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The stability and compressibility of MgAl_2O_4 high-pressure polymorphs

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Abstract High-pressure and high-temperature experiments using a laser-heated diamond anvil cell (LHDAC) and synchrotron X-ray diffraction have revealed a phase transition in MgAl_2O_4 . CaTi_2O_4 -type MgAl_2O_4 was found to be stable at pressures between 45 and at least 117 GPa. The transition pressure of CaTi_2O_4 -type phase in MgAl_2O_4 is much lower than that in the natural N-type mid-oceanic ridge basalt composition. The Birch–Murnaghan equation of state for CaTi_2O_4 -type MgAl_2O_4 was determined from the experimental unit cell parameters with $K_0 = 219(\pm 6)$ GPa, $K_0' = 4$ (constrained value), and $V_0 = 238.9(\pm 9)$ Å³. The observed compressibility was in agreement with the theoretical compressibility calculated in a previous study. ϵ - MgAl_2O_4 was observed at pressures between 40 and 45 GPa, which has not been reported in natural rock compositions. The gradient (dP/dT slope) of the transition from the ϵ -type to CaTi_2O_4 -type MgAl_2O_4 had a positive value. These results should resolve the dispute regarding the stable high-pressure phase of MgAl_2O_4 , which has been reported in earlier studies using both the multi-anvil press and the diamond anvil cell.

Keywords MgAl_2O_4 polymorphs · Phase transition · Compressibility · High pressure · Diamond anvil cell

Introduction

The high-pressure polymorphs of MgAl_2O_4 are important minerals, and are host phases of the alumina component of aluminous rocks, such as the basalts and sediments that are found in the lower mantle (e.g., Irifune and Ringwood 1993; Irifune et al. 1994; Kesson et al. 1994; Ono et al. 2001, 2005a; Guignot and Andraut 2004). Therefore, both the phase transitions and the elastic properties of the MgAl_2O_4 high-pressure phases are the subject of intense experimental and theoretical investigations (e.g., Liu 1978; Irifune et al. 1991; Funamori et al. 1998; Akaogi et al. 1999; Catti 2001; Irifune et al. 2002; Gracia et al. 2002; Guignot and Andraut 2004).

A spinel-type structure (space group = $Fd\bar{3}m$) is stable under ambient conditions. Reid and Ringwood (1969) suggested that a possible post-spinel of the MgAl_2O_4 phase would be similar to CaTi_2O_4 -, CaFe_2O_4 -, or CaMn_2O_4 -type structures, with the space group being $Cmcm$, $Pnma$, and $Pbcm$, respectively. Actually, high-pressure experiments have shown that spinel-type MgAl_2O_4 decomposes into an assemblage of periclase (MgO) and corundum (Al_2O_3) at pressures above 15 GPa (Liu 1975; Akaogi et al. 1999). At pressures in the range 25–28 GPa, MgO and Al_2O_3 react to form CaFe_2O_4 -type MgAl_2O_4 (Akaogi et al. 1999; Irifune et al. 2002). CaTi_2O_4 -type MgAl_2O_4 has also been reported by Funamori et al. (1998). In contrast, Liu (1978) observed ϵ - MgAl_2O_4 at pressures above 25 GPa, which is inconsistent with data from other multi-anvil press experiments.

With regard to the basalt composition, it is known that the CaFe_2O_4 -type aluminous phase is a major host mineral for the alumina component in the lower mantle (Irifune and Ringwood 1993; Kesson et al. 1994; Ono et al. 2001). Recently, Ono et al. (2005a) reported that the CaTi_2O_4 -type aluminous phase appeared at pressures above 120 GPa. Therefore, the physical properties of the high-pressure phases of MgAl_2O_4 in the condi-

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tions that exist throughout the mantle are the subject of major geophysical interest.

We performed our experiments using a laser-heated diamond anvil cell (LHDAC), which made it possible to acquire precise data on samples at high pressures and temperatures, and we also employed intense X-rays from a synchrotron radiation source. In this work, we report on the results of in situ X-ray observations of the high-pressure phases of MgAl_2O_4 . We also discuss the pressure-induced phase transition sequence, and the compressibility of MgAl_2O_4 .

