Post-garnet Transition in the System $\text{MgSiO}_3\text{-Al}_2\text{O}_3$

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Phase relations of the $\text{MgSiO}_3\text{-Al}_2\text{O}_3$ system were examined with special interest of post garnet transition. High pressure experiments were performed using 6-8 type multianvil apparatus based on conventional quenching method at pressures of 26 to 37 GPa and 1600 to 1800°C. It was observed that pyrope dissociates into perovskite solid solution plus corundum solid solution above about 26.5 GPa, and it was suggested that this phase boundary has a very small negative slope. The stability field of single phase perovskite solid solution in the system $\text{MgSiO}_3\text{-Al}_2\text{O}_3$ extends as pressure increases, and perovskite solid solution isochemical with pyrope stabilizes at about 37 GPa and 1600°C.
[post-garnet transition, phase relation, pyrope, perovskite, corundum]

1. Introduction

It is generally accepted that majorite garnet, one of the major constituents in the upper mantle, transforms to perovskite at the lower mantle conditions. However, details of this post-garnet transition are not known in spite of several previous studies by diamond-anvil experiments. Recent study by Irifune et al. (1996) [1] using 6-8 multianvil apparatus contributed to the study of the post garnet transition by precise determination of phase relations in the $\text{MgSiO}_3\text{-Al}_2\text{O}_3$ system at 1500°C, but there still remain many things to be examined concerning phase relations. In this study, phase relations of the $\text{MgSiO}_3\text{-Al}_2\text{O}_3$ system were examined using 6-8 type multianvil systems with the aim of more precise determination of pressure and temperature dependence of phase relations, and it was examined whether perovskite solid solution isochemical to pyrope is stabilized or not at above 27 GPa.

2. Experimental

High pressure experiments were performed using 6-8 type multianvil apparatus at Gakushuin University with tungsten carbide anvils with truncated edge length of 1.5 mm. A semi-sintered MgO octahedron with edge length of 4.7 mm was used as a pressure transmitting medium. A cylindrical Re heater of 0.7 mm in diameter and 3.8 mm in length was used. A LaCrO_3 sleeve was placed outside of the Re heater for thermal insulation. The powdered sample was directly put into the Re heater. Temperature was measured with a Pt/Pt-13% Rh thermocouple at the outer surface of the heater. Pressure was calibrated using semiconductor - metal transitions in ZnS (15.5 GPa), GaAs (18.7 GPa) and GaP (23 GPa) and ilmenite - perovskite transition in MgSiO_3 (22.5 GPa) at 1800°C. High pressure experiment was also performed using 6-8 type multianvil apparatus at ISEI, Okayama University with sintered diamond anvils with truncated edge length of 2.0 mm. Details of sample assembly and pressure calibration are described in elsewhere [2].

Two kinds of starting materials were used. One was synthetic pyrope, which was synthesized at 5.5 GPa and

1000°C using glass with pyrope composition as a starting material. Powder X-ray diffraction study confirmed that the synthesized product had the garnet structure and no other phases coexisted. EPMA analysis revealed that the garnet phase had pyrope composition within the analytical error, and small amount of platinum used as a thermocouple, relict corundum, and Si-rich phase were also observed. The others were mechanical mixtures of MgSiO_3 clinoenstatite, Al_2O_3 corundum and $\text{Al}(\text{OH})_3$ with compositions of $\text{MgSiO}_3 : \text{Al}_2\text{O}_3 = 9 : 1$ with 1 wt% H_2O and 7.5 : 2.5 with 2 wt% H_2O . Small amount of water added promoted grain growth of coexisting phases. Clinoenstatite was synthesized at atmospheric pressure and 1500°C using glass with enstatite composition as a starting material. Powder X-ray diffraction and EPMA analysis confirmed that the product was clinoenstatite plus small amount of protoenstatite, and no relict phase was observed.

