Equation of State of MgAl2O4 Spinel to 1473K and 9.5 GPa

Jeremy Smith, Michael Vaughan, and Ganglin Chen
Center for High Pressure Research, State University of New York, Stony Brook, NY, 11794-2100, USA

Volume measurements of $MgAl_2O_4$ spinel as a function of pressure and temperature ranging from ambient conditions to 9.5 GPa and 1473 K were measured using synchrotron X-ray radiation at the National Synchrotron Light Source in a DIA-type cubic anvil apparatus (SAM-85) using a powder sample. The volumes were fit with a Birch-Murnaghan equation of state, fixing K_0' to 4, yielding $K_0 = 191 \pm 3$ GPa, $\partial K/\partial T = -0.009 \pm 0.02$ GPa/K, $V_0 = 528.8 \pm 0.2$ Å^3, $\alpha_0 = 2.03 \pm 0.15 \times 10^{-5}$ K^{-1}, $\alpha_1 = 1.0 \pm 0.17 \times 10^{-8}$, and $\partial^2 K/\partial T \partial P = -2.5 \pm 2.1 \times 10^{-3}$ GPa/K.

1. Introduction

While $MgAl_2O_4$ spinel is a widely studied compound, it is a very interesting material, worthy of further study. It is useful as a reference material as there are many compounds which form in the spinel structure. It is also stable over a high pressure and temperature range. Additionally, there is evidence that this is a highly irregular material. High pressure ultrasonic studies [*Yoneda*, 1990; *Chang and Barsch*, 1972] have suggested a vanishing bulk modulus, yet high pressure x-ray diffraction experiments [*Kruger et al.*, 1997] found none (Fig. 1). A discontinuity in thermal expansion has been demonstrated by Brillouin spectroscopy to 1273 K [*Askarpour et al*., 1993] and by dilatometry to 1173 K [*Suzuki and Kumazawa*, 1980]. However, Peterson *et al*. [1991] found no discontinuity by means of *in situ* time of flight neutron powder diffraction to 1273 K. It is clear that this compound requires further study.

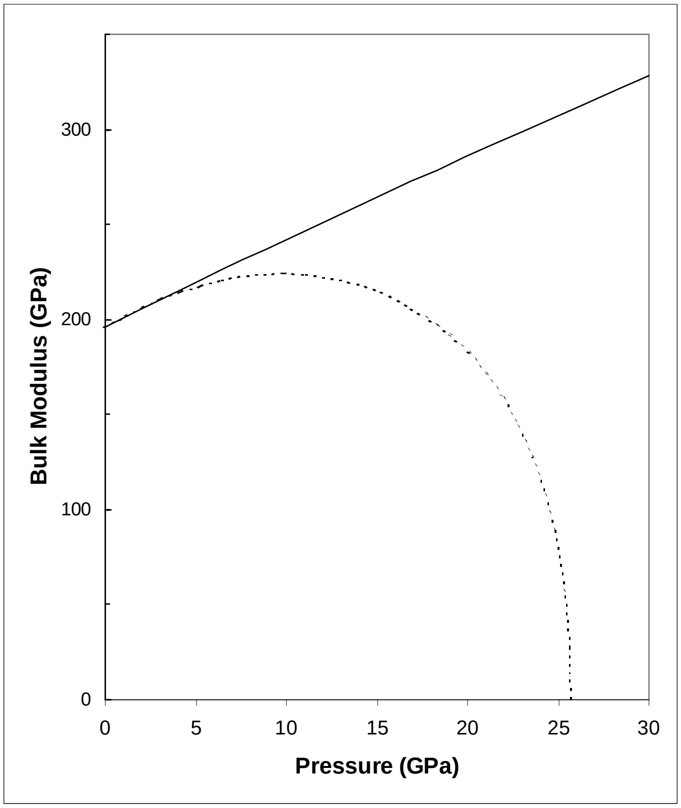

Fig. 1
Extrapolation of the bulk modulus of spinel. Solid line corresponds to that of Kruger *et al* [1997], dashed line corresponds to that of Yoneda [1990], who predicts a softening over 10 GPa.

In the present study, we use *in situ* x-ray diffraction to measure the response of $MgAl_2O_4$ spinel to high pressure and temperature. Previous experiments have concentrated on high pressure [*e.g. Kruger et al.*, 1997] or high temperature [*e.g. Askarpour et al.*, 1993] alone. While many of the pressure experiments were performed with more advanced techniques such as ultrasonics [*e.g. Yoneda*, 1990], the present study is the first to combine high pressure and high temperature to find the equation of state of $MgAl_2O_4$ spinel.

