Crystal structure of CaMg₂Al₆O₁₂, a new Al-rich high pressure form

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ABSTRACT

The crystal structure of $CaMg_2Al_6O_{12}$, a new high-pressure phase synthesized at 21.8 GPa and 1200 °C using a multi-anvil apparatus, was solved by a newly developed structure program and refined by Rietveld analysis of the powder X-ray diffraction profile. The structure is hexagonal with cell constants $a = 8.7616(2)$ and $c = 2.7850(1)$ Å, and space group $P6_3/m$. The structure of this phase contains double chains of edge shared AlO_6 octahedra running along the c axis. Three double chains share corners to form sixfold positions in which octahedrally coordinated Mg atoms reside. The large Ca atoms are randomly distributed at ninefold sites with half-occupancy in the hexagonal tunnel. Previously reported Al-rich silicate phases could possibly have the same structure. This structure could thus qualify as one of the possible major host phases for aluminum in the lower mantle.

INTRODUCTION

The possible host minerals for Al in the Earth's lower mantle are debated, especially as related to the fate of the subducting slab in the lower mantle (Madon et al. 1989; Ahmed-Zaid and Madon 1991; Irifune et al. 1991; Irifune 1994; Funamori et al. 1998; Hirose et al 1999; Miyajima et al. 1999). Recent high pressure and high temperature experiments indicate that a significant amount of aluminium can be incorporated into $(Mg,Fe)SiO_3$ perovskite (Ahmed-zaid and Madon 1995; Kesson et al. 1995; Irifune et al. 1996). However, it is not clear what other phases could host large amounts of Al in the lower mantle and how these might be related to the bulk chemistry of the subducting slab.

The phase equilibrium study of the system $MgAl_2O_4$-$CaAl_2O_4$ (Akaogi et al. 1999) produced a new high-pressure phase ($CaMg_2Al_6O_{12}$) with hexagonal symmetry in the intermediate composition of this system. The X-ray diffraction (XRD) pattern of the $CaMg_2Al_6O_{12}$ suggests that its structure differs from that of the calcium ferrite phase. This paper presents the crystal structure of this phase determined by a newly developed program for crystal structure analysis using the combined methods of Monte Carlo and R-factor, and refined with Rietveld Analysis. Characteristics of the structure are compared to other related high-pressure structures, and its implications as the major host phase for Al in the lower mantle are discussed.

SYNTHESIS AND X-RAY DIFFRACTION STUDY

The starting material was prepared from a mixture of high-purity reagents of $CaCO_3$, $Mg(OH)_2$, and α-Al_2O_3 in the molar ratio 0.35:0.65:1.00, and was heated at 1000 °C, for 10–15 hours. Powder XRD showed that the heated sample was a mix-

ture of MgO, CaO, and α-Al_2O_3 with small amounts of $MgAl_2O_4$ spinel and $CaAl_2O_4$ stuffed tridymite. A 6–8 type multi-anvil apparatus at Gakushuin University was used to synthesize the high-pressure phases. The powdered starting material was packed into a sample chamber in the central part of a cylindrical Pt furnace placed in the MgO octahedron. Temperature was measured with a Pt/Pt-13%Rh thermocouple in contact with the outer surface of the furnace. Pressure was calibrated at room temperature using pressure-fixed points. The sample was held at 21.8 GPa and 1200 °C for 2 hours, and then quenched isobarically (Akaogi et al. 1999). X-ray powder diffraction data were collected on a diffractometer with Cr$K\alpha$ radiation (45 kV, 250 mA), using a step scanning method with a 2θ range of 15° to 145°. The step size was 0.01° and the count time was 5 s/step. The X-ray intensity was counted after monochromatization by pyrolytic graphite. The observed powder diffraction pattern showed a new phase with trace amounts of $CaAl_2O_4$ with the calcium ferrite structure. The XRD pattern of the new phase is similar to that of $CaAl_2O_4$ although some of the peaks differ. In particular, the d-values and relative intensities of several strong diffraction peaks of $CaMg_2Al_6O_{12}$ resembled that of $CaAl_2O_4$, suggesting that the fundamental atomic arrangements are similar in both structures. Microprobe analysis indicated that the composition of the new phase was $Ca_{0.33}Mg_{0.67}Al_2O_4$ or $CaMg_2Al_6O_{12}$. The powder XRD pattern of the new phase was successfully indexed to a hexagonal lattice with cell parameters $a = 8.7616(2)$ and $c = 2.7850(1)$ Å (Akaogi et al. 1999). The observed and calculated d-values and indexes are listed in Table 5 in Akaogi et al. (1999).

