

LETTER

A new high-pressure CaGe_2O_5 polymorph with 5- and 6-coordinated germaniumPÉTER NÉMETH,^{1,2,*} KURT LEINENWEBER,² THOMAS L. GROV,² AND PETER R. BUSECK^{1,2}¹School of Earth and Space Exploration, Arizona State University, Tempe, Arizona 85287-1404, U.S.A.²Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287-1604, U.S.A.

ABSTRACT

We discovered a new CaGe_2O_5 polymorph in high-pressure experiments (above 8 GPa). The phase is orthorhombic, space group *Pbam*, with $a = 7.306(2)$, $b = 8.268(2)$, $c = 5.714(1)$ Å, $V = 345.2(1)$ Å³, and $Z = 4$. The new phase, which we call post-titanite CaGe_2O_5 , is the high-pressure polymorph of titanite CaGe_2O_5 . The structure of this new polymorph is based on a network of 5- and 6-coordinated Ge polyhedra and 8-coordinated Ca atoms. Following the germanate analog to silicate, post-titanite CaSi_2O_5 could be expected to form at high-pressure conditions and thus might exist in Earth's mantle.

Keywords: CaGe_2O_5 polymorph, post-titanite, 5- and 6-coordinated Ge, Earth's mantle

INTRODUCTION

The phase transitions of many germanates are similar to those of silicates but occur at lower pressure, and therefore germanates have been used in the geosciences as analogs of silicates (e.g., Ross and Navrotsky 1988). Germanate with CaGe_2O_5 composition has not been studied in high-pressure (HP) experiments. At ambient pressure (Aust et al. 1976; Malcherek and Bosenick 2004), it is isostructural with the mineral titanite (CaTiSiO_5). CaSi_2O_5 , a possible silicate component in Earth's mantle (e.g., Angel et al. 1996), also adopts a titanite-type structure at HP (Angel 1997; Kudoh and Kanzaki 1998).

Here we report the crystal structure of a new HP polymorph of CaGe_2O_5 . This phase has 5- and 6-coordinated Ge. Because it is the HP polymorph of titanite CaGe_2O_5 , we call it post-titanite CaGe_2O_5 . The post-titanite structure is known from analogs, but this is the first time it has been identified as a HP product of a phase with titanite structure. The significance of the post-titanite germanate is that it indicates the possible presence of post-titanite silicate in the mantle.

EXPERIMENTAL METHODS

The starting material for the HP syntheses was a powder sample of composition CaGe_2O_5 formed by reacting CaCO_3 and GeO_2 in a Pt crucible at 1593 K for 5 hours. The presence of CaGe_2O_5 titanite (ICSD no. 14005, Aust et al. 1976) was confirmed using a Siemens D-5000 powder X-ray diffractometer in Bragg-Brentano geometry with Cu radiation.

We placed 35 mg of starting material in a Pt capsule and then welded both ends using Pt foils. The HP syntheses were done at several pressures and temperatures (Table 1) using a Walker-style 6–8 multianvil pressure device (Walker 1991) with WC cubes truncated to 8 mm edge lengths. The sample was contained in an injection-molded MgO + spinel octahedron surrounded by pyrophyllite gaskets. A graphite box furnace (type "G2," Leinenweber and Parise 1995) was used to heat the samples, and either a type-S (Pt-Pt10%Rh) or a type-C (W5%Re-W26%Re) thermocouple was placed axially outside the capsule to measure the temperature.

For obtaining large single crystals, we also added 10% Ca(OH)_2 and excess GeO_2 powder to the starting materials of some HP runs (Table 1). The Ca(OH)_2 allowed a hydrous melt to occur at our run temperatures, which fluxed the growth of the crystals. The X-ray powder diffractograms of the recovered materials

revealed titanite or post-titanite CaGe_2O_5 depending on the conditions of the syntheses (Table 1).

We selected a lamellar single crystal ($0.27 \times 0.12 \times 0.03$ mm) from the R515 run (Table 1) and measured it with a Bruker SMART APEX single-crystal diffractometer using $\text{MoK}\alpha$ radiation, a graphite monochromator, and a 2000K CCD detector. 3114 reflections from $h = -9$ to 9, $k = -10$ to 10, $l = -7$ to 7 were collected, from which 438 were independent reflections, and 428 were considered as observed. Raw intensity data were corrected for absorption (Blessing 1995) using the program SADABS (Sheldrick 1996).

We solved the structure using direct methods. We utilized SHELXTL (Sheldrick 2001) for the structure solution and subsequent refinement using neutral atomic scattering factors. A final $R(F)$ of 0.0159 and a goodness of fit of 1.227 were obtained. Further details of the refinement are listed in Table 2.

