Effects of non-stoichiometry on the spinel structure at high pressure: Implications for Earth’s mantle mineralogy

Fabrizio Nestola a,*, Joseph R. Smyth b, Matteo Parisatto a, Luciano Secco a, Francesco Princivalle c, Marco Bruno d, Mauro Prencipe d, Alberto Dal Negro a

a Dipartimento di Geoscienze, Università di Padova, Via Giotto 1, I-35137 Padova, Italy
b Department of Geological Sciences, University of Colorado, Boulder, CO 80309, USA
c Dipartimento di Scienze della Terra, Università di Trieste, Via Weiss 8, Trieste, Italy
d Dipartimento di Scienze Mineralogiche e Petrologiche, Università di Torino, Via Valperga Caluso (35), I-10125 Torino, Italy

Received 18 June 2008; accepted in revised form 3 November 2008; available online 8 November 2008

Abstract

A non-stoichiometric sample of spinel with composition \( T(Mg_{0.4}Al_{0.6})M(Al_{1.8}h_{0.2})O_4 \) was investigated by single-crystal X-ray diffraction in situ up to about 8.7 GPa using a diamond anvil cell. The \( P(V) \) data were fitted using a third-order Birch–Murnaghan equation of state and the unit-cell volume \( V_0 \), the bulk modulus \( K_{T0} \) and its first pressure derivative \( K' \) were refined simultaneously providing the following coefficients: \( V_0 = 510.34(6) \) Å\(^3\), \( K_{T0} = 171(2) \) GPa, \( K' = 7.3(6) \). This \( K_{T0} \) value represents the lowest ever found for spinel crystal structures. Comparing our data with a stoichiometric and natural \( MgAl_2O_4 \) (pure composition) we observe a decrease in \( K_{T0} \) by about 11.5% and a strong increase in \( K' \) by about 33%. These results demonstrate how an excess of Al accompanied by the formation of significant cation vacancies at octahedral site strongly affects the thermodynamic properties of spinel structure. If we consider that the estimated mantle composition is characterized by 3–5% of \( Al_2O_3 \) this could imply an Mg/Al substitution with possible formation of cation vacancies. The results of our study indicate that geodynamic models should take into account the potential effect of Mg/Al substitution on the incompressibility of the main mantle-forming minerals (olivine, wadsleyite, ringwoodite, Mg-perovskite).

© 2008 Elsevier Ltd. All rights reserved.

1. INTRODUCTION

Previous studies (Brodholt, 2000; Ross et al., 2002) have shown that the presence of defects like cation or oxygen vacancies in a crystal increases the compressibility of the structure and may affect the thermodynamic properties of the material. Further, it appears that structural vacancies become increasingly important in the temperature–pressure regime of the Earth’s transition zone and the surrounding regions, affecting silicate perovskites, ringwoodite, wadsleyite, and olivine. In perovskite structures, oxygen vacancies can allow substitution of monovalent cations in the 8-fold site or trivalent cations in the octahedral site as in the perovskite (\( CaTiO_3 \))–brownmillerite (\( Ca_2Fe_2O_5 \)) system. Oxygen vacancies in this system sharply decreases the bulk modulus (Ross et al., 2002). In the silicate spinel ringwoodite (\( Mg_2SiO_4 \)) vacancies allow the incorporation of H (Smyth et al., 2003) in correspondence of vacant sites. Such hydration mechanism is also important in other mantle minerals: wadsleyite (Holl et al., 2008), olivine (Smyth et al., 2006), orthopyroxene (Smyth et al., 2007), and clinopyroxene (McCormick et al., 1989; Smyth et al., 1991). However, vacancies are also formed by the Mg/Al substitution (e.g. in spinel structure a \( 3Mg^{2+} \) by \( 2Al^{3+} + \square \) substitution at octahedral site; the symbol \( \square \) = cation vacancy) and as \( Al_2O_3 \) is believed to be present in significant amounts for all mantle compositions (up to 3–5% by weight) (Anderson, 1989), previous works have focussed on the effects of Al incorporation on physical properties of mantle silicates (Xu et al.,...
1998; Zhang and Weidner, 1999; Brodholt, 2000). Therefore, for the Mg-phases stable at the mantle conditions a significant Mg/Al substitution (with Al cation strongly smaller than Mg) could occur in radii 0.535 Å and 0.720 Å in octahedral coordination, respectively, Shannon, 1976) accompanied by the formation of cation vacancies could strongly influence the rheology of minerals assemblages of the deep Earth.