CRYSTAL STRUCTURE ANALYSIS

Structure model construction

The number of formula units $CaMg_2Al_6O_{12}$ per unit cell, $Z = 1$, was derived from the observed cell volume, yielding a spe-

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cific gravity is of 3.97 g/cm^3. The electron-diffraction pattern of $hk0$ indicates a sixfold axis on the (001) plane and no mirror plane parallel to the c axis (Fig. 1a). This means that the Laue group is 6/m or $\bar{3}$. However, the observed systematic absence of l = 2n + 1 for 00l by the X-ray and electron diffractions (Figs. 1b and 1c) specifies the Laue group as 6/m. This Laue group combined with the systematic absence constrains the possible space group as $P6_3$ or $P6_3/m$.

The number of formula units (Z = 1) indicates that there is one Ca atom per unit cell. However, neither space groups $P6_3$ nor $P6_3/m$ has a Wyckoff position such as 1a or 1b for one Ca atom per unit cell. This dilemma can be solved by the statistical distribution of Ca atoms between equivalent positions with a partial occupation. The projection of the Ca and Fe positions onto (001) in the calcium ferrite structure (Decker and Kasper 1957) produces a hexagonal structure if oxygen atoms are neglected (Fig. 2). In three dimensions, it is not really a hexagonal structure because Z-coordinates of three Ca atoms are 0.25 and those of the remaining Ca atoms are 0.75. However, if all Ca atoms at the corners of the hexagonal cell are located on the positions of Z = 0.25 and Z = 0.75 randomly with half-occupancy, it is possible to take a hexagonal structure. Therefore, Wyckoff positions 2a and 2b in space groups $P6_3$ and $P6_3/m$

might be the potential candidates for Ca sites, assuming that Ca occupies these Wyckoff positions randomly with half-occupancy.