Experimental

High-pressure X-ray diffraction experiments were performed using the LHDAC high-pressure apparatus. A symmetric-type diamond cell (SYNTEC Co. Ltd, Japan) with a 60° conical aperture was used (Ono et al. 2005b). Synthetic powdered MgAl_2O_4 was loaded into a 50–100 μm diameter hole that was drilled into a rhenium gasket. The MgAl_2O_4 starting material had a spinel structure, space group $Fd\bar{3}m$, which is the stable phase under ambient conditions. Platinum powder was mixed with the sample to absorb the laser radiation and to provide a heat source. It was also used as an internal pressure calibrant. The powders were comminuted in an agate mortar to ensure homogeneity and a small grain size. Argon, NaCl, or MgO was used as the pressure-transmitting medium to reduce any deviatoric stress and temperature gradients occurring across the sample. The samples were heated with either an YLF or YAG laser to overcome any potential kinetic effects on any potential phase transitions. The size of the heating spot was about 20–30 and 50–100 μm for the YLF and YAG lasers, respectively. The maximum laser power of the YLF and YAG lasers was 40 and 100 W, respectively.

The sample was initially compressed to the desired pressure at room temperature and the load on the DAC maintained at a constant level. After being kept at the desired pressure and temperature for a given time period, the samples were quenched by shutting off the laser. The sample temperature was measured using the spectroradiometric method (Ono et al. 2005a). The spectroradiometric system consisted of a thermoelectrically cooled CCD detector and a spectrograph. A 300-g/mm grating was used, which covered the wavelength range of $\lambda = 460\text{--}925$ nm with a central wavelength at $\lambda = 700$ nm. The spectrometer allowed us to measure the temperature profile across a laser-heated spot. The entrance slit of the spectrograph was used to select a thin line that traversed the laser spot. A temperature profile across the hotspot was measured in 2.5 μm steps. The Temperature was determined by fitting the thermal radiation spectrum between $\lambda = 600$ and 800 nm to the Planck radiation function:

$$I = 2\pi hc^2 \varepsilon(\lambda) \lambda^{-5} / [\exp(hc/k\lambda T) - 1],$$

where I is the spectral intensity, ε emissivity, λ wavelength, and T temperature (e.g., Shen et al. 2001; Kavrner and Panero 2004). The system response was calibrated using a tungsten filament lamp of known radiance that was calibrated relative to an NIST standard. The emissivity of tungsten (De Vos 1954) was used to model the radiation spectrum from the heated sample.

The heated samples were probed using angle-dispersive X-ray diffraction at the synchrotron beam lines BL13A, Photon Factory (Ono et al. 2005c), and BL10XU, SPring-8 (Ono et al. 2005d), located in Japan. A monochromatic incident X-ray beam was collimated to a diameter of 16–30 μm , and the angle-dispersive X-ray diffraction patterns were obtained on an imaging plate (Rigaku) or on an X-ray CCD detector (Bruker). The observed intensities on the imaging plates were integrated as a function of 2θ using the ESRF Fit2d software code (Hammersley et al. 1996) to obtain conventional, one-dimensional diffraction profiles. To adjust the sample position in the X-ray beam precisely, we monitored the X-ray beam intensity distribution transmitted through the DAC by scanning the DAC stage. The shape of the sample and the gasket hole were reflected in the two-dimensional map of the transmitted X-ray intensity, and we could position the sample in the X-ray beam using this X-ray map.

The pressure was estimated from the observed unit cell volumes using the equation of state of platinum (Holmes et al. 1989) employing an electronic thermal pressure correction (Tsuchiya and Kawamura 2002). The uncertainty in the pressure was dependent on the experimental temperature, because of the use of the equation of state. Moreover, a pressure gradient may have existed in the sample, even at high temperatures. We estimated that the typical pressure error at high pressures and temperatures was 2–3 GPa.