2. Experimental Procedure

Experiments were performed on the powder sample of spinel using a DIA-type cubic anvil high-pressure apparatus (SAM-85) with white synchrotron radiation from the superconducting wiggler port (X-17 beamline) at NSLS. Diffraction patterns were collected with collection times of about 1 minute by means of energy dispersive analysis with a two theta angle of 7.5°. Pressure was calculated by Decker's equation of state [*Decker*, 1971] using the internal NaCl standard. The system is described in greater detail by *Weidner et al.* [1992a,b]. The cell assembly used in this study is also described elsewhere by *Weidner et al.* [1998].

In this experiment, the sample was first compressed to 9.5 GPa then heated to about 1473 K. Diffraction patterns were collected at about every 200 K during the cooling cycle. Data is collected during the cooling cycle to minimize deviatoric stress, which is found to relax during heating [*Wang et al.,* 1998]. At room tem-

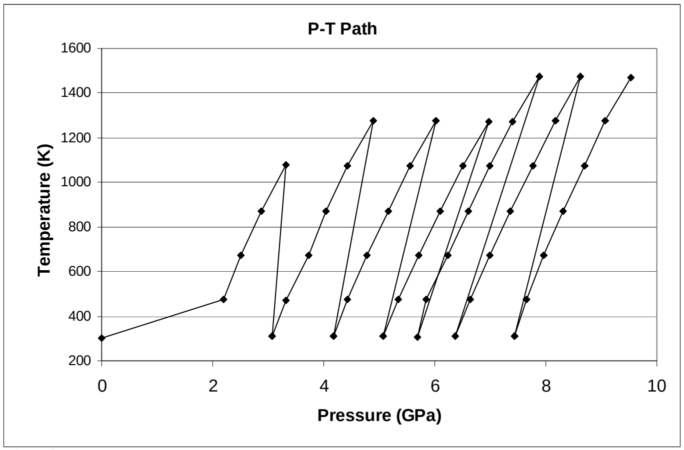

Fig. 2
The pressure and temperature path of spinel. The ambient condition data was taken first, then the highest pressure and temperature. The temperature was dropped in 200 K intervals until room temperature where the pressure was relaxed slightly and the sample was reheated. Data points were collected on cooling cycles to minimize deviatoric stress.

perature, the pressure was relaxed and the sample was reheated in preparation for another cooling cycle. This was repeated several times to cover the P-T range (Fig. 2).

Pressure (GPa)	Temperature (K)	Cell Volume (Å3)	Error
0.001	303.1	528.2087	0.1283
9.525	1470.02	517.9313	0.1186
9.061	1274.48	516.8651	0.1822
8.695	1073.55	515.0472	0.1416
8.311	873.15	513.6863	0.1561
7.953	673.93	512.321	0.119
7.645	473.45	511.3134	0.1953
7.442	311.85	510.0693	0.1669
8.63	1473.4	520.4007	0.1889
8.169	1276.98	519.2462	0.1927
7.76	1073.66	517.442	0.108
7.366	872.74	516.0957	0.1758
6.993	674.45	514.7352	0.1362
6.636	473.81	513.2149	0.1525
6.369	311.28	512.5659	0.21
7.892	1475.53	522.3477	0.1546
7.405	1273.07	521.3958	0.2045
6.996	1072.3	519.5574	0.117
6.611	872.13	517.7764	0.0978
6.232	673.4	516.6283	0.1972
5.854	473.81	515.2077	0.1752
5.686	308.46	514.4982	0.2019
6.978	1273.72	522.4714	0.2005
6.5	1075.33	520.92	0.1249
6.099	873.15	519.3257	0.1596
5.71	673.56	517.8159	0.1271
5.333	472.85	516.4789	0.1012
5.062	309.4	515.8699	0.1593
6.013	1276.71	524.6741	0.1245
5.545	1073.45	523.321	0.1502
5.157	873.21	521.7505	0.1981
4.775	671.03	520.1389	0.1119
4.434	473.75	518.7966	0.1094
4.169	309.11	518.0742	0.1101
4.899	1275.08	527.8004	0.1257
4.432	1073.19	526.6859	0.1528
4.033	872.8	524.9255	0.1446
3.721	673.66	523.3733	0.145
3.324	471.59	522.2238	0.1662
3.073	308.9	521.2699	0.1263
3.318	1076.84	529.219	0.2279
2.868	871.87	527.6307	0.1746
2.509	673.66	526.3622	0.1597
2.187	473.63	525.0978	0.1324