High pressure experiments were performed based on conventional quenching method at pressures of 26 to 27 GPa and temperatures of 1600 and 1800°C at Gakushuin University, and 37 GPa and 1600°C at ISEI, Okayama University. Run durations were 30 to 120 minutes. Quenched samples were recovered to atmospheric pressure, and then polished to examine by micro-focused X-ray diffractometer with a rotating anode. For large-grained samples, compositions of coexisting phases were measured by EPMA. For the run product synthesized at ISEI, Okayama University, powder X-ray diffraction study was also carried out.

3. Results and discussion

Table 1 lists the experimental conditions and phases observed in the central part of run products. The following phases were observed in the central part of run products; pyrope, majorite garnet, perovskite solid solution (with some alumina content), corundum solid solution (with some enstatite content) and stishovite solid solution (with some alumina content). It was observed that pyrope dissociates into perovskite solid solution plus corundum solid solution above about 26.5

Table 1. Experimental conditions and results

Run no.	Pressure (GPa)	Temperature (°C)	Time (min)	Phases	Alumina contents of phases (mol%)*
<i>pyrope</i>					
py1	26.5	1800	42	py + pv(tr) + co(tr)	
py3	27.0	1800**	120	pv + co	
py4	27.0	1600	66	pv + co	
py5	26.5	1600	79	py + pv(tr) + co(tr)	
py6	26.5	1600	60	pv + co	
py7	26.5	1800	61	pv + co	
pyISEI	37.0	1600**	30	pv + st(tr)	
<i>hydrous mixture of 75En25Co-2wt% H₂O composition***</i>					
pyM1	27.0	1800**	30	pv + co + st(tr)	pv:12(2), co:70(1)
pyM4	27.0	1600	60	pv + co	pv:8(1), co:80(2)
<i>hydrous mixture of 90En10Co-1wt% H₂O composition***</i>					
en9co1M1	26.0	1600	120	pv + ga + co(tr) + st(tr)	pv:1(1), ga:21(2)

* Error in parentheses is one standard deviation

** Temperature estimated from power supply

*** $X\text{En}(100-X)\text{Co}$ represents composition of X mol% $\text{MgSiO}_3 \cdot (100-X)$ mol% Al_2O_3

Abbreviations: py; pyrope, pv; perovskite, co; corundum, st; stishovite, ga; garnet, tr; trace

GPa. Inconsistent results of resultant phases at 26.5 GPa imply that these experiments were performed at the conditions close to the phase boundary between the stability field of pyrope and that of perovskite plus corundum, though it also represents experimental limitation for control of high-pressure and high-temperature conditions. Perovskite solid solution isochemical with pyrope was synthesized at about 37 GPa. Details of perovskite with pyrope composition synthesized in this study are described elsewhere [2]. Small amount of stishovite was often observed especially in the run products synthesized from hydrous mixtures. The main reason of production of stishovite is not clear, but it can be said that H_2O in the sample may be somewhat concerned.

Fig. 1a shows the back-scattered electron image (BEI) of dissociated product of assemblage of perovskite and corundum, observed at the central part of the run product synthesized at 26.5 GPa and 1600°C for 60 minutes using starting material of pyrope (Run py6). This was the most well-crystallized dissociated-product in this study, although all phases in this photograph had grain sizes not larger than 5 micrometer (except for relict corundum). Thus it can be said that the rates of dissociation of pyrope and grain growth of perovskite and corundum are very slow. On the other hand, run products of the assemblage of perovskite and corundum derived from starting materials of hydrous mixtures of clinoenstatite, corundum and $\text{Al}(\text{OH})_3$ had grain sizes relatively large (about 5 to 20 micrometers). This discrepancy would originate from the difference of chemical reaction of formation of perovskite plus corundum; i.e. the former was the dissociation reaction of pyrope while the latter was the solid-solid reaction. In the latter reaction, it may be thought that clinoenstatite

Fig. 1. Back-scattered electron images (BEI) of the recovered sample quenched at 26.5 GPa and 1600°C (Run py6). (a) At the location of central part. Small bright grains correspond to corundum, and relatively large and dark matrix with many cracks is perovskite. Large grains are relict corundum which would exist in the starting material. (b) At the location of middle part. Left side in the image corresponds to the high-temperature portion in the sample. Worm-like grains (those exist at the right side of the image separately, while they gather at the left side) are the assemblage of dissociated products, perovskite plus corundum, and large crater-like matrix is pyrope. Bright spots are platinum which would exist in the starting material of synthetic pyrope.

in the hydrous mixture first transformed to perovskite with enstatite composition, and then it reacted with coexisting corundum by atomic diffusion.

