Nitrogen Solubility in Spinel Mg_2SiO_4 Studied at High Pressure and High Temperature in the Diamond Anvil Cell

E. Soignard [1], D. Machon [2], D. Daisenberger [2], P.F. McMillan[2,3]
1. Arizona State University, Department of geological sciences, Tempe, AZ, USA
2. University College London, Department of Chemistry, London, UK
3. Davy Faraday Research Laboratory, Royal Institution, London, UK

Introduction

A silicate spinel phase is an important component of the Earth's mantle between 400 and 650 km depth, and the high pressure stability and elastic properties of spinels in the Mg_2SiO_4-Fe_2SiO_4-$MgAl_2O_4$ system have been studied extensively. Recently, it has been shown that silicon nitride (Si_3N_4) transforms into a spinel structure at high pressure and high temperature. The low pressure phenacite-structured β-form of silicon nitride is an important refractory ceramic technological material, and the new family of nitride spinels (Si_3N_4, Ge_3N_4, Sn_3N_4, Si_2GeN_4) is being examined for potential technological properties. However, the existence of the new Si_3N_4 spinel also opens up the possibility for the spinel structure to act as a source or sink of nitrogen in the mantle, which is of great geochemical interest. Currently, the only demonstrated repository for nitrogen in the mantle is diamond [1]. Thus, Javoy has estimated the mantle content 35 ppm from the chondrites composition and the nitrogen content in diamond [1-2]. However, if another major mantle mineral could dissolve significant structurally bound nitrogen, this would considerably change models for the nitrogen budget, and the interpretation of $\delta^{15}N$ isotopic ratios. Here we propose to investigate the dissolution of Si_3N_4 component in Mg_2SiO_4 spinel, by high pressure-high temperature synthesis experiments using laser heating in DAC and in situ X-ray diffraction.

Experimental Method

The sample was loaded into a cylindrical diamond anvil cell with 0.3 carats diamond anvils. The diamond culet diameter was 300 μm. The sample was loaded into a 130 μm diameter hole drilled into a pre-indented rhenium gasket. The pressure medium was either argon or nitrogen depending upon the experiment.

The samples were mixtures of silicon nitride and Mg_2SiO_4. The sample pressure was determined using ruby fluorescence at room temperature and Pt at high temperature.

The samples were first pressurised and then laser heated using a double sided YLF laser heating system. The temperature was determined using thermal emission spectroscopic methods.

The diffraction patterns were collected at a wavelength of 0.3344 Å.

Results and discussion

While performing the experiment it was extremely difficult to control the temperature correctly due mainly to the sample. The sample were mixed with some amorphous platinum in order to couple with the laser. Therefore, the heating was not very homogenous.

We could easily transform the $Mg_2SiO_4 + Si_3N_4$ sample into the spinel phases: γ-Mg_2SiO_4 and γ-Si_3N_4 at 23 GPa. The diffraction patterns were showing clearly two spinel phases. Therefore if there was reaction between the silicon nitride and the silicate, the reaction was only very limited and was not consuming the entire silicon nitride component of the sample.

We repeated the experiment with a range of Si_3N_4 / Mg_2SiO_4 mixture loaded into an Ar pressure medium and always obtained a mixture of the two spinel phases.

At high pressure it is not always possible to completely eliminate the possibility of nitrogen entering the silicate crystallographic network since the lattice parameter is dependent upon pressure and temperature. Therefore, for each experiment we collected diffraction patterns upon decompression in order to obtain the compressibility data on the spinel phase. The data did not positively indicate whether or not nitrogen entered the lattice. We released pressure and observed that the lattice parameter of the silicate and nitride were within error identical to those previously reported. Therefore we do not have any evidence for any solubility of silicon nitride spinel into the magnesium silicate spinel phase.

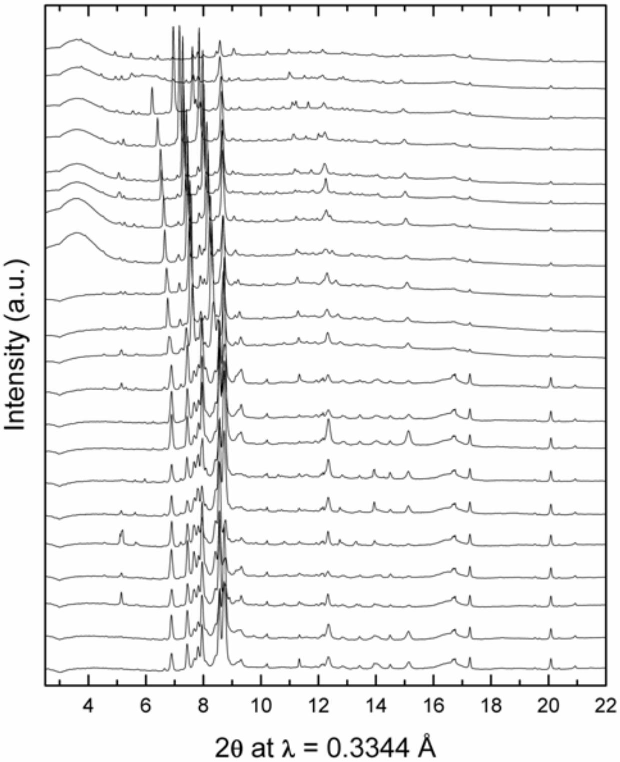

Fig. 1, Diffraction pattern of Mg_2SiO_4 at 23.5 GPa followed by decompression. The broad feature at low 2 θ appears at 15 GPa and remains down to room pressure.

We further pursued the experiment by loading a mixture of $Mg_2SiO_4 + Si_3N_4$ into a nitrogen pressure medium. The sample was pressurised up to about 25 GPa heated to temperatures above 2000 K and slowly decompressed down to room pressure. Upon decompression, we observed the appearing of a broad features and the disappearance of the crystalline diffraction pattern. Therefore, we concluded that the sample was not pure Mg_2SiO_4 since there are no report of amorphisation of γ-Mg_2SiO_4 or γ-Si_3N_4 upon decompression.

All these results are still part of on going research at University College London.

Acknowledgments

This work was performed at GeoSoilEnviroCARS (Sector 13), Advanced Photon Source (APS), Argonne National Laboratory. GeoSoilEnviroCARS is supported by the National Science Foundation - Earth Sciences (EAR-0217473), Department of Energy - Geosciences (DE-FG02-94ER14466) and the State of Illinois. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38. This research was supported by the UK EPSRC by grand (GR-R65206) to PFM and also by the Wolfson-Royal Society Research Merit Award (PFM).

References

[1] M. Javoy, Earth Planet. Sci. Lett **329**, 537-555 (1999).
[2] P. Cartigny, N. Jendrzejewski, F. Pineau, E. Petit, M. Javoy, Earth Planetary Sci. lett. **194**, 241-257 (2001).