In order to quantify the effect of an excess of Al and relative cation vacancies on the high-pressure behaviour of spinel crystal structure we have investigated a single-crystal sample containing spinel Mg0.4Al2.4O4 (where apical T and M indicate the tetrahedral and octahedral sites, respectively) in situ at high-pressure by X-ray diffraction using a diamond anvil cell (DAC). The sample shows a strong excess of Al with respect to MgAl2O4 and a significant amount of cation vacancies at octahedral site. Moreover, as MgAl2O4 is a natural common phase and often used as a pressure medium, hydrostatic up to the maximum pressure reached in this work (Angel et al., 2007), and a crystal of quartz was loaded in the DAC together with the spinel sample as an internal pressure standard (Angel et al., 1997).

The unit-cell parameters and crystal structure data (reported in Table 1) were determined at 12 different pressures up to about 8.7 GPa and room temperature on a STOE STADI4 four-circle diffractometer (monochromatized MoKα radiation) equipped with an Oxford Diffraction CCD detector. The unit-cell edge and intensity data were collected up to 2θmax = 60° using an exposure time of 60 s and an ω-scan of 0.2° in order to obtain the highest possible precision in cell-edge determination. The sample-detector distance was 60 mm. The CrysAlis Red program (Oxford Diffraction) was used to integrate the intensity data applying the Lorentz-polarization correction. The absorption correction for crystal, DAC, and gasket shadowing was performed using Absorb 6.0 (Angel, 2004). Weighted structural anisotropic refinements were done using the SHELXL-97 software (Sheldrick, 1997) starting from the atomic coordinates of the same crystal fragment previously published (Lenaz et al., 2008) in Fd3m space group; no violation in symmetry from this space group was detected to the maximum pressure reached. Concerning the cation distribution, we started from the same published work (Lenaz et al., 2008). The refined site occupancies did not show any variation as a function of pressure with respect to those of room pressure, consistently with previous results (Lenaz et al., 2008).

### 2. ANALYTICAL PROCEDURES

A colourless synthetic single-crystal of spinel (space group Fd3m) with composition T(Mg0.4Al0.6)M(Al1.8H0.2)O4 (where apical T and M indicate the tetrahedral and octahedral sites, respectively) was selected for an in situ, high-pressure, X-ray diffraction investigation. The sample is a fragment of the same sample previously investigated at ambient conditions (Lenaz et al., 2008). As the authors report in their paper this sample shows a very limited amount of water, e.g. 90 ppm of H2O; however such amount of water if compared with the vacancy concentration cannot influence the high-pressure crystal structure evolution of a rigid structure like spinel. Unfortunately, there are not available data so far on the effect of water on the high-pressure behaviour of spinel. However, if we consider that, for example, for forsterite the bulk modulus decreases by 3.5% for a sample containing 9000 ppm (Jacobsen et al., 2008), we are confident that the effect of 90 ppm on a structure could be considered negligible in measuring its bulk modulus as in this work. For our sample cation vacancies are located primarily at the octahedral site, so that the formation mechanism of the defect is essentially a 3Mg2+ by 2A13+ + □ substitution. The crystal was twin- and inclusion-free, with a crystal size of 180 × 90 × 50 μm. It was loaded in an ETH-type (DAC) using a T301 steel foil as gasket, which was pre-indented to 90 μm with a hole 250 μm in diameter. A mixture of methanol:ethanol:water with ratio 16:3:1 was used as a pressure medium, hydrostatic up to the maximum pressure reached in this work (Angel et al., 2007), and a crystal of quartz was loaded in the DAC together with the spinel sample as an internal pressure standard (Angel et al., 1997).

The sample-detector distance was 60 mm. The CrysAlis Red program (Oxford Diffraction) was used to integrate the intensity data applying the Lorentz-polarization correction. The absorption correction for crystal, DAC, and gasket shadowing was performed using Absorb 6.0 (Angel, 2004). Weighted structural anisotropic refinements were done using the SHELXL-97 software (Sheldrick, 1997) starting from the atomic coordinates of the same crystal fragment previously published (Lenaz et al., 2008) in Fd3m space group; no violation in symmetry from this space group was detected to the maximum pressure reached. Concerning the cation distribution, we started from the same published work (Lenaz et al., 2008). The refined site occupancies did not show any variation as a function of pressure with respect to those of room pressure, consistently with previous results (Lenaz et al., 2008).