Centrosymmetry was assumed and $P6_3/m$ was selected to represent the space group of this phase. In this space group, the Ca atom should be located on a 2a or 2b position. Mg atoms could be located on a 2c or 2d position and Al atoms could be located on a 6g or 6h position. The possible Wyckoff position or combinations of two Wyckoff positions for oxygen atoms was 12i, 6g + 6h, or 6h + 6h. All the possible arrangements of Wyckoff positions and coordinates were examined by the newly developed Structure Model-Assembly Program (Miura and Kikuchi 1999). This program automatically constructs a crystal structure model for the object material which satisfy XRD data, cell constants, a space group, chemical formula, and Z-number according to the following procedure. In the initial stage, Wyckoff positions and coordinates of independent atoms in a unit cell are generated by Monte Carlo and its XRD pattern is calculated. Then the R-factors based on the calculated and observed XRD data are compared. Numerous models are made by Monte Carlo trials, and the best three hundred models with low R-value are selected and stored. As each atom concentrates in a particular area with increasing number of Monte Carlo trials, search areas are restricted to the vicinity of these atoms. The Wyckoff positions were fixed to 2a for Ca, 2d for Mg, 2h for Al, and 6h + 6h for O in the later stage of the calculation because this arrangement gave a low R-value and the same procedures were repeated to reduce the R-value. After 24 hours of calculation, the program found a structure model which has a reasonably low R-value (R = 0.168). As temperature factors were not optimized in the calculation, the obtained model did not completely match the observed XRD pattern.
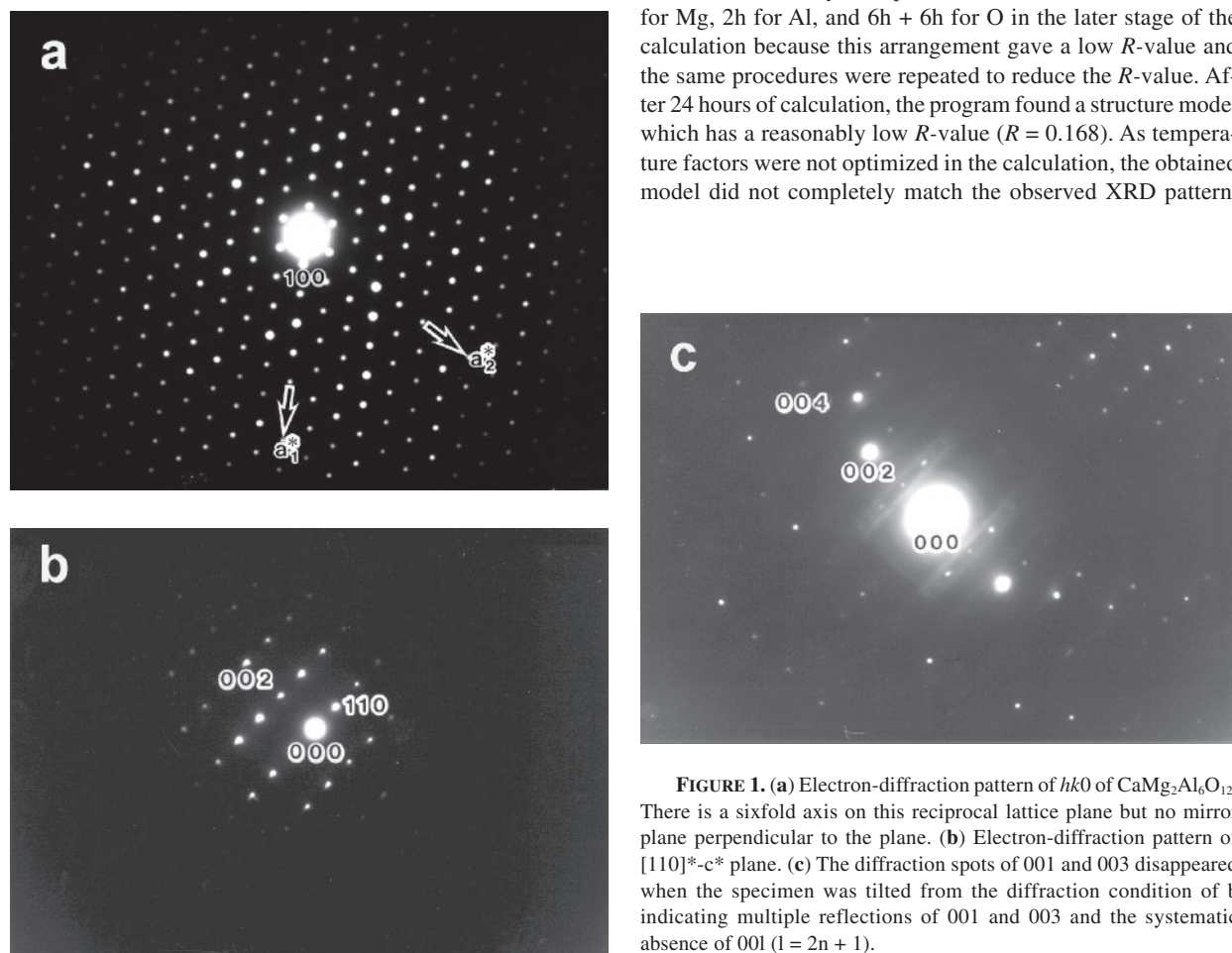

FIGURE 1. (a) Electron-diffraction pattern of $hk0$ of CaMg$_2$Al$_6$O$_{12}$. There is a sixfold axis on this reciprocal lattice plane but no mirror plane perpendicular to the plane. **(b)** Electron-diffraction pattern of [110]*-c* plane. **(c)** The diffraction spots of 001 and 003 disappeared when the specimen was tilted from the diffraction condition of b indicating multiple reflections of 001 and 003 and the systematic absence of 00l (l = 2n + 1).
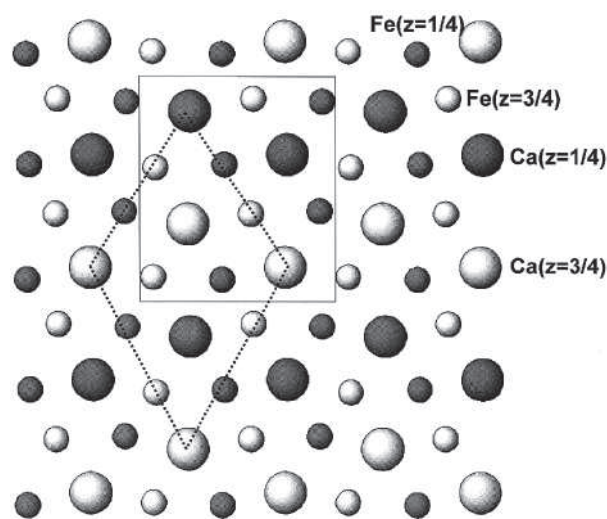
FIGURE 2. Model structure of the hexagonal phase derived from the calcium ferrite structure. Ca and Fe positions in the calcium ferrite structure (solid line is the unit cell) reported by Decker and Kasper (1957) make a hexagonal lattice (dotted line) if all the Ca atoms are located on the positions of Z = 1/4 and Z = 3/4 randomly with half an occupancy.

