Post-garnet Transition of Almandine at High Pressure: Phase Equilibrium and Calorimetric Studies

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High pressure high temperature transition of almandine garnet ($\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) was examined at 20-23.5 GPa at 1200-1600° C in the oxygen fugacity of iron-wustite buffer, using a multi-anvil apparatus. It was found that almandine dissociates into a mixture of wustite, corundum and stishovite. The dissociation boundary is placed at 20-21 GPa at 1200-1600° C with a slightly negative slope. Enthalpy of formation of almandine was measured by high temperature solution calorimetry and thus enthalpy of the almandine dissociation was obtained. The thermodynamically calculated dissociation boundary agrees with that determined by the phase equilibrium experiments. This dissociation boundary may be used as a pressure standard at around 20 GPa at high temperature. The present results in combination with those on pyrope suggest that almandine-pyrope garnet is stable in a depth range down to the upper part of the Earth's lower mantle.

[high pressure transition, phase equilibrium, almandine, enthalpy, thermodynamic calculation]

1. Introduction

Phase transitions of garnet in the system MgSiO_3 - FeSiO_3 - CaSiO_3 - Al_2O_3 at high pressures and high temperatures are of great interest to clarify mineralogy of the lower mantle and dynamics of slab subduction. Almandine ($\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) is one of the important endmembers of the mantle garnet. However, the phase transition of almandine is still the subject of debate. Liu [1] reported that almandine decomposed into stishovite and graphite with a hydrogarnet structure at about 15 GPa, while Kesson et al.[2] proposed that almandine dissociated into either a mixture of wustite, corundum and stishovite or a mixture of wustite, stishovite and FeAl_2O_4 (calcium ferrite structure). Both of the studies were performed, using the diamond anvil cell with laser heating system. It has been suggested that there still exist several problems in laser heating experiments of iron-containing samples such as almandine due to effective absorption of laser radiation.

In this study, using a multi-anvil apparatus, we have carried out high pressure phase equilibrium experiments of almandine with precise control of pressure and temperature in a larger sample volume, compared with the diamond anvil cell. We have found that almandine dissociates into wustite, corundum and stishovite and have determined precisely the equilibrium dissociation boundary. Next, we have measured formation enthalpy of almandine by high temperature solution calorimetry, and have determined the dissociation boundary by thermodynamic calculation. Both of the

boundaries are consistent with each other, suggesting reliability of the determination of the boundary. Finally, stability of garnet in the system $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ (almandine)- $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ (pyrope) in the lower mantle is discussed.

2. Experimental Methods

High pressure high temperature phase equilibrium experiments were carried out using the multi-anvil apparatus with tungsten carbide anvils of 1.5 mm-truncated edge length in combination with a MgO octahedron of 4.7 mm on edge. Pressure was calibrated against press load at room temperature by using pressure-fixed points, ZnS (15.5 GPa), GaAs (18.3 GPa) and GaP (23 GPa), and further corrected at 1400° C by the ilmenite-perovskite transition of MgSiO_3 [3]. Synthetic almandine was mixed with wustite and metallic iron of about 5-8 wt% each, and used as the starting material for normal runs. Similarly, a mixture of wustite, corundum and stishovite with the almandine stoichiometry was further mixed with wustite and metallic iron of about 5-8 wt%, and used for reverse runs. The addition of wustite and metallic iron was to keep the oxygen fugacity of the iron-wustite buffer in the sample during the run. The starting material was put into a tubular rhenium furnace, and the run temperature was measured at the central part of the furnace with a Pt/Pt-13%Rh thermocouple. No correction was made on the emf of the thermocouple. The sample was held at 20.3-23.5 GPa and 1200-1600° C for 10-120 min, and quenched.

Phase identification in the central part of the recovered samples was made by microfocussed x-ray diffractometry with x-ray beam of $50\ \mu\text{m}$ in diameter. In some runs, lattice parameters of the phases in the central part were measured by powder x-ray diffraction method. Both of the x-ray diffraction experiments were performed using a Rigaku 2500V x-ray diffractometer with a rotating Cr anode operated at 45 kV and 250 mA.

