Synthesis of high-TiO₂ pyrope-grossular garnet at 10 GPa

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A high-titanium containing garnet, SiO₂(40.6), TiO₂(6.3), Al₂O₃(18.8), MgO(14.3), CaO(20.21), (wt%) has been synthesized at 10 GPa and 1500°C. Unit cell parameter of this synthetic garnet is determined to be 11.812 Å by micro-focused X-ray diffractometry and this value is intermediate between those of pyrope and grossular. These results indicate that pyrope-grossular garnet potentially can accommodate TiO₂ up to 6.3 wt% at the high of 10 GPa.

Keywords: High-titanium garnet, High-pressure, Solid solution, Cell parameter

I. Introduction

Phase relations of CaMgSi₂O₆-CaTiAl₂O₆ system have been experimentally studied at the atmospheric pressure to clarify the behavior of titanium in alkaline igneous rocks and Ca-Al-rich inclusions in carbonaceous chondrites (Yagi and Onuma, 1967, 1969; Onuma *et al.*, 1978). Furthermore, it has been expected that perovskite, garnet and corundum would stable at high-pressure greater than 2.5 GPa (Yagi and Onuma, 1967). However, mineral assemblage and contents of TiO₂ in each phases produced under high-pressure conditions have not been clarified experimentally.

The experimental studies have been performed at 10 GPa and 1500°C on a starting composition of CaMgSi₂O₆ (80 wt%) • CaTiAl₂O₆ (20 wt%) which contains pyroxene and rare perovskite (Yagi and Onuma, 1967). Furthermore, a supplemental high-pressure experiment was

conducted on a garnet phase which is present in the run product for examination by microfocused X-ray diffraction to determine the cell parameter.

II. Experimental methods

High-pressure and high-temperature experiments were performed by a multi-anvil apparatus at Tohoku University. Tungsten carbide cubes of 3.5 mm truncation and magnesia octahedron with incorporated graphite were used as the second stage anvil and as a cell assembly, respectively. Sample pressure was calibrated against oil pressure of the hydraulic press. Pressure calibration curve for was constructed by detecting phase transitions of Bi I-II (2.55 GPa) and Bi III-V (7.7 GPa) at room temperature and then the curve was modified for high-temperature experiments by detecting phase transition of forsterite- modified spinel at 14.6 GPa and 1600°C (Katsura and Ito, 1989).

Two starting compositions were prepared: (1) a composition of $\text{CaMgSi}_2\text{O}_6$ (80 wt%); $\text{CaTiAl}_2\text{O}_6$ (20 wt%); and (2) a composition of garnet, which is present in the run product of the starting composition (1). The starting material (1) was prepared by crystallization of a glass at 1100°C for three day. The starting material (2) was a glass with the garnet composition produced at 10 GPa and 1500°C (Table 1). The glasses were made by fusion of the appropriate oxide or carbonate mixtures, SiO_2 , MgO , TiO_2 , MgO and CaCO_3 . The starting material (1) was held in a sealed Pt capsule, and the material (2) in a carbon capsule. The run duration was 1 hour and temperature was monitored by thermocouple of W3%Re97%-W25%Re75% in both experiments. Temperature gradient in the sample is estimated to be more than 50°C of the nominal temperature of 1500°C. Chemical analyses of the run product of (1) was performed with electron microprobe analyzers.

III. Results

Perovskite, clinopyroxene and garnet were identified with electron microprobe analyzer in the run product. Mass balanced chemical compositions are shown in Table 1. Proportion of abundance of perovskite, clinopyroxene and garnet are approximately 8, 72 and 20 in wt%, respectively. A surprising result is that the garnet contains 8 wt% TiO_2 . Titanium-rich garnet was reported as andradite or schorlomite in alkaline igneous rocks and skarn deposits (Deer *et al.*, 1978), or in a synthetic garnet at high-pressure (Ringwood and Lovering, 1970). It is noted, however, that iron is essential to these high-titanium bearing garnet. In contrast to the garnets previously reported, this is the first report of the high-titanium garnet crystallized in a iron-free system. Therefore, a supplement high-pressure experiment to synthesize the garnet and X-ray

Table 1. Starting composition and representative analyses of phases produced at 10 GPa and 1500°C

wt%	S.C.	perovskite	Cpx	garnet
SiO_2	44.39	3.62	50.33	39.18
TiO_2	6.72	51.63	1.83	8.11
Al_2O_3	8.57	1.08	5.38	16.85
MgO	14.89	1.59	16.84	14.52
CaO	25.43	51.63	23.49	16.85
total	100.00	96.94	97.87	98.36
Si		0.332	3.700	2.883
Ti		3.557	0.101	0.449
Al		0.117	0.466	1.461
Mg		0.217	1.846	1.592
Ca		3.830	1.851	1.553
total		8.052	7.965	7.938
proportion of abundance				
in wt%		8	72	20
S.C: starting composition				

diffraction examination have been performed to determine the lattice parameter.