RESULTS AND DISCUSSION

Structure of post-titanite CaGe_2O_5

The structural information and bond valence sums from single-crystal X-ray diffraction are given in Table 3. Anisotropic thermal parameters for all atoms and selected interatomic distances with the calculated bond valences are reported in Tables 4 and 5, respectively.

The structure of post-titanite CaGe_2O_5 is based on a network of 5- and 6-coordinated Ge polyhedra (Fig. 1a). Chains of GeO_6 octahedra, which share a common edge along the c axis, connect the corners of the 5-coordinated Ge square pyramids parallel to (001). Pairs of Ge pyramids also share edges, forming bridges between the octahedral chains. Other prominent structural features are channels occupied by 8-coordinated Ca atoms along the c axis (Fig. 1a).

Titanite and post-titanite CaGe_2O_5

Titanite CaGe_2O_5 is triclinic ($a = 6.5286$, $b = 8.7863$, $c = 6.8616$ Å, $\alpha = 88.215^\circ$, $\beta = 113.026^\circ$, $\gamma = 90.988^\circ$, and space

TABLE 1. Summary of the HP experiments

HP Run Number	P (GPa)	T (K)	Duration (hours)	Product	
				titanite	post-titanite
R506	8	1473	24		Yes
R507	8	1273	4		Yes
R510*	8	1773	1.5	Yes	
R513*	7.5	1473	8	Yes	
R515*	8.5	1423 (est.)	2		Yes

Notes: est. = Temperature estimated from power relation.

* Starting material with Ca(OH)_2

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group $\bar{C}1$, Malcherek and Bosenick 2004) at ambient temperature. At 714 K a transformation to a high-temperature modification occurs. Above this temperature titanite CaGe_2O_5 is monoclinic ($a = 6.5699$, $b = 8.8212$, $c = 6.8845$ Å, $\beta = 112.955^\circ$, and space group $C2/c$, Malcherek and Bosenick 2004). In contrast to both of the above, the recovered post-titanite CaGe_2O_5 synthesized in this work is orthorhombic ($a = 7.306$, $b = 8.268$, $c = 5.714$ Å, with space group $Pbam$).

The structures of the triclinic and monoclinic CaGe_2O_5 titanites are similar. A comparison to the monoclinic titanite serves to show the unique features of the post-titanite CaGe_2O_5 . The volume difference at ambient pressure and temperature between the post-titanite and titanite CaGe_2O_5 phases is 4.9%. The smaller volume of post-titanite is achieved by increases in coordination numbers and by a closer packing of the polyhedra. At ambient pressure the titanite CaGe_2O_5 has 4- and 6-coordinated Ge, and 7-coordinated Ca (Fig. 1b). In the HP polymorph, the coordination numbers of Ge are 5 and 6, and that of Ca is 8. The linkage of Ge polyhedra differs between the low-pressure and HP polymorphs. In the monoclinic titanite structure, the Ge tetrahedra share corners with the octahedra, but they are isolated from each other (Fig. 1b). Ge octahedra also form a chain along the c crystallographic axis (Fig. 1b) of titanite CaGe_2O_5 , but the connection is via corner sharing rather than the edge-sharing that occurs in post-titanite CaGe_2O_5 (Fig. 1a).

Isostructural compounds

Post-titanite CaGe_2O_5 is isostructural with materials such as BiMn_2O_5 (Niizeki and Wachi 1968) and rare earth alumin-

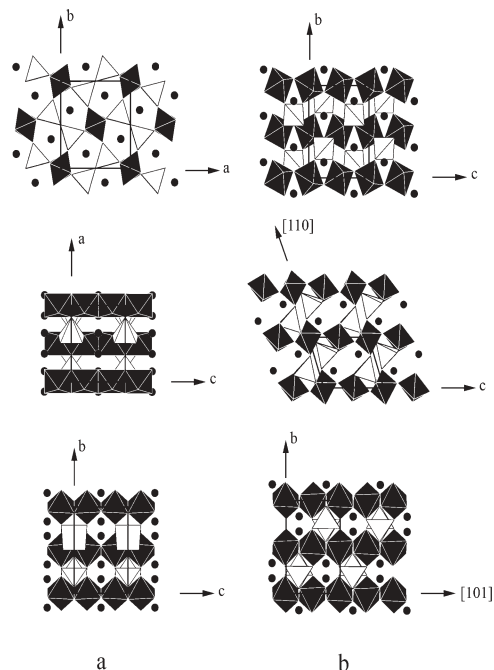


FIGURE 1. Structure models of two polymorphs of CaGe_2O_5 . Black rectangular lines mark unit cells. (a) Post-titanite CaGe_2O_5 ; black and white polyhedra are GeO_6 octahedra and GeO_5 pyramids, respectively. (b) Titanite CaGe_2O_5 ; black and white polyhedra are GeO_6 octahedra and GeO_4 tetrahedra, respectively. Black circles mark Ca sites for both structures.

germanates (Jarchow et al. 1981). Ge is 5-coordinated and Al occupies the octahedral sites in the structures of the rare earth aluminogermanates. Thus, 5-coordinated Ge is not unique, and several phases with 6-coordinated Ge are known (e.g., Sasaki et al. 1983). However, we are not aware of other compounds with 5- and 6-coordinated Ge in the same structure.