Enthalpies of solution for almandine, fayalite, corundum and quartz were measured at 702°C using a Calvet-type microcalorimeter. The heats of solution in $2\text{PbO}\cdot\text{B}_2\text{O}_3$ solvent for quartz and corundum were measured by standard solution calorimetry method. The enthalpies of solution of almandine and fayalite in the solvent were measured in purified Ar atmosphere to prevent oxidation of the samples. In the measurements of heats of solution, a powder sample of about 4–19 mg was used for each solution run. All of the above powder samples were dissolved within about 40 min in the solvent.

3. Results and discussion

All of the run products of the phase equilibrium experiments contained both of wustite and metallic iron. This confirmed that the samples were in the oxygen fugacity of the iron-wustite buffer. Table 1 shows the x-ray diffraction data of the run product synthesized at 23.5 GPa and 1400°C for 60 min. Stishovite, wustite, corundum and almandine were observed in addition to metallic iron. This shows that almandine dissociates into the mixture of wustite, corundum and stishovite at the P,T conditions. Lattice parameters of stishovite, corundum, wustite and almandine are also shown in Table 1. The cell parameters indicate that stishovite is pure SiO_2 , while corundum contains a small amount of impurities. Although we tried to analyse the phases of the dissociation products with EPMA, it was difficult due to the small grain sizes. The composition of wustite was estimated to be $\text{Fe}_{0.95}\text{O}$ from the cell parameter-composition relationship of nonstoichiometric wustite [4].

Figure 1 shows the results of the phase equilibrium experiments. The dissociation boundary was tightly constrained with the normal and reverse runs. The dissociation occurs at 20–21 GPa at 1200–1600 $^\circ\text{C}$, and the boundary has a slightly negative slope. The density increase of 10.6 % is associated with this decomposition

reaction.

All of our run products showed no evidence for melting of the samples. However, in Kesson et al.'s [2] diamond anvil experiments on almandine at 60 GPa and high temperature, fibrous and spherulitic intergrowths of wustite, corundum, and stishovite and amorphous materials were observed. This suggests that partial melting occurred in Kesson et al.'s sample presumably at higher temperature than those in our study. The decomposition of almandine at about 15 GPa in Liu's [1] experiments may be attributed to partial melting and associated reduction of ferrous iron in the sample, as suggested by Kesson et al. [2]. It is likely that both of the results by Kesson et al. and Liu were caused by effective absorption of laser radiation in almandine.

The enthalpies of solution in $2\text{PbO}\cdot\text{B}_2\text{O}_3$ at 702°C , measured with the Calvet-type microcalorimeter, were $78.8 \pm 3.8\ \text{kJ/mol}$ for $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ (almandine), $19.9 \pm 0.9\ \text{kJ/mol}$ for Fe_2SiO_4 (fayalite), $-3.7 \pm 0.1\ \text{kJ/mol}$ for SiO_2 (quartz), and $32.1 \pm 0.7\ \text{kJ/mol}$ for Al_2O_3 (corundum). Using these data, enthalpy of formation of almandine from the mixture of fayalite, corundum and quartz was obtained as

Fig. 1. Phase diagram for dissociation of almandine into the mixture of wustite, corundum and stishovite determined by high pressure phase equilibrium experiments. Circles and squares represent normal and reverse runs, respectively. Open and closed areas in each symbol correspond to the abundance of the mixture of wustite, corundum and stishovite and that of almandine, respectively. Alm: almandine, Wu: wustite, Cor: corundum, St: stishovite.

Table 1. Powder x-ray diffraction data of the run product at 23.5 GPa and 1400° C.