TABLE 1. Structural data of high pressure hexagonal $CaMg_2Al_6O_{12}$ obtained by the Rietveld analysis

Atom	site	Occ	x	y	z	B
Ca	2a	0.5	0.000	0.000	0.250	2.9(5)
Mg	2d	1.0	0.666	0.333	0.250	1.8(3)
Al	6h	1.0	−0.010(1)	0.342(1)	0.250	1.5(2)
O1	6h	1.0	0.134(1)	0.601(1)	0.250	0.0(3)
O2	6h	1.0	0.306(1)	0.197(1)	0.250	0.5(3)

Notes:

$$R_{WP} = \sqrt{\frac{\sum_i W_i[y_i(o) - y_i(c)]^2}{\sum_i W_i[y_i(o)]^2}} = 22.29\%, \quad R_i = \frac{\sum_k |I_k(o) - I_k(c)|}{\sum_k I_k(o)} = 6.86\%$$

$$R_F = \frac{\sum_k |[I_k(o)]^{1/2} - [I_k(c)]^{1/2}|}{\sum_k [I_k(o)]^{1/2}} = 5.11\%.$$

Isotropic temperature factor = $\exp(-B \sin^2\theta/\lambda^2)$

$Y_i(O)$ and $Y_i(c)$ are observed and calculated intensities, respectively, at point i. W_i is the weight assigned each step intensity. $I_k(O)$ and $I_k(C)$ are the observed and calculated intensity, respectively, for Bragg reflection.

TABLE 2. Interatomic distances of high pressure hexagonal $CaMg_2Al_6O_{12}$

Atoms	Distance (Å)	Atoms	Distance (Å)
Ca-O2 ×3	2.36(2)	Al-O1	1.97(2)
Ca-O2 ×6	2.74(2)	Al-O1 ×2	1.97(2)
avg Ca-O	2.61	Al-O2	1.86(2)
		Al-O2 ×2	1.86(2)
Mg-O1 ×6	2.09(2)	avg Al-O	1.92

However, it was accurate enough to be used as a starting model for the Rietveld Analysis.

Rietveld analysis

The refinement of the structure was carried out by the program RIETAN-94 (Kim and Izumi 1994). The intensity data of every 0.02° step in 2θ were used for the calculation because the observed data of every 0.01° is too large to calculate in a personal computer. As a trace amount of $CaAl_2O_4$ (calcium ferrite structure) peaks were observed, the refinement of $CaAl_2O_4$ was also included in the Rietveld calculation. The initial structure parameters for $CaAl_2O_4$ were derived from the structural data reported by Decker and Kasper (1957). Background parameters, profile parameters, preferred orientation parameter, atomic coordinates, temperature factors and mass fractions of compounds were refined. Cell constants were also calculated in the Rietveld analysis. However, the Si corrected data by Akaogi et al.(1999) were adopted as crystallographic data. The final *R*-values and mass fraction becomes 0.051 and 0.955 for the hexagonal phase and 0.117 and 0.045 for the calcium ferrite phase, respectively. Figure 3 shows the observed and calculated X-ray diffraction patterns. The refined atomic parameters and selected bond distances are given in Table 1 and 2, respectively. The polyhedral representation of the structure projected along the *c* axis is shown in Figure 4.