### 3. DISCUSSION AND CONCLUSIONS

The evolution of the unit-cell volume as a function of pressure is shown in Fig. 1, whereas pressure–volume

<table>
<thead>
<tr>
<th>P (GPa)</th>
<th>V (Å³)</th>
<th>u</th>
<th>V_M (Å³)</th>
<th>V_T (Å³)</th>
<th>Un. Refl.</th>
<th>R_l (%)</th>
<th>GooF</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00010(1)</td>
<td>510.34(6)</td>
<td>0.2585(3)</td>
<td>9.55(2)</td>
<td>3.24(1)</td>
<td>49</td>
<td>3.31</td>
<td>1.256</td>
</tr>
<tr>
<td>1.835(6)</td>
<td>505.05(8)</td>
<td>0.2586(3)</td>
<td>9.44(3)</td>
<td>3.21(1)</td>
<td>42</td>
<td>2.60</td>
<td>0.977</td>
</tr>
<tr>
<td>2.470(10)*</td>
<td>503.32(6)</td>
<td>0.2585(4)</td>
<td>9.42(3)</td>
<td>3.19(1)</td>
<td>40</td>
<td>3.41</td>
<td>1.054</td>
</tr>
<tr>
<td>2.610(13)</td>
<td>502.98(7)</td>
<td>0.2587(4)</td>
<td>9.39(3)</td>
<td>3.20(1)</td>
<td>40</td>
<td>4.32</td>
<td>1.235</td>
</tr>
<tr>
<td>3.316(9)*</td>
<td>501.25(7)</td>
<td>0.2585(5)</td>
<td>9.39(4)</td>
<td>3.18(1)</td>
<td>39</td>
<td>3.75</td>
<td>1.290</td>
</tr>
<tr>
<td>3.471(13)</td>
<td>500.85(8)</td>
<td>0.2584(4)</td>
<td>9.39(4)</td>
<td>3.17(1)</td>
<td>39</td>
<td>4.09</td>
<td>1.261</td>
</tr>
<tr>
<td>3.828(9)*</td>
<td>499.93(8)</td>
<td>0.2583(5)</td>
<td>9.38(4)</td>
<td>3.16(1)</td>
<td>38</td>
<td>4.22</td>
<td>1.293</td>
</tr>
<tr>
<td>4.200(12)</td>
<td>498.95(6)</td>
<td>0.2587(4)</td>
<td>9.32(3)</td>
<td>3.18(1)</td>
<td>39</td>
<td>3.34</td>
<td>1.233</td>
</tr>
<tr>
<td>5.194(8)*</td>
<td>496.52(6)</td>
<td>0.2581(4)</td>
<td>9.33(3)</td>
<td>3.12(1)</td>
<td>39</td>
<td>4.05</td>
<td>1.268</td>
</tr>
<tr>
<td>6.212(5)</td>
<td>494.06(7)</td>
<td>0.2581(3)</td>
<td>9.29(3)</td>
<td>3.11(1)</td>
<td>43</td>
<td>2.66</td>
<td>1.009</td>
</tr>
<tr>
<td>7.634(8)*</td>
<td>490.98(7)</td>
<td>0.2581(3)</td>
<td>9.24(2)</td>
<td>3.09(1)</td>
<td>42</td>
<td>3.45</td>
<td>1.122</td>
</tr>
<tr>
<td>8.698(10)</td>
<td>488.70(8)</td>
<td>0.2580(3)</td>
<td>9.21(2)</td>
<td>3.06(1)</td>
<td>46</td>
<td>2.89</td>
<td>0.992</td>
</tr>
</tbody>
</table>

* Data measured during decompression.
The evolution of the unit-cell volume with pressure shows a marked curvature, and there are no evidence of phase transitions in the pressure range investigated. The unit-cell volume decreases by 4.4% to the maximum pressure reached. The $P(V)$ data were fitted using a third-order Birch–Murnaghan equation of state (BM3-EoS) (Birch, 1947) and the EOSFIT 5.2 program (Angel, 2002) was used to refine the experimental data. The unit-cell volume, $V_0$, the bulk modulus, $K_{T0}$, and its first pressure derivative, $K'_0$, were simultaneously refined providing the following EoS coefficients: $V_0 = 510.34(6) \text{ Å}^3$, $K_{T0} = 171(2) \text{ GPa}$, $K'_0 = 7.3(6)$. To our knowledge, the $K_{T0}$ value determined in this work represents the lowest ever found for spinel structures, which are relatively stiff ones based, as they are, on a close-packed array of oxygen atoms. To be remarked that the refined $V_0$ value is equal to the experimental one. The calculated volume compressibility $\nu_v$, with $\nu_v = 1/K_{T0}$, has a value of 0.005585(2) GPa$^{-1}$. Fig. 2 is an $f_E$–$F_E$ plot of the data, where $F_E$ is the normalized pressure defined as $P/3 \times f_E \times (1 + 2f_E)^{5/2}$. Such plot provides a useful diagnostic tool in order to compare the refined and the experimental EoS coefficients (Angel, 2000). In this figure, all data points lie on a positively inclined straight line indicating that the BM3-EoS we used in this work, well describes our experimental data, and confirms that the value of the first pressure derivative is markedly higher than 4.