Table 1.
Cell Volumes of Spinel

3. Results and Discussion

The P-V-T data (table 1) were fit to a high temperature Birch-Murnaghan equation of state. We use the Birch-Murnaghan equation of state that has the form:

$$P = \frac{3}{2} K_0 \left[\left(\frac{V}{V_0} \right)^{-7/3} - \left(\frac{V}{V_0} \right)^{-5/3} \right] \cdot \left\{ 1 + \frac{3}{4} (K_0' - 4) \cdot \left[\left(\frac{V}{V_0} \right)^{-2/3} - 1 \right] \right\}$$

and we replace the room temperature parameters with their high temperature counterparts given by:

$$K_T = K_0 + \left(\frac{\partial K_T}{\partial T} \right)_P (T - 300) \quad , \quad K_T' = K_0' + \left(\frac{\partial K_T'}{\partial T} \right)_P (T - 300)$$

and

$$V_T = V_0 \left[\exp\left(\int_{300}^{T} \alpha(T) dT \right) \right]$$

where α(T) is given by:

$$\alpha(T) = \alpha_0 + \alpha_1 T$$

Using a least-squares fit, fixing *K’*=4, we calculated the coefficients in Table 2. Previous high-pressure x-ray diffraction studies [*Kruger et al.*, 1997] yielded a K_0=196(±1), K_0’=4.7(±0.3), and KK_0”l6. Unfortunately, the resolution of our data was insufficient to accurately determine even K_0’. If K_0’ was not fixed to 4, the iteration returned the very uncertain, low value of .2(±1.6). Previous high-temperature studies [*e.g. Suzuki and Kumazawa*, 1980] found an anomaly in the thermal expansion around 930 K. While this temperature is in our P-T range, our data was unable to resolve decisively an anomalous thermal expansion.

We found that our analysis would be greatly enhanced if we had precise isobaric and isothermal lines. To achieve this, we set our data into a P-T grid (Fig. 3), with an effort to minimize the

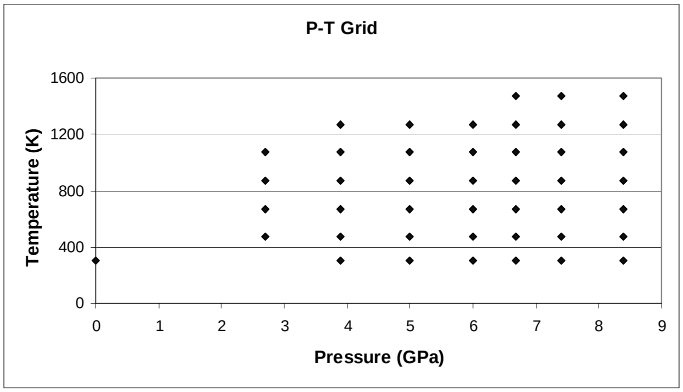

Fig. 3
Pressure and temperature grid to which the cell volumes were fitted.

change in both pressure and temperature. Leaving the cell volumes unaltered, we added the gridded points to our data and ran this extended list through an iteration of the high-temperature Birch-Murnaghan equation of state fixing the coefficients to the values in Table 2. From the iteration, we determined the deviation of each cell volume from the model. The cell volumes of the gridded data were then adjusted by the difference of this deviation and the deviation of the original data point from its model. This gives the gridded data the same deviation from the model as the original data point. This is illustrated in Fig. 4 where a data point is chosen (6.5 GPa and 1075.33 K) which is gridded to 6 GPa and 1073 K. It can be seen that the deviation from their respective models is exactly the same. We tested the fit by putting the new data points through a least squares iteration and comparing the new coefficients with those we obtained from the ungridded data. We found all of the coefficients to be within two standard deviations of the ungridded ones.

	Present Study	Yoneda	Kruger et al.
K_0 (GPa)	191(±3)	196.4	196(±1)
K_0’	[4]	5.68	4.7(±0.3)
K_0’’		-0.64	≈-0.03
$(\partial K/\partial T)_P$	-.009(±.02)		
V_0 (Œ^3)	528.8(±.2)	528.22	
α_0 10^{-5} (K^{-1})	2.03(±.15)		
α_1 10^{-8} (K^{-1})	1.0(±.17)		
$\partial^2 K/\partial T\partial P$ (10^{-3})	-2.5(±2.1)		

Table 2.
Birch-Murnaghan equation-of-state parameters of spinel at high temperature