The non-centrosymmetric model, $P6_3$ was also examined by the Rietveld method. As the origin of the *Z*-coordinate was not determined uniquely in this space group, the *Z*-coordinate of Ca was fixed and those of the remaining atoms were analyzed. However, the correlation factors among the *Z*-coordinates of independent atoms were very high (0.99–1.00) and the refined *Z*-coordinates showed very large standard deviations. Therefore, it is concluded that the hexagonal phase has centrosymmetry.

DISCUSSION

In the new hexagonal structure (Fig. 4), a pair of AlO_6 octahedra share edges to form a long double chain elongated parallel to the *c* axis. Three double chains share corners to form sixfold positions in which Mg atoms reside. The large Ca atoms are located in the ninefold positions. For comparison, the crystal structure of calcium ferrite, $CaFe_2O_4$, (the CF structure) reported by Decker and Kasper (1957) is shown in Figure 5. The differences between these two structures are summarized as the following three points. (1) In the CF structure, the Ca atoms, representing all divalent cations, are coordinated by eight oxygen atoms. However, in the hexagonal phase, the Ca atoms which represent one-third of divalent cations, are coordinated by nine oxygen atoms while the Mg atoms which are the remaining two-thirds of divalent cations in the hexagonal structure, exist in two sixfold-coordinated positions. Thus the three symmetrically equivalent Ca positions in the CF structure break down into two sixfold positions and one ninefold position, as a consequence of different ionic radii of Ca and Mg. (2) Although these two structures are made up of the arrangements of FeO_6 or AlO_6 double chains, the arrangement of the double-chains are different. In the CF structure four double chains share corners around Ca atoms, whereas in the hexagonal phase three double chains share corners around Mg atoms and six around Ca atoms. (3) In the CF structure, large Ca atoms are distributed periodically in the pseudo-triangular tunnel along the *c* axis, whereas in the hexagonal phase Ca atoms are disordered
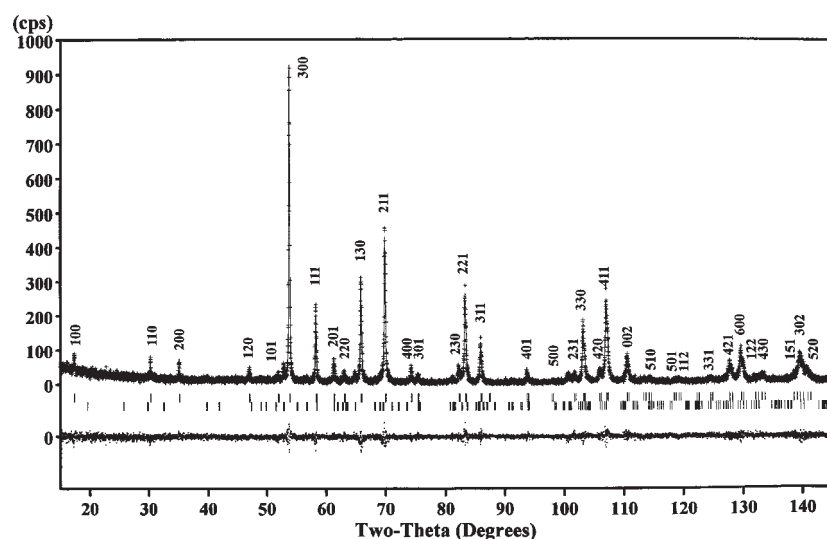
FIGURE 3. Results of Rietveld analysis of the high pressure hexagonal form of CaMg$_2$Al$_6$O$_{12}$. The observed (crosses) and calculated (solid line) powder X-ray diffraction data. The vertical lines below the diffraction peaks mark the positions of the Bragg reflections of Cr$K\alpha_1$ and $K\alpha_2$ for CaMg$_2$Al$_6$O$_{12}$ (upper) and CaAl$_2$O$_4$ (lower), respectively. The plots near the bottom of the figure is the difference between the observed and calculated patterns.
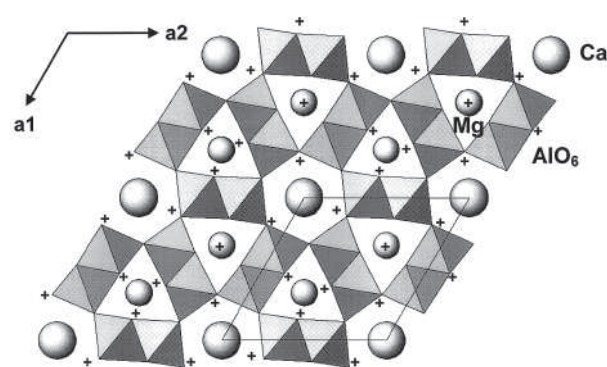

FIGURE 4. Crystal structure of CaMg$_2$Al$_6$O$_{12}$ is made up of linked AlO$_6$ double chains. Mg atoms are located in a position surrounded by three double chains. Ca atoms are located in a large tunnel made up of the radial arrangement of six AlO$_6$ double chains. +: z = 0.75.