Stability of the post-titanite CaGe_2O_5

Our experimental data provide limited information about the stability field of post-titanite CaGe_2O_5 . We recovered the post-

TABLE 2. Summary of X-ray diffraction data for post-titanite CaGe_2O_5

Crystal data			
Color	Colorless	V (Å ³)	345.2(1)
Morphology	Platy	Z	4
Size (mm)	$0.27 \times 0.12 \times 0.03$	Stoichiometric formula	CaGe_2O_5
Cell setting	Orthorhombic	Formula weight M_r	265.26
Space group	$Pbam$	Calculated density	5.104
		(g/cm ³)	
a (Å)	7.306(2)	$F(000)$	496
b (Å)	8.268(2)	Absorption coefficient	18.788
		μ (mm ⁻¹)	
c (Å)	5.714(1)	Temperature (K)	298(2)
Data Collection			
Radiation type	MoK α	Number of independent reflections	438
Data collection wavelength (Å)	0.71073	Number of observed reflections	428
Radiation source	fine-focus sealed tube	Observed criterion	$>2\sigma(I)$
Radiation monochromator type	graphite	Absorption correction type	empirical
Measurement device	Bruker SMART APEX	Absorption correction details	Bruker SADABS
Measurement method	ω scan	Number of frames collected	1818
Cell measurement ω_{\min}	3.57	Frame width (ω)	0.3°
Cell measurement ω_{\max}	27.49	Exposure time/frame	10 s
Number of measured reflections	3114		
Refinement			
Parameters Refined	45	wR_{all}	0.0445
R_{all}	0.0164	wR_{obs}	0.0443
R_{obs}	0.0159	Goodness of fit (S)	1.227

TABLE 3. Atomic coordinates, equivalent isotropic displacement parameters (U_{iso} in Å²), and bond valence sums calculated using the program Eutax (M. O'Keeffe, personal communication) for CaGe_2O_5

Atom	x	y	z	U_{iso}	Bond valence sum
Ge1	0	0	0.25331(5)	0.0045(2)	4.013
Ge2	0.89175(4)	0.64576(4)	0	0.0045(2)	3.922
Ca	0.1355(1)	0.66590(9)	0.5	0.0062(2)	2.380
O1	0.1055(3)	0.2076(2)	0.2389(3)	0.0066(4)	2.003
O2	0	0.5	0.2071(5)	0.0074(5)	2.113
O3	0.1567(3)	0.9446(3)	0.5	0.0060(5)	2.153
O4	0.6564(3)	0.5719(3)	0	0.0064(5)	2.041

Note: The site occupancy factors are all 1.

TABLE 4. Anisotropic displacement parameters (in Å²) for CaGe_2O_5

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ge1	0.0055(2)	0.0045(2)	0.0036(2)	0.000	0.000	-0.0001(1)
Ge2	0.0045(2)	0.0048(2)	0.0041(2)	0.000	0.000	-0.0001(1)
Ca	0.0069(3)	0.0058(3)	0.0059(4)	0.000	0.000	0.0006(2)
O1	0.0105(9)	0.0052(8)	0.0041(8)	0.0013(6)	-0.0001(6)	-0.0009(6)
O2	0.009(1)	0.008(1)	0.005(1)	0.000	0.000	0.0019(8)
O3	0.006(1)	0.008(1)	0.004(1)	0.000	0.000	0.0010(9)
O4	0.006(1)	0.009(1)	0.004(1)	0.000	0.000	-0.0008(9)

titanite phase from HP runs at 8 GPa and at both 1273 and 1473 K (Table 1), but we found the titanite phase in the HP runs at the same pressure and at higher temperature (1773 K). Therefore, the titanite and post-titanite CaGe_2O_5 probably have a phase boundary with a positive dP/dT slope (Fig. 2).

Post-titanite silicate in Earth's mantle?