Results

Seven runs were carried out at loading pressures between 35 and 120 GPa (Table 1). In the first set of experiments (#1) using argon as the pressure-transmitting medium, the pressure was increased directly to 60 GPa at room temperature, and the X-ray diffraction pattern of the sample was recorded. After the desired pressure was achieved, the sample was heated to relax the differential stress and to overcome potential kinetic effects on any phase transitions. The typical heating time was 5–10 min at each P – T condition. After heating, the pressure was decreased to about 5 GPa, and the diffraction peaks were observed to sharpen due to the relaxation of the differential stress. In addition to peaks arising from the platinum and argon, some new peaks were observed in the diffraction pattern after heating (Fig. 1). This indicates that the starting material had transformed into a high-pressure phase. Most of the new peaks belonged to an orthorhombic symmetry compound having space

Table 1 Experimental conditions

Run	P (GPa) range	T (K) range	PM ^a
#1	47.3–70.0	300–2210	Ar
#2	42.8–53.1	300–2730	Ar
#3	61.6–66.5	300–c.a.2000	Ar
#4	42.0–68.4	300–2130	Ar
#5	55.3–118.8	300–2780	Ar
#6	34.5–51.7	300–2020	MgO
#7	29.4–45.3	300–2520	NaCl

^aPM is pressure-transmitting medium

group $Cmcm$ (Table 2), which was assigned to CaTi_2O_4 -type MgAl_2O_4 , where the Al^{3+} cations exhibit sixfold coordination to the oxygen ions, and the Mg^{2+} cations are located between the edge-sharing AlO_6 octahedra.

In addition to peaks from CaTi_2O_4 -type MgAl_2O_4 , some of the newly formed peaks belonged to a cubic symmetry phase with space group $Fm-3m$. These cubic phase peaks showed good agreement with peaks expected from platinum carbide (Ono et al. 2005b), and these can be explained by a small amount of platinum that was mixed with the sample having reacted with the

carbon of the diamond anvils during heating. After the diffraction patterns were measured, the pressure was decreased to 45 GPa, and then the sample was heated again. The CaTi_2O_4 -type phase remained stable under this condition. The CaTi_2O_4 -type phase could be quenched on reducing the pressure to ambient.

In a second experimental run (#2), the pressure was increased directly to 45 GPa at room temperature, and then the sample was heated. During the heating stage, the diffraction pattern was measured at temperatures between 1,470 and 2,530 K. Diffraction peaks arising from the CaTi_2O_4 -type phase were detected both during and after heating. Further experimental runs (#3–5) were performed to a pressure of 117 GPa at 2,780 K. No transition was observed in these runs.

The next experimental run (#6) used MgO as the pressure-transmitting medium. The pressure was increased directly to 40 GPa at room temperature, and then the sample was heated. The diffraction pattern of the sample was different to that of the CaTi_2O_4 -type phase (Fig. 2). In addition to peaks assigned to platinum, MgO, and corundum, unassignable peaks were also observed, and these unassignable peaks were recoverable after the pressure had been quenched to ambient. The diffraction pattern of the new phase under ambient conditions was most likely that of ϵ - MgAl_2O_4 , which has an orthorhombic symmetry, as reported by Liu (1978). However, all diffraction peaks of the unidentified phase at high pressure could not be indexed using the ϵ - MgAl_2O_4 structure.

It is possible that the unidentified phase was the result of a reaction between the sample and the MgO pressure-transmitting medium, and therefore another run (#7) using NaCl pressure-transmitting medium was performed, it was observed that the new phase coexisted with MgO and corundum. The observed diffraction peaks of new phase in this run were same as those in the previous run using an MgO pressure-transmitting medium. This indicated that the new phase was not the result of a reaction between the sample and the pressure-transmitting medium.

The experimental conditions used are shown in Fig. 3. The phase boundary between ϵ - MgAl_2O_4 and the CaTi_2O_4 -type phase has a positive dP/dT gradient. The phase boundary was estimated to be $P(\text{GPa}) = 45.5 + 0.0046 \times [T(\text{K}) - 2000]$. In contrast, the dP/dT gradient between the CaFe_2O_4 -type phase and ϵ - MgAl_2O_4 was negative.

The effect of pressure on the unit cell parameters and the volume of the CaTi_2O_4 -type phase is shown in the data listed in Table 3. Both heating and data collection were performed at pressures > 40 GPa, which corresponds to the stability field of the CaTi_2O_4 -type phase, because there is the possibility that the CaTi_2O_4 -type phase could transform to form other phases under metastable conditions. The observed change in volume is plotted as a function of pressure in Fig. 4. The P – V data were fitted to the Birch–Murnaghan equation of state to determine the elastic parameters:

