Random Si distribution between the T-site and M-site of $MgAl_2O_4$-spinel at high P-T conditions

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$MgAl_2O_4$-spinel is geologically important. Its cation order-disorder behaviour can affect a large range of physical and chemical properties, so that it has been extensively investigated. How its minor component such as SiO_4 is hosted by the crystal structure is largely unknown.

In this study, we synthesized a series of Si-bearing $MgAl_2O_4$-spinels at 1500-1650 °C and 3-6 GPa. These spinels had SiO_2 contents up to ~1.03 wt%, and showed a substitution mechanism of $Si^{4+} + Mg^{2+} = 2Al^{3+}$.

Unpolarized Raman spectra were collected from the experimental products, and a new set of well-defined Raman peaks at ~823, 856, 920 and 968 cm^{-1} were observed. Comparing these peaks with the Raman features of natural Si-free $MgAl_2O_4$-spinel, synthetic Si-free $MgAl_2O_4$-spinel, natural low quartz, synthetic coesite, synthetic stishovite and synthetic forsterite, we infer that they should belong to the SiO_4 groups. The correlations between the Raman intensities and SiO_2 contents of the Si-bearing $MgAl_2O_4$-spinels suggest that at some P-T conditions some Si cations must start to adopt the M-site and form SiO_6 groups. Unlike the SiO_4 groups with very intense Raman signals, the SiO_6 groups are largely Raman-silent.

Our experimental data suggest that the Si cations in the $MgAl_2O_4$-spinel primarily appear on the T-site at P-T conditions < ~3-4 GPa and 1500 °C, but soon attain a random

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distribution between the T-site and M-site of the $MgAl_2O_4$-spinel at P-T conditions > ~5-6 GPa and 1630-1650 ^oC.