FIGURE 5. Crystal structure of CaFe$_2$O$_4$ reported by Dacker and Kasper (1957) is made up of FeO$_6$ double chains. The eightfold-coordinated Ca atoms are located in a triangle tunnel consisting of two double chains and two octahedra, which belong to different double chains.

at 2a sites on a 6$_3$ axis in the triangular tunnel.

The structure feature of random distributions of Ca atoms with half-occupancy in the hexagonal phase seems to be rather unique among the high-pressure structures. The geometrical reason for this is that the distance between the symmetrically equivalent positions of 2a, (0,0,1/4) and (0,0,3/4), is too small (1.39 Å) for the simultaneous occupation of Ca atoms at 2a positions, given that the radius of Ca is 1.26 Å (Whittaker and Mutus 1970). Ca atoms are packed closely in ninefold tunnels and the dense structure was attained. The three nearest oxygen neighbors are so close to Ca and CaO$_9$ polyhedron seems distorted. If Ca atoms move off the center of the polyhedron, the distance between Ca and nearest oxygen becomes more reasonable. However, crystal structure model with Ca on (0,0,z)
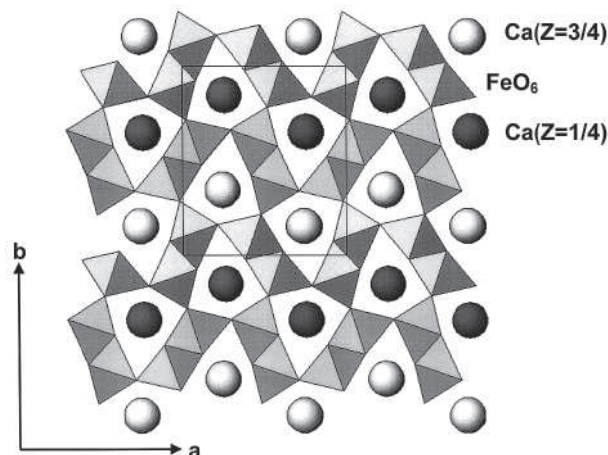
did not show good *R*-value. The reason why the stability field of this phase expands from CaMg$_2$Al$_6$O$_{12}$ toward Mg$_3$Al$_6$O$_{12}$ (Akaogi et al.1999), and not toward Ca$_3$Al$_6$O$_{12}$, may be attributed to the fact that the number of Ca larger than 1 on the formula unit cannot occupy the ninefold sites nor the smaller sixfold sites. However, small Mg atoms can enter into smaller sixfold sites. The absence of CaMg$_2$Al$_6$O$_{12}$ phase with the CF structure from the experiments (Akaogi et al. 1999) may indicate that the hexagonal structure is preferred over the CF structure when different divalent cations have significantly different ionic radii.

This new hexagonal phase has several similarities with the silicate NAL phase M$_3$Al$_4$Si$_{1.5}$O$_{12}$ (M = Mg, Fe, Ca, Na, K) synthesized at 30–50 GPa by Miyajima et al. (1999) in high-pres-

sure phase assemblage of natural garnet. NAL has also space group of $P6_3/m$ or $P6_3$ and its lattice parameters, $a = 8.85(2)$, $c = 2.78(2)$ Å, are similar to those of the hexagonal phase. Although the chemistry of NAL slightly different from that of the hexagonal phase ($CaMg_2Al_6O_{12}$), the chemistry of NAL can be derived from that of the hexagonal phase by the cation substitution, $4Al = 3Si$ for one third of Al with some additional mono- and divalent cation substitutions. Therefore, NAL would have the same structure with the new hexagonal phase with Si and Al randomly occupying 11/12 of the octahedral sites.