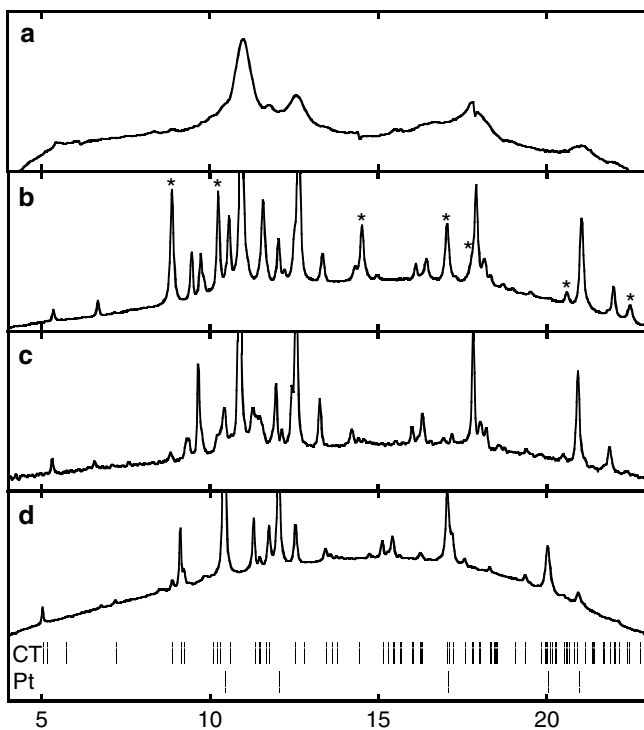


Fig. 1 Examples of the observed X-ray diffraction patterns of CaTi_2O_4 -type MgAl_2O_4 at 300 K. **a** Before heating at a pressure of about 60 GPa. **b** After the first heating at a pressure of 55.8 GPa. **c** After the second heating at a pressure of 47.4 GPa. **d** After decompression at a pressure of 0 GPa. The stars denote the peaks from the high-pressure phase of platinum carbide. The vertical bars indicate the calculated positions of the diffraction lines of the CaTi_2O_4 -type phase ($a = 2.779$ Å, $b = 9.186$ Å, and $c = 9.373$ Å) and platinum ($a = 3.923$ Å). Abbreviations of bars are as follows: CT CaTi_2O_4 -type phase; and Pt platinum. The wavelength of the monochromatic incident X-ray beam was $\lambda = 0.4122$ Å.

Table 2 Observed and calculated X-ray diffraction pattern of CaTi₂O₄-type MgAl₂O₄ at 0 GPa and room temperature

<i>hkl</i>	<i>d</i> _{obs} Å	<i>d</i> _{cal} Å	<i>d</i> _{obs} − <i>d</i> _{cal}	<i>I</i> _{obs}	<i>I</i> _{cal}
002	4.7045	4.7023	0.0022	25	9
022	3.2884	3.2885	0.0001	5	3
110	2.6625	2.6622	0.0003	15	11
023	2.5922	2.5906	0.0016	100	83
111	2.5633	2.5616	0.0017	25	14
040 ^a		2.3003			7
024	2.0940	2.0936	0.0004	85	50
130	2.0609	2.0603	0.0006	10	30
131	2.0129	2.0125	0.0004	65	100
132	1.8875	1.8871	0.0004	65	86
114	1.7620	1.7623	0.0003	15	17
025	1.7426	1.7410	0.0016	5	6
133	1.7185	1.7217	−0.0032	<5	6
006	1.5667	1.5674	−0.0007	25	21
134	1.5503	1.5495	0.0008	5	10
115	1.5364	1.5362	0.0002	35	42
151	1.5152	1.5147	0.0005	<5	10
152	1.4577	1.4590	−0.0013	10	23
062	1.4577	1.4580	−0.0003	10	6
200 ^a		1.3906			33
135 ^a		1.3891			16
153	1.3792	1.3784	0.0008	45	32
063	1.3792	1.3776	0.0016	45	40
116	1.3506	1.3507	−0.0001	10	11
046	1.2953	1.2953	0.0000	5	16
223	1.2253	1.2252	0.0001	10	21

Calculated *d*-spacings are based on orthorhombic unit cell dimensions of *a*=2.7812 Å, *b*=9.2013 Å, *c*=9.4047 Å, and *V*=240.67 Å³. *I*_{obs} and *I*_{cal} are observed and calculated peak intensities

