution, carried out in the $Fd\bar{3}m$ space group, was obtained via direct methods and refined by a full-matrix least-squares method using the SHELXT

software, with the chemical constraint of $MgAl_{1.98}Cr_{0.02}O_4$ (see the main text for the compositional data). All the heavy atoms were first located unambiguously in the Fourier maps, and then the O atoms were found in the subsequent difference maps. All atoms were refined with anisotropic displacement parameters. The refined parameters were the oxygen positional parameter (u), bond distances of the T-site and M-site, and anisotropic displacement parameters.

As the value of the inversion parameter x directly obtained from the structure refinement process should be of high uncertainty due to the similar X-ray scattering factors of Mg and Al, we also calculated the x with the bond-length method of Carbonin et al. [1]. In the calculation, we used the ionic radii from Ref. [2]. The x value was calculated by minimizing the following function which took structural and chemical data into account [1],

$$\mathrm{F}(X_i) = \sum_j \left\{ \left[O_j - C_j(X_i) \right] / \delta_j \right\}^2$$

where O_j were observed quantities with their standard deviations as δ_j, i.e. T-O and M-O bond lengths, mean atomic numbers of the T-site and M-site, number of charges for charge balance, and atomic proportions obtained from microprobe analysis. $C_j(X_i)$ were the corresponding quantities calculated by variable cation fractions X_i.

In the minimization, some assumptions were made according to Ref. [1]: (a) Mg, Al, Fe^{2+}, Fe^{3+} and vacancies would occupy both the T-site and M-site, that was to say, those were variables in our calculation; (b) Cr, Ti and Ni occupied the M-site only; (c) Bond lengths were a linear combination of site atomic fractions multiplied by their characteristic bond distances in the 2-3 spinels.

After several iterative operations with these two methods, $F(X_i)$ were achieved as less than 1δ between the calculated and observed quantities. The final cycles of the least-squares refinement converged at R_1 = 0.0164, wR_2 = 0.0730, and S = 1.065 (see STable 1 and STable 2 for the crystal structure refinement details and results, respectively). The cations on the T-site and M-site were determined as $Mg_{0.836}Al_{0.162}Fe^{3+}_{0.002}$ and $Mg_{0.157}Al_{1.823}Cr_{0.018}Ti_{0.001}Ni_{0.001}$, respectively. Eventually, the cation fraction of Al on the T-site, or the inversion parameter x, was determined as

0.162, a value compatible with our Raman spectroscopic data.

STABLE 1. Details of structure refinement

Empirical formula	$(Mg_{0.993}Fe_{0.002}Ti_{0.001}Ni_{0.001})(Al_{1.983}Cr_{0.018})O_4$	
Formula weight	141.205	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Cubic	
Space group	$Fd\bar{3}m$	
Unit cell dimensions	a = 8.0728(9) Å	α = 90 °
	b = 8.0728(9) Å	β = 90 °
	c = 8.0728(9) Å	γ = 90 °
Volume	526.11(10) $Å^3$	
Z	8	
Density (calculated)	3.566 kg/m^3	
Absorption coefficient	1.217 mm^{-1}	
F(000)	561.8	
Crystal size	100 x 80 x 50 μm^3	
Theta range for data collection	4.37 to 28.30 °	
Index ranges	$-10 \leq h \leq 8$, $-10 \leq k \leq 9$, $-10 \leq l \leq 10$	
Reflections collected	1090	
Independent reflections	47 [R(int) = 0.0562]	
Completeness to theta = 28.30 °	100%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	47 / 0 / 8	
Goodness-of-fit on F^2	1.065	
Final R indices [I>2sigma(I)]	R_1 = 0.0164, wR_2 = 0.0730	

R indices (all data)	R_1 = 0.0173, wR_2 = 0.0740
Largest diff. peak and hole	0.216 and -0.219 e $Å^{-3}$

STABLE 2. Structural data of N-Sp

Lattice parameter (Å)	8.0728(9)
O atom position *u*	0.26329(24)
Inversion parameter *x*	0.162
T-O (Å)	1.93367(13)
M-O (Å)	1.9169(3)
V_T ($Å^3$)	3.7105
V_M ($Å^3$)	9.3915
U_{iso} (oxy)	0.0041(9)
U_{iso} (tet)	0.0039(10)
U_{iso} (oct)	0.0034(8)
R_p	0.0173

References

1. Carbonin, S.; Russo, U.; Giusta, A.D. Cation distribution in some natural spinels from X-ray diffraction and Mössbauer spectroscopy. *Mineral. Mag.* **2016**, *60*, 355-368.
2. Lavina, B.; Salviulo, G.; Giusta, A.D. Cation distribution and structure modelling of spinel solid solutions. *Phys. Chem. Mineral.* **2002**, *29*, 10-18.