Observed		Stishovite ^a			Corundum ^a				Wustite ^a			Almandine ^a		
I/I_{100}	d/Å	d/Å	hkl	I/I_{100}	d/Å	hkl	I/I_{100}		d/Å	hkl	I/I_{100}	d/Å	hkl	I/I_{100}
100	2.955	2.954	110	100										
30	2.882											2.883	400	40
70	2.579											2.579	420	100
30	2.555				2.556	104	100							
35	2.486								2.488	111	80			
15	2.383				2.383	110	21							
20	2.354											2.354	422	20
15	2.263											2.262	510	20
25	2.248	2.247	011	22										
60	2.156								2.155	200	100			
30	2.107											2.105	521	20
30	2.089				2.089	113	66							
20	2.029 ^b													
30	1.9794	1.9790	111	38										
20	1.8695	1.8685	120	12								1.8707	611	30
15	1.7431				1.7428	024	34							
10	1.6639											1.6646	444	30
20	1.6044				1.6040	116	89							
20	1.5994											1.5992	640	40
25	1.5410											1.5411	642	50
60	1.5299	1.5299	121	37										
25	1.5245								1.5238	220	60			
20	1.4770	1.4771	220	11										
5	1.4420											1.4415	800	20
10	1.4067				1.4068	124	23							
15	1.3760				1.3760	030	27							
10	1.3326	1.3327	002	7										

a: The d-values were calculated using the following lattice parameters determined by least squares fitting of the observed major reflections which did not overlap with those of the coexisting phases. Stishovite, $a=4.178(1)\text{\AA}$, $c=2.665(1)\text{\AA}$; corundum, $a=4.766(1)\text{\AA}$, $c=13.014(4)\text{\AA}$; wustite, $a=4.178(1)\text{\AA}$; almandine, $a=11.532(1)\text{\AA}$. The relative intensities are from JCPDS No. 45-1374 (stishovite), 46-1212 (corundum), 6-615 (wustite), and 9-427 (almandine).

b: The reflection (110) of α -iron.

-22.5 ± 4.0 kJ/mol. Based on the data together with enthalpy of formation of fayalite from wustite + quartz [5] and enthalpy of the quartz-stishovite transition [6], enthalpy ($\Delta H'_{298}$) for the following reaction,

is calculated to be 178.9 ± 5.6 kJ/mol. Entropy change ($\Delta S'_{298}$) for the reaction (1) is also obtained as -34.1 ± 3.1 J/mol.K from the published entropy data of the phases in (1) [5,6,7].

The dissociation boundary of almandine into wustite, corundum and stishovite was calculated by the same method as in [6], using the above obtained thermodynamic data. Effects of temperature on $\Delta H'$ and $\Delta S'$ were corrected using the heat capacity equations of the relevant phases. Effect of pressure on molar volume of each phase was calculated using the Birch-Murnaghan equation of state, and effect of temperature on molar volume was calculated by thermal expansivities. These physical properties of the phases used in the thermodynamic calculation are listed in Table 2. The calculated boundary shown by a solid curve in Fig. 2 is placed at about 20-21 GPa at 1000-1800 °C with a slight negative slope. The uncertainty of dissociation pressure of the calculated boundary is about ± 0.8 GPa which is derived from both of the errors of $\Delta H'$ and $\Delta S'$ and, is shown by error bars in Fig. 2. In this calculation, stoichiometric wustite was assumed as one of the dissociation products. However, nonstoichiometric wustite of the composition $\text{Fe}_{0.95}\text{O}$ was synthesized, as described above. Therefore, we calculated the dissociation boundary for $\text{Fe}_{0.95}\text{O} + 0.05\text{Fe}$ instead of the stoichiometric wustite, using thermodynamic model and data for nonstoichiometric wustite by [5]. The calculated boundary of this case shown with a dotted curve in Fig. 2 is only 0.3-0.7 GPa higher than that for the stoichiometric wustite. These calculations show that the calculated boundaries are in good agreement with the boundary determined by the phase equilibrium experiments shown in Fig. 1. This indicates that the dissociation boundary has been tightly constrained by both of the phase equilibrium and calorimetric studies. This boundary can be used as a pressure calibration standard at high temperatures at around 20 GPa, because the boundary is accurately determined as shown

above, and the boundary slope is rather insensitive to temperature.