^aPeaks of CaTi₂O₄-type MgAl₂O₄ were interfered with those of platinum

$$P = 1.5K_0(x^{-7} - x^{-5})[1 + 0.75(K_0' - 4)(x^{-2} - 1)],$$

where $x = (V/V_0)^{1/3}$; and *V*₀, *K*₀, and *K*₀' are the volume, the isothermal bulk modulus, and the first pressure derivative of the isothermal bulk modulus, respectively. When the value of *K*₀' was set to *K*₀'=4, the isothermal bulk modulus and the volume at ambient pressure were determined to be *K*₀=219(6) GPa and *V*₀=238.9(9) Å³, respectively (Fig. 4). The bulk modulus determined in this study is in agreement with the theoretical predictions of 248 and 222 GPa of Catti (2001), and 214.8 GPa of Gracia et al (2002).

Discussion

Using a LHDAC, Liu (1978) reported that ϵ -type MgAl₂O₄ with orthorhombic symmetry was observed at pressures greater than 25 GPa. In contrast, Akaogi et al. (1999) and Irifune et al. (2002) confirmed that CaFe₂O₄-type MgAl₂O₄ is stable at pressures corresponding to those used in the synthesis of ϵ -MgAl₂O₄ of Liu (1978). In this study, ϵ -type MgAl₂O₄ was observed at pressures between 40 and 45 GPa (Fig. 3). Our observation is not inconsistent with the data from in situ experiments using a multi-anvil press (Irifune et al. 2002), because the

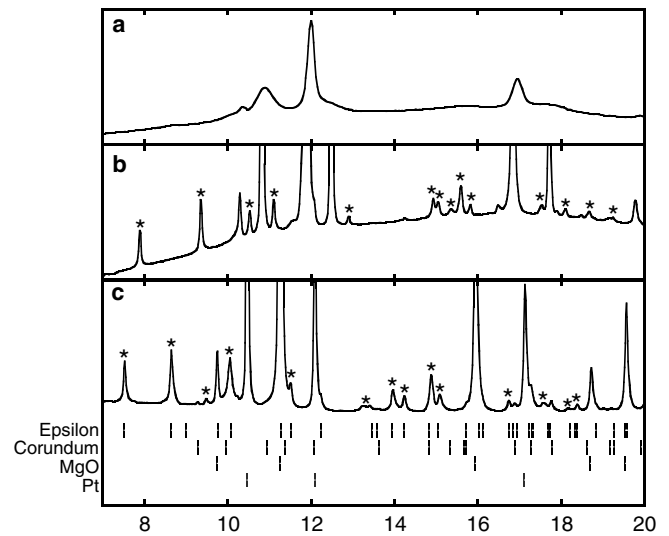


Fig. 2 Examples of the observed X-ray diffraction patterns of ϵ -MgAl₂O₄ at 300 K: **a** before heating at a pressure of about 40 GPa; **b** after heating at a pressure of 34.5 GPa; and **c** after decompression at a pressure of 0 GPa. The stars denote the ϵ -MgAl₂O₄ peaks. The vertical bars indicate the calculated positions of the diffraction lines of ϵ -MgAl₂O₄ (Liu 1978), corundum, MgO, and platinum under ambient conditions. The wavelength of the monochromatic incident X-ray beam was $\lambda = 0.4130\text{\AA}$

maximum pressure of the existence of CaFe₂O₄-type MgAl₂O₄ that was determined using that technique was about 35 GPa. The uncertainty in the experimental method used by Liu (1978) was large, because the pressure was estimated from the length of the spring of