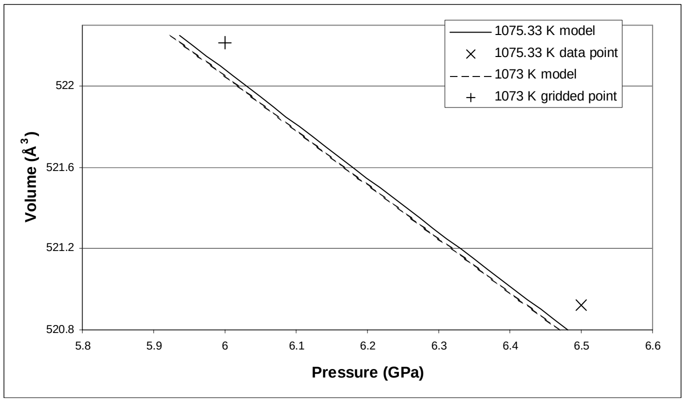

Fig. 4
Example of the gridding procedure. The gridded point (6 GPa and 1073 K) has the same deviation from the 1073 K model as the ungridded point (6.5 GPa and 1075.33 K) has from the 1075.33 K model.

With our grid, we are able to perform accurate comparisons with previous room temperature studies. A very clear comparison can be made if the P-T data is changed in terms of the Eulerian strain parameter ($f=[(V_0/V)^{2/3}-1]/2$) and normalized pressure ($F=P/[3f(1+2f)^{5/2}]$) [*Birch*, 1978]. We combine our room temperature data with the high-pressure x-ray diffraction study of *Kruger et al.* [1997], using our best estimate of their V_0 (529.5 Å^3) and a fit to the coefficients of *Yoneda* [1990] (Fig. 5) using a fourth-order Birch-Murnaghan equation of the form:

$$P=\frac{3}{2}K\left[\left(\frac{V}{V_0}\right)^{-7/3}-\left(\frac{V}{V_0}\right)^{-5/3}\right]\cdot\left\{1+\frac{3}{4}(K'-4)\cdot\left[\left(\frac{V}{V_0}\right)^{-2/3}-1\right]+\frac{3}{8}\left(KK''+K'(K'-7)+\frac{143}{9}\right)\cdot\left[\left(\frac{V}{V_0}\right)^{-2/3}-1\right]^2\right\}$$

Yoneda [1990] predicts a vanishing bulk modulus which *Kruger et al.* [1997] do not see. The two models are very different at high strain, but are unfortunately quite similar at low strain. The resolution of our study is not good enough to differentiate between the two models; our data could fit either model.

Using the gridded values, we can make a plot of ln(V) vs. T at constant pressure (Fig. 6). Within the resolution of our data, we see no evidence of a discontinuity in thermal expansion, but instead see a consistent curvature which lends credence to the α_1 term.

While our data is of insufficient resolution to distinguish between the high-pressure models or to confidently support or contradict a non-linearity in thermal expansion, it is a good first step in high pressure and high temperature *in situ* x-ray diffraction experiments on spinel. It is clear that further study is needed, especially hydrostatic experiments at higher pressure.

4. Acknowledgements

We would like to thank Donald Weidner for his helpful assistance and use of his regression software.

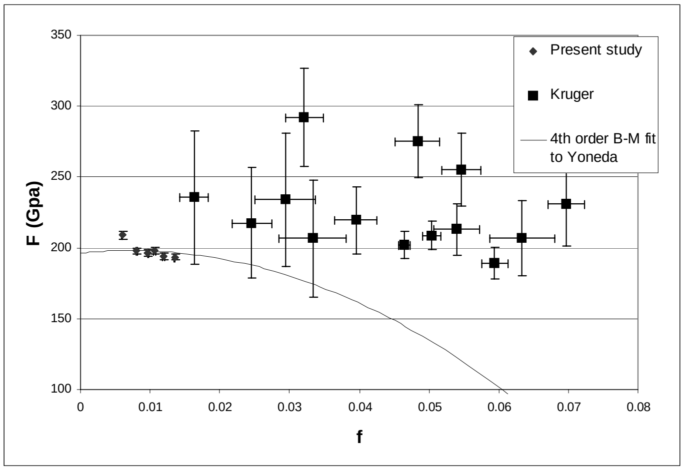

Fig. 5
Room temperature equation of state of $MgAl_2O_4$ using the normalized pressure (F) and Eulerian strain (f) parameters defined in the text. The solid line is a fourth-order Birch-Murnaghan equation of state based on the elastic moduli given by Yoneda [1990].