Synthetic garnet

The starting composition for the synthetic garnet is given in Table 1. A polished section was made from the recovered sample, after an hour under 10 GPa and 1500°C. Chemical analysis and micro-focused X-ray diffractometry were performed on same garnets in a region of the surface of the sample section. The chemical composition and the diffraction pattern and d (lattice spacing) and I (relative peak intensity) values are shown in Table 2 and 3, respectively. No other phase than the garnet was confirmed. It is noted that the chemical composition of synthesized garnet are slightly different from the starting composition (Table 2). This implies the compositional differences in the garnets due to the thermal gradient in the sample.

The possible cation distribution in three kinds of site: dodecahedral, octahedral and tetrahedral site in the garnet are expressed, in consideration of a site preference of the ele-

Table 2. Chemical composition of the synthesized garnet (N=9)

	Average	1-s	min.-max.
SiO ₂	40.59	0.40	39.99 - 41.12
Al ₂ O ₃	18.83	0.75	17.02 - 19.55
TiO ₂	6.25	0.68	5.73 - 7.79
MgO	14.25	0.26	14.00 - 14.75
CaO	20.21	0.45	19.50 - 20.93
total	100.47	0.72	99.49-101.35

Numbers of ions on the basis of 12 oxygen.

Si	2.9394	0.0124
Al	1.6336	0.0558
Ti	0.3080	0.0392
Mg	1.5398	0.0247
Ca	1.5152	0.0333
total	7.9358	0.0123

N: number of analysis

1-s: one standard deviation of 9 analyses

Mol per cent of end-components

ZTi ⁽⁺⁾ Al ₂ SiO _n	9.4
ZMgTiSi ₃ O _n	5.7
ZTi ⁽⁺⁾ Si ₃ O _n	6.8
ZAl ₂ Si ₃ O _n	78.1

Z=(Ca_{1.515} Mg_{1.485})

ments (Huggins *et al.*, 1977), as follow :

This garnet solid solution cannot be represented only by the components of $\text{Z}_3\text{MgTiSi}_3\text{O}_{12}$, $\text{Z}_3\text{Ti}_2\text{Al}_2\text{SiO}_{12}$ and $\text{Z}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, (Z=Ca, Mg). If we assume a component of $\text{Z}_3\text{Ti}_2\text{Si}_3\text{O}_{12}$ in which titanium has trivalence, although we do not have evidence for presence of trivalence titanium in the garnet at present, then the garnet solid solution can be represented by above four garnet components (Table 2). The *d* value of the synthetic garnet intervenes between those of pyrope and grossular, and cell parameter: 11.812 Å is a intermediate value between those of pyrope (11.459 Å) and grossular (11.855 Å). The success of synthesizing

Table 3. Observed X-ray diffraction data for synthetic garnet (λ) = 1.54056 Å)

2-theta	<i>l</i>	<i>d</i> (ods.)	hkl
30.22	20	2.955	400
33.92	63	2.641	420
35.66	16	2.516	332
37.30	22	2.409	422
38.88	24	2.314	431
41.90	13	2.154	521
47.50	36	1.913	611
53.86	24	1.701	444
56.26	57	1.634	640
58.60	100	1.574	642
63.10	15	1.472	800
71.64	24	1.316	842
73.72	32	1.284	921
75.78	15	1.254	851
79.92	14	1.199	941

Ti-rich garnet in this study suggests that pyrope-grossular garnet solid solution can potentially accommodate titanium up to 6.3 wt% as TiO₂ at the pressure of 10 GPa and that further characterization of crystal chemistry of the Ti-garnet is required by a single crystal X-ray diffractometry to determine the valency state of titanium in the garnet solid solution.

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10 GPa における高 TiO_2 ゃくろ石の合成

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$\text{CaMgSi}_2\text{O}_6$ - $\text{CaTiAl}_2\text{O}_6$ 系中の組成 [$\text{CaMgSi}_2\text{O}_6$ 成分(80 wt%)・ $\text{CaTiAl}_2\text{O}_6$ 成分(20 wt%)] の 10 GPa, 1500°C における相平衡関係を実験的に決定した。その結果、輝石、ペロプスカイトと多量の TiO_2 を含むざくろ石が認められた。このざくろ石の存在の確証とセルパラメーターの決定のため、改めてこのざくろ石の組成のガラスから 10 GPa, 1500°C においてざくろ石の合成を試みた。その結果、6.3 wt% の TiO_2 を含むざくろ石が合成され、セルパラメーターは 11.812 Å であった。