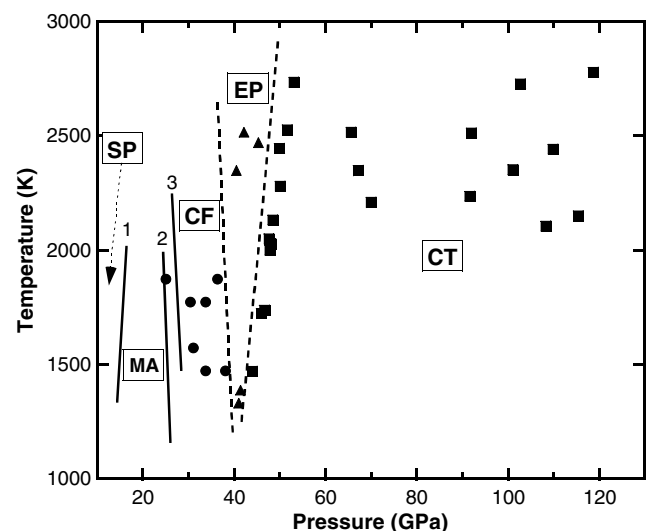


Fig. 3 The experimental high P–T conditions. The solid squares and triangles denote the CaTi₂O₄-type and ϵ -type phases, respectively. The solid circles denote in situ observations of the CaFe₂O₄-type phase (after Irifune et al. 2002). Key to phases: SP spinel-type; CF CaFe₂O₄-type; EP ϵ -type MgAl₂O₄; MA, MgO + Al₂O₃; and CT, CaTi₂O₄-type. The lines show the phase boundaries reported by previous studies: 1 decomposition of the spinel-type phase (Akaogi et al. 1999); 2 two oxides—CaFe₂O₄-type (Irifune et al. 2002); and 3 two oxides—CaFe₂O₄-type (Akaogi et al. 1999)

Table 3 Lattice parameters and volumes of CaTi₂O₄-type MgAl₂O₄ to 91 GPa at 300 K

<i>P</i> (GPa)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	Volume (Å ³)
0.0	2.781(1)	9.201(4)	9.405(3)	240.7(2)
0.0	2.779(1)	9.186(5)	9.373(2)	239.3(1)
42.7	2.636(3)	8.810(37)	8.874(10)	206.0(9)
42.8	2.636(3)	8.801(34)	8.869(11)	205.7(9)
47.4	2.631(1)	8.695(6)	8.979(3)	203.1(2)
55.3	2.625(1)	8.657(6)	8.844(2)	201.0(2)
55.8	2.617(1)	8.644(18)	8.822(1)	199.6(1)
60.2	2.607(1)	8.609(5)	8.792(3)	197.3(1)
66.1	2.598(1)	8.559(4)	8.754(2)	194.6(1)
66.5	2.600(2)	8.560(5)	8.747(3)	194.7(2)
67.7	2.599(0)	8.573(1)	8.759(1)	195.2(0)
75.7	2.585(0)	8.520(2)	8.710(1)	191.8(1)
84.5	2.570(1)	8.451(3)	8.666(2)	188.3(1)
91.2	2.560(0)	8.437(2)	8.629(1)	186.4(0)

Numbers in parentheses represent the error of lattice parameter and volume of CaTi₂O₄-type MgAl₂O₄. Pressures were determined from the observed unit cell volume of platinum using the platinum equation of state (Holmes et al. 1989)

the diamond anvil cell, which was only calibrated at room temperature. Such an old technique is not used in the most recent reliable studies. Moreover, a high temperature correction was not taken into account in Liu's study. It is known that the pressure in a diamond anvil cell is different before and after heating (Andrault et al. 1998; Kavner and Duffy 2001). Therefore, it is likely that the observed phase at pressures greater than 25 GPa by Liu (1978) is inconsistent with the data from that other studies.

In this study, ϵ -type MgAl₂O₄ was observed to coexist with periclase and corundum. This indicates a the direct transition from the spinel-type to the ϵ -type MgAl₂O₄ did not occur. The spinel-type MgAl₂O₄ first decomposed to a metastable assemblage of periclase and corundum. The two component oxides then reacted to

form the stable ϵ -type MgAl₂O₄ phase. The decomposition from the spinel-type MgAl₂O₄ phase to form a metastable two oxide mixture before the formation of CaFe₂O₄-type MgAl₂O₄ was reported by Irifune et al. (2002). Therefore, our observation of a metastable assemblage is likely to be due to the same kinetic effect as reported in a previous study using a multianvil press. Most of the diffraction peaks from the ϵ -type MgAl₂O₄ observed at ambient conditions in this study were same as those reported by Liu (1978). However, the diffraction peaks observed at high pressures in this study could not be identified using the orthorhombic structure suggested by Liu (1978). This implies that the crystal structure reported by Liu (1978) was not ϵ -type MgAl₂O₄. The chemical composition of ϵ -type MgAl₂O₄ could not be detected using an electron probe micro-analyzer, because the grain size of this phase was too small. The unit cell volume of ϵ -type MgAl₂O₄ estimated by Liu (1978) is about 10% smaller than that of periclase and corundum. However, the unit cell volume of the ϵ -type phase is much smaller than that of the higher-pressure CaTi₂O₄-type MgAl₂O₄ phase. Therefore, the unit cell volume of the ϵ -type phase estimated by the previous study is incorrect.