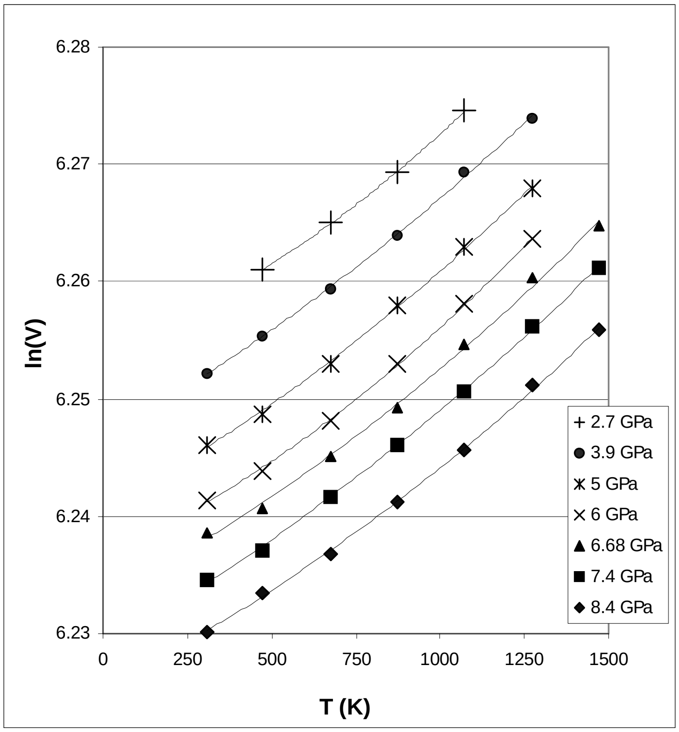

Fig. 6
Natural log of volume vs. temperature at constant pressure. The isobars are fitted with a quadratic curve. We see no discontinuity in thermal expansion, but we do see a systematic increase.

5. References

Askarpour, V., Manhgnani, M.H., Fassbender, S., and Yoneda, A. (1993) Elasticity of Single-Crystal $MgAl_2O_4$ Spinel up to 1273 K by Brillouin Spectroscopy. Physics and Chemistry of Minerals, 19, 511-519.

Birch, F. (1978) Finite Strain Isotherm and Velocities for Single-Crystal and Polycrystalline NaCl at High Pressures and 300° K. Journal of Geophysical Research, 83, 1257-1268.

Chang, Z.P., and Barsch, G.R. (1972) Pressure Dependence of Single-Crystal Elastic Constants and Anharmonic Properties of Spinel. Journal of Geophysical Research, 78, 2418-2433.

Decker, D.L. (1971) High-Pressure Equation of State for NaCl, KCl and CsCl. Journal of Applied Physics, 42, 3239-3244.

Kruger, M.B., Nguyen, J.H., Caldwell, W., and Jeanloz, R. (1997) Equation of State of $MgAl_2O_4$ spinel to 65 GPa. Physical Review, B56.

Suzuki, I. and Kumazawa, M. (1980) Anomalous Thermal Expansion in Spinel

$MgAl_2O_4$: A Possibility for a Second Order Phase Transition? Physics and Chemistry of Minerals, 5, 279-284.

Wang, Y., Weidner, D.J., and Meng, Y. (1998) Advances in Equation-of-State Measurements in SAM-85. Properties of Earth and Planetary Materials at High Pressure and Temperature, Geophysics Monograph Series, 101, 365-372.

Weidner, D.J., Vaughan, M.T., Ko, J., Wang, Y., Liu, X., Yeganeh-Haeri, A., Pacalo, R.E., and Zhao, Y. (1992a) Characterization of stress, pressure, temperature in SAM-85, a DIA type high pressure apparatus. High Pressure Research: Applications to Earth and Plane tary Sciences, Geophysics Monograph Series, 67, 13-17.

Weidner, D.J., Vaughan, M.T., Ko, J., Wang, Y., Leinenweber, K., Liu, X., Yeganeh-Haeri, A., Pacalo, R.E., and Zhao, Y. (1992b) Large volume high pressure research using the wiggler port at NSLS. High Pressure Research, 8, 617-623.

Weidner, D.J., Wang, Y., Chen, G., Ando, J., and Vaughan, M.T. (1998) Rheology Measurements at High Pressure and Temperature. Properties of Earth and Planetary Materials at High Pressure and Temperature, Geophysics Monograph Series, 101, 473-482.

Yoneda, A. (1990) Pressure Derivatives of Elastic Constants of Single Crystal MgO and $MgAl_2O_4$. Journal of Physics of the Earth, 38, 19-55.