Textural observation of the experimental charge of Run py6 by SEM and EPMA mapping analysis revealed that there was no distinctive phase boundary between the central region (where perovskite plus corundum existed, Fig. 1a) and the end region (where only unreacted pyrope existed) of the sample in spite of the rapid decrease in temperature away from centrally located hot region within the small cylindrical heater (the size of which recovered to atmospheric pressure was about 0.5 mm in diameter and 2.6 mm in length). Three-phase coexisting field (pyrope + perovskite + corundum) was observed at the middle region (located about 0.8–1.1 mm far from the central part) which is shown in Fig. 1b. These results indicate that the absolute value of dP/dT for this boundary is very small. This three-phase field may correspond to the phase boundary between the stability field of pyrope and that of perovskite plus corundum. We have no experimental evidence to maintain that dP/dT for this boundary is positive. So we suggest that this phase boundary has a very small negative slope, and a phase diagram of the $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ composition shown in Fig. 2 is determined.

Fig. 3 shows phase relations in the system MgSiO_3 – Al_2O_3 at 1600°C and 1800°C. The stability field of single phase perovskite solid solution extends to Al_2O_3 -rich side as pressure increases, and perovskite solid solution isochemical with pyrope is stabilized at about 37 GPa and 1600°C. Thus the results by diamond anvil experiments concerned with the formation pressure of perovskite solid solution isochemical to garnet composition (e.g. O'Neill and Jeanloz, 1994 [3]) are inconsistent with our results. It is also clarified in this study that the stability field of single phase perovskite solid solution extends as temperature increases. If we consider the fact that the location of the phase boundary between the stability field of perovskite and perovskite plus corundum at 1600°C determined in this study is almost consistent with that determined by Irifune et al. (1996) [1], we support their results that the entire inventory of Al_2O_3 in a pyrolite-peridotite lower mantle could be accommodated in solid solution in magnesian silicate perovskite along the geotherm. The stability field of corundum solid solution also extends to MgSiO_3 -rich side as temperature increases, though pressure dependence is not clarified in this study. More precise determination of location of phase boundaries especially in the Al_2O_3 -rich side is needed in future study.

References

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Fig. 2. The P-T diagram of $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$. Circular and square symbols indicate runs using starting materials of pyrope and hydrous mixture of $\text{MgSiO}_3 : \text{Al}_2\text{O}_3 = 7.5 : 2.5$ composition containing 2 wt% H_2O , respectively. Solid symbols indicate perovskite plus corundum, while open symbols indicate pyrope. Abbreviations: Py; Pyrope, Pv; Perovskite, Cor; Corundum, s.s.; solid solution.

Fig. 3. Phase relations in the system MgSiO_3 – Al_2O_3 at 1600°C (dashed lines) and 1800°C (dotted lines). Circular symbols indicate runs using starting material of pyrope. Square symbol indicates runs using starting material of mixture of $\text{MgSiO}_3 : \text{Al}_2\text{O}_3 = 7.5 : 2.5$ composition containing 2 wt% H_2O . Rhombus symbol indicates the run using starting material of $\text{MgSiO}_3 : \text{Al}_2\text{O}_3 = 9 : 1$ composition containing 1 wt% H_2O . Solid symbols indicate existence of perovskite. Diagonal symbols indicate existence of corundum. Open symbols indicate existence of garnet. Cross (+) and X symbols indicate compositions of product phases at 1600 and 1800°C determined by EPMA measurements.