Recently, Sueda et al. (2004) reported that a new MgAl₂O₄ phase, whose structure was not identified, was observed at 40 GPa and a temperature of 2,100 K using a multi-anvil press and in situ X-ray measurements. The *P*-*T* conditions of Sueda et al. observations of a new phase are in good agreement with those of the ϵ -type phase observed in our study. Although the structure of the ϵ -type MgAl₂O₄ phase could not be resolved in our experiments, the structure should be reinvestigated using good quality diffraction data. In our study, single-phase ϵ -type MgAl₂O₄ could not be synthesized, because MgO and corundum always coexisted with the ϵ -type MgAl₂O₄ phase. It is likely that the influence of the transition kinetics is not negligible, because a large temperature inhomogeneity must exist in the sample chamber of the LHDAC. As there is a possibility that the ϵ -type MgAl₂O₄ phase is metastable, it is necessary to investigate the stability of this phase in future studies.

Catti (2001) calculated that CaTi₂O₄-type MgAl₂O₄ is stable at pressures above 39 GPa compared to the two oxide MgO and Al₂O₃ assemblage. However, Gracia et al. (2002) predicted that the assemblage of the two MgO and Al₂O₃ oxides is stable, and that the volume of the two-oxide assemblage is smaller than that of CaTi₂O₄-type MgAl₂O₄ under high pressures. Thus, the theoretical data of the high-pressure phase of MgAl₂O₄ are controversial. In our study, CaTi₂O₄-type MgAl₂O₄ was stable at pressures from 40 to 120 GPa. The change in volume from the two-oxide assemblage to the CaTi₂O₄-type MgAl₂O₄ phase observed in our experiments is in agreement with that predicted by Catti (2001). It is likely that the calculations of Gracia et al. (2002) involved significant difficulties due to the incomplete optimization of the unit-cell coordinates in the MgAl₂O₄ polymorph structures.

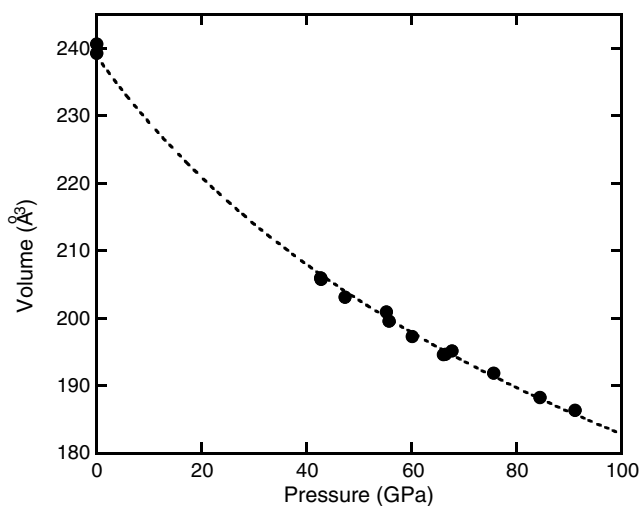


Fig. 4 Pressure–volume data for CaTi₂O₄-type MgAl₂O₄ at 300 K. The dashed curve denotes the Birch–Murnaghan equation fit with $K_0 = 219$ GPa and $K_0' = 4$ (fixed value), respectively

As the aluminous phases of MgAl_2O_4 polymorph structures appear in the subducted oceanic crust, it is important to know the compressibility of MgAl_2O_4 polymorph structures to improve our understanding of dynamics of the subducted slab in the lower mantle (Kesson et al. 1994; Ono et al. 2001). However, there are contradictions in the bulk modulus data of the CaFe_2O_4 -type phase in the mid-oceanic ridge basalt (MORB) composition, and its value is claimed to be in the range 184–243 GPa (Ono et al. 2002; Guignot and Andraut 2004; Ono et al. 2005a).