Previous data on a stoichiometric disordered spinel MgAl$_2$O$_4$ (Nestola et al., 2007) showed a bulk modulus $K_{T0} = 193 \text{ GPa}$ and a first pressure derivative $K'_0 = 5.4$, with a compressibility of 0.00518 GPa$^{-1}$. Therefore, our data demonstrate that for the defect-bearing spinel the compressibility increases by 12.9%, with a 35% increase of $K'$. In Fig. 1 the relative unit-cell volume compression for the stoichiometric samples is shown together with that of the non-stoichiometric sample here studied. The figure clearly shows the higher compression of the defect sample. $K_{T0}$ and its first pressure derivative $K'_0$ are strongly correlated so, in order to obtain a reliable comparison between the stoichiometric and the defect spinel, a confidence ellipse taking into account such correlation for both the samples is shown in Fig. 3. The confidence ellipses clearly show that the differences both in $K_{T0}$ and $K'_0$ between the vacancy—free and vacancy—bearing spinels are significant.

We also determined the changes in the crystal structure of the defect spinel as a function of pressure (Table 1). The atomic coordinate of the oxygen $u$ (the unique variable beyond the unit-cell edge in the spinel structure, where the atomic coordinates are $x = y = z = u$) shows only a slight decrease to the maximum pressure. Concerning the polyhedral compressibility, our data show linear compressibilities of about 0.0064 and 0.0041 GPa$^{-1}$ for the tetrahedron and octahedron, respectively. For the vacancy-free spinel the tetrahedral and octahedral volumes compress by similar rates with linear compressibilities of 0.0049 and 0.0045 GPa$^{-1}$, respectively. These results clearly indicate that the higher bulk compressibility showed by the defect spinel is mainly accommodated by the greater compressibility of the tetrahedron.

Our data on a non-stoichiometric spinel with composition $\gamma(Mg_{0.4}Al_{1.6})_{2.2}O_4$ clearly show that a com-

Fig. 1. Unit-cell volume relative compression for the vacancy-bearing Mg$_{0.4}$Al$_{2.4}$O$_4$ (filled squares) and vacancy-free MgAl$_2$O$_4$ spinel (Nestola et al., 2007) (open circles).

Fig. 2. $f_E$–$F_E$ plot for the vacancy-bearing spinel Mg$_{0.4}$Al$_{2.4}$O$_4$.

Fig. 3. Confidence ellipses for $\Delta = 2.3$ relative to the vacancy-bearing Mg$_{0.4}$Al$_{2.4}$O$_4$ and vacancy-free spinel MgAl$_2$O$_4$ (Nestola et al., 2007); (the symbol $\Delta$ indicates the level confidence, e.g. $\Delta = 2.3$ is for a confidence level of 68.3%, the equivalent of 1$\sigma$ for a normal distribution of a single variable, see for more details, Angel, 2000).
bined effect of excess of Al and cation vacancies strongly decrease the bulk modulus with respect to a stoichiometric spinel. Our results can be applied to the analogue crystal structure of ringwoodite, the most abundant phase of the Earth’s transition zone. If, for ringwoodite, the same vacancy formation mechanism as in MgAl2O4 spinel (e.g. 3Mg2+ + 2Al3+ + 6H2O in its crystal structure. Recently, ringwoodite has been synthesized with 2% of H2O by weight (Kudoh et al., 2000), thus having a chemical formula characterized by 0.11 p.f.u. of cation vacancies, 0.11 of which are concentrated at the octahedral site. Of course, the formation mechanism for a hydrous ringwoodite is quite different with respect to that observed in ringwoodite for a 50% of Fe/Mg substitution (Hazen, 1993). These results may also be of significance for hydrous ringwoodite, which even if in case of absence of Al, can be characterized by cation vacancies due to the presence of H2O in its crystal structure. Recently, ringwoodite has been synthesized with 2% of H2O by weight (Kudoh et al., 2000), thus having a chemical formula characterized by 0.13 p.f.u. of cation vacancies, 0.09 of which are concentrated at the octahedral site. Of course, the formation mechanism for a hydrous ringwoodite is quite different with respect to that of an Al-rich one, however, based on our data we do not exclude that a decrease of K’0 for a hydrous ringwoodite could be mainly related to the cation vacancies.

ACKNOWLEDGMENTS

Financial support has been provided by MIUR – PRIN 2006 to A. Dal Negro and E. Bruno and by US National Science Foundation Grant EAR07-11165 to J.R. Smyth. We thank two anonymous referees and Dr. Vaughan for their help in strongly improving this manuscript.

REFERENCES


Angel R. J. (2004) EOSFIT v. 5.2 program. Crystallography Laboratory, Virginia Tech, Blacksburg, USA.


Associate editor: David J. Vaughan