Based on the similarity of the powder X-ray diffraction data and chemistry, it is also suggested that the Al-rich phase $[(Ca_{0.27}Na_{0.73})_{0.89} Mg_2(Fe_{0.033}Al_{0.679}Si_{0.288})_{5.79}O_{12}]$ with a calcium ferrite-like structure synthesized at about 25–28 GPa from the MORB composition by Irifune and Ringwood (1993) would have the same structure as the hexagonal phase (Akaogi et al. 1999). It is possible that the $(Mg,Ca)Al_2SiO_6$ phase with an unknown structure synthesized at 40–50 GPa from natural garnet by Ahmed-Zaid and Madon (1995) would also have the same structure as the hexagonal phase, because their phase is similar in composition and synthesis condition to the NAL phase by Miyajima et al. (1999). These results suggest that the newly identified aluminous phase with the hexagonal structure could be an important host for aluminum in the lower mantle, particularly in the subducted basaltic crust.

REFERENCES CITED

Ahmed-Zaid, I. and Madon, M. (1991) A high-pressure form of Al_2SiO_5 as a possible host of aluminum in the lower mantle. Nature, 353, 426–428.
———(1995) Electron microscopy of high-pressure phases synthesized from natural garnets in a diamond anvil cell: Implications for the mineralogy of the lower mantle. Earth and Planetary Science Letter, 129, 233–247.

Akaogi, K., Hamada, Y., Suzuki, T., Kobayashi, M., and Okada, M. (1999) High pressure transitions in the system $MgAl_2O_4$-$CaAl_2O_4$: A new hexagonal aluminous phase with implication for the lower mantle. Physics of the Earth and Planetary Interior, 117, 67–77.
Decker, B.F. and Kasper, J.S. (1957) The structure of Calcium Ferrite, Acta Crystallographica, 10, 332–337.
Funamori, N., Jeanloz, R., Nguyen, J. H., Kavner, A., Caldwell, W. A., Fujino, K., Miyajima, N., Shinmei, T., and Tomioka, N. (1998) High-pressure transformations in $MgAl_2O_4$. Journal of Geophysical Research, 103, 20813–20818.
Hirose, K., Fei, Y., Ma, Y., and Mao, H. (1999) The fate of subducted basaltic crust in the Earth's lower mantle. Nature, 397, 53–56.
Irifune, T. (1994) Absence of an aluminous phase in the upper part of the Earth's lower mantle. Nature, 370, 131–133.
Irifune, T. and Ringwood, A.E. (1993) Phase transformations in subducted oceanic crust and buoyancy relationships at depths of 600–800 km in the mantle. Earth and Planetary Science Letters, 117, 101–110.
Irifune, T., Fujino, K., and Ohtani, E. (1991) A new high-pressure form of $MgAl_2O_4$. Nature, 349, 409–411.
Irifune, T., Koizumi, T., and Ando, J. (1996) An experimental study of the garnet-perovskite transformation in the system $MgSiO_3$-$Mg_3Al_2Si_3O_{12}$. Physics of Earth and Planetary Interior, 96, 147–157.
Kesson, S.E., Fitz Gerald, J.D., Shelly, J.M.G., and Withers, R.L. (1995) Phase relations, structure and crystal chemistry of some aluminous silicate perovskites. Earth and Planetary Science Letters, 134, 187–201.
Kim, Y.I. and Izumi, F. (1994) Structure Refinements with a new version of the Rietveld-Refinement program RIETAN, Journal of the Ceramic Society of Japan, 102,401–404.
Madon, M., Castex, J., and Peyronneau, J. (1989) A new aluminocalcic high-pressure phase as a possible host of calcium and aluminum in the lower mantle. Nature, 342, 422–425.
Miura, H. and Kikuchi, T. (1999) Crystal Structure Model-Assembly Program Using the Monte Carlo and the R-factor Method, The Journal of Chemical Software, 5, 163–172.
Miyajima, N., Fujino, K., Funamori, N., Kondo, T., and Yagi, T. (1999) Garnet-perovskite transformation under the Earth's lower mantle conditions: An analytical transmission electron microscopy study. Physics of the Earth and Planetary Interor, 116, 117–131.
Whittaker, N.J.W. and Muntus, R. (1970) Ionic radii for use in geochemistry. Geochimica et Cosmochimica Acta, 34, 945–956.