Figure 5 shows the change in volume of the aluminous phases that appear in the MORB composition (Ono et al. 2005a). These are compared with the change in volume of pure MgAl_2O_4 polymorphs at pressures corresponding to those existing in the mantle. In general, the bulk modulus increases when a pressure-induced phase transition occurs, because the more dense structure is less compressible at higher pressures. As the CaFe_2O_4 -type phase appears at low pressures compared to the CaTi_2O_4 -type phase, it is reasonable that the bulk modulus of the CaFe_2O_4 -type phase is smaller than that of the CaTi_2O_4 -type phase. Therefore, the high value of the bulk modulus of the CaFe_2O_4 -type phase in the MORB composition reported by Ono et al. (2002) is not acceptable, because the bulk modulus of CaTi_2O_4 -type MgAl_2O_4 determined in this study was 219(6) GPa. Thus, the values of 184–200 GPa reported by Guignot

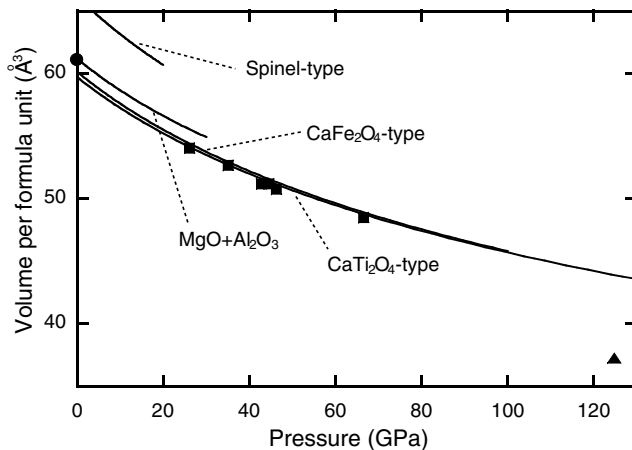


Fig. 5 Comparison of the volume change of MgAl_2O_4 polymorphs and aluminous phases in natural MORB composition at 300 K. The *solid curves* denote the volume change of pure MgAl_2O_4 polymorphs and $\text{MgO} + \text{Al}_2\text{O}_3$. The *circle* denotes the volume of aluminous phase with a CaFe_2O_4 -type structure in MORB under ambient condition (Ono et al. 2002). The *squares* and *triangle* show the volumes of the aluminous phase with the CaFe_2O_4 -type and CaTi_2O_4 -type structures in MORB under high pressure (Ono et al. 2005a). The bulk modulus (K_0) and volume (V_0) CaFe_2O_4 -type phase in MORB were 184(± 8) GPa and 243.0(± 1.3) \AA^3 , respectively, when the first pressure derivative of the bulk modulus (K') was fixed to 4. The equations of state for pure MgAl_2O_4 polymorphs and $\text{MgO} + \text{Al}_2\text{O}_3$ were obtained from: Finger et al. (1986), Spinel-type; Dewaele et al. (2000) and Richet et al. (1988), $\text{MgO} + \text{Al}_2\text{O}_3$; Irifune et al. (2002), CaFe_2O_4 -type; this study, CaTi_2O_4 -type

and Andraut (2004) and Ono et al. (2005a) are more likely to be correct.

Although we have shown that the CaTi_2O_4 -type phase in pure MgAl_2O_4 is stable at pressures greater than 45 GPa at high temperatures, the CaFe_2O_4 -type phase is stable at pressures up to 100 GPa in the natural MORB composition (Kesson et al. 1994). Recently, the CaTi_2O_4 -type phase was reported to exist at 140 GPa in the MORB composition (Ono et al. 2005a). The ϵ -type phase however, has not been reported in the natural composition. These differences between pure MgAl_2O_4 and the natural composition are most likely due to differences in their chemistry. The NaAlSiO_4 component seems to play an important role in determining the bulk modulus of the CaFe_2O_4 -type phase (Guignot and Andraut 2004). This component may also affect the transition pressure of the MORB composition. It is known that the solubility of the NaAlSiO_4 component influences the phase transition between the CaFe_2O_4 -type and the hexagonal aluminous phase (Litasov and Ohtani 2005). In Fig. 5, the volume of the CaTi_2O_4 -type pure MgAl_2O_4 phase is compared to that of the MORB composition, as reported by Ono et al. (2005a). There was about a 15% difference in volume between these two observations. This value seems to be very large, because the difference in volume between pure and natural composition CaFe_2O_4 -type phases is about 1%. As it is difficult to explain this difference in volume by the effect of the structural transition alone, the influence of the chemical composition in natural MORB should be considered.

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