CaSi_2O_5 is the silicate analog of CaGe_2O_5 . Silicate with CaSi_2O_5 composition has not been found at ambient pressure. It is a HP product (Kanzaki et al. 1991; Angel et al. 1996) that forms when perovskite CaSiO_3 , a mantle component, breaks down below 10–16 GPa and 1000–2800 K (Gasparik et al. 1994). Above 0.205 GPa, CaSi_2O_5 has the monoclinic titanite-type structure with both 4- and 6-coordinated Si (Angel 1997), and it can occur up to 15 GPa (Shim et al. 2000). Upon decompression the titanite-type CaSi_2O_5 phase undergoes a structural distortion, and it becomes triclinic with 4-, 5-, and 6-coordinated Si (Angel et al. 1996). Five-coordinated Si is believed to play a central role in oxygen diffusion in Earth's mantle and is suspected to be a component of aluminosilicate melts and glasses (Stebbins and

McMillan 1989; Xue et al. 1991, Stebbins and Poe 1999).

Details of the phase relations between CaSiO_3 perovskite and CaSi_2O_5 titanite are unresolved (e.g., Shim et al. 2000). Therefore, a Ca-silicate with the post-titanite CaGe_2O_5 structure might occur at HP and thus exist in Earth's mantle. If this phase occurs, it would be a new silicate with 5-coordinated Si. A further significance arises from the Ca substitutions. Rare earth elements can occupy Ca sites, and thus the post-titanite phase might be a carrier of rare earth elements in the mantle.

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REFERENCES CITED

- Angel, R.J. (1997) Transformation of fivefold-coordinated silicon to octahedral silicon in calcium silicate, CaSi_2O_5 . *American Mineralogist*, 82, 836–839.
- Angel, R.J., Ross, N.L., Seifert, F., and Fliervoet, T.F. (1996) Structural characterization of pentacoordinate silicon in a calcium silicate. *Nature*, 384, 441–444.
- Aust, H., Völlenne, H., and Wittmann, A. (1976) Die Kristallstruktur der Hoch- und der Tieftemperaturform von CaGe_2O_5 . *Zeitschrift für Kristallographie*, 144, 82–90.
- Blessing, R.H. (1995) An empirical correction for absorption anisotropy. *Acta Crystallographica*, A51, 33–38.
- Gasparik, T., Wolf, K., and Smith, C.M. (1994) Experimental determination of phase relations in the CaSiO_3 system from 8 to 15 GPa. *American Mineralogist*, 79, 1219–1222.
- Jarchow, O., Klaska, K.H., and Werk, M. (1981) Erste Selten Erden-Aluminium-Germanate vom Typ REAlGeO_5 . *Naturwissenschaften*, 68, 92.
- Kanzaki, M., Stebbins, J.F., and Xue, X. (1991) Characterization of quenched high pressure phases in CaSiO_3 system by XRD and ^{29}Si NMR. *Geophysical Research Letters*, 18, 463–466.
- Kudoh, Y. and Kanzaki, M. (1998) Crystal chemical characteristics of α - CaSi_2O_5 , a new high pressure calcium silicate with five-coordinated silicon synthesized at 1500 °C and 10 GPa. *Physics and Chemistry of Minerals*, 25, 429–433.
- Leinenweber, K. and Parise, J. (1995) High-pressure synthesis and crystal structure of $\text{CaFeTi}_2\text{O}_6$, a new perovskite structure type. *Journal of Solid State Chemistry*, 114, 277–281.
- Malcherek, T. and Bosenick, A. (2004) Structure and phase transition of CaGe_2O_5 revisited. *Physics and Chemistry of Minerals*, 31, 224–231.
- Niizeki, N. and Wachi, M. (1968) The crystal structures of $\text{Bi}_2\text{Mn}_4\text{O}_{10}$, $\text{Bi}_2\text{Al}_4\text{O}_9$ and $\text{Bi}_2\text{Fe}_4\text{O}_9$. *Zeitschrift für Kristallographie*, 127, 173–187.
- Ross, N.L. and Navrotsky, A. (1988) Study of the MgGeO_3 polymorphs (orthopyroxene, clinopyroxene, and ilmenite structures) by calorimetry, spectroscopy, and phase equilibria. *American Mineralogist*, 73, 1355–1365.
- Sasaki, S., Prewitt, C.T., and Liebermann, R.C. (1983) The crystal structure of CaGeO_3 perovskite and the crystal chemistry of GdFeO_3 -type perovskites. *American Mineralogist*, 68, 1189–1198.
- Sheldrick, G. M. (1996) SADABS. University of Göttingen, Germany.
- (2001) SHELXTL PC, Version 6.12, An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data. Bruker Analytical X-Ray Instruments, Inc., Madison, Wisconsin.
- Shim, S.H., Duffy, T.S., and Shen, G. (2000) The stability and P - V - T equation of state of CaSiO_3 perovskite in the Earth's lower mantle. *Journal of Geophysical Research*