This study shows that the dissociation of almandine occurs at 20-21 GPa at 1000-1800 °C. Irifune et al. [8] found that $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ pyrope dissociates into perovskite and corundum solid solutions in the system $\text{MgSiO}_3\text{-Al}_2\text{O}_3$ at about 27 GPa and 1500 °C. Kubo et al. [9] have shown that the boundary of this dissociation reaction has a slope of almost zero. Combining the present results on almandine with those of pyrope, it is concluded that garnet in the almandine-pyrope system is stable at pressures below about 27-30 GPa in a wide range of temperature. This indicates that the almandine-pyrope garnet can be stable in a depth range from the upper mantle to the upper part of the lower mantle (down to about 700-800 km depth). On the contrary, O'Neill and Jeanloz [10] reported that in the diamond cell experiments at about 50 GPa and 1000-2000 °C a natural garnet in the pyrope-almandine system transformed to aluminous perovskite and that garnet still survived at the P,T conditions. They proposed therefore that stability of garnet in the lower mantle down to the depth range of

Fig. 2. Phase boundaries for dissociation of almandine calculated using thermodynamic data. A solid curve shows the calculated boundary using $\Delta H'_{298}$ of 178.9 kJ/mol and $\Delta S'_{298}$ of -34.1 J/mol.K, with the error bars showing the uncertainties of the dissociation pressure due to errors of $\Delta H'_{298}$ and $\Delta S'_{298}$. A dotted curve represents the calculated boundary for nonstoichiometric wustite ($\text{Fe}_{0.95}\text{O}$) plus 0.05Fe, see text.

Table 2. Physical properties used for calculation of the phase boundaries.

Phase	V'_{298} (cm^3/mol)	$\alpha = a_0 + a_1 T + a_2 T^{-2}$ (K^{-1})			K_{T298} (GPa)	K_T'	$(\partial K_T / \partial T)_P$ (MPa/K)
		$a_0 \times 10^5$	$a_1 \times 10^9$	$a_2 \times 10$			
$\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ (alm)	115.44 ^a	1.776	12.140	-5.071 ^c	176 ^e	5.5 ^e	-27.0 ^e
FeO (wu)	12.25 ^b	1.688	2.040	0.190 ^d	153 ^f	4.9 ^f	-27.2 ^g
Al_2O_3 (cor)	25.58 ^c	2.276	4.198	-0.897 ^c	253 ^h	5.0 ^h	-31.3 ⁱ
SiO_2 (st)	14.01 ^c	1.053	9.031	1.220 ^b	302 ^j	5.3 ^j	-47.0 ^d
Phase	$C_p = A + BT^{-0.5} + CT^{-2} + DT^{-3}$ (J/mol.K)						
	$A \times 10^{-2}$	$B \times 10^{-3}$	$C \times 10^{-6}$	$D \times 10^{-8}$			
$\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ (alm)	5.377	0.0	-40.549	71.378 ^b			
FeO (wu)	0.857	-0.871	0.0	3.954 ^b			
Al_2O_3 (cor)	1.550	-0.828	-3.861	4.091 ^k			
SiO_2 (st)	0.858	-0.346	-3.605	4.511 ^l			

a: This study, b: [11], c: JCPDS 46-1212, d: [12], e: [13], f: [14], g: Same as MgO in [15], h: [16], i: [15], j: [17], k: [18], l: [6].

about 1200 km. Based on our results shown above, such stability of pyrope-almandine garnet in the deep part of the lower mantle is unlikely. We suggest that the garnet in the run product at 50 GPa in O'Neill and Jeanloz's experiments would be an untransformed starting material due to slow transition kinetics and/or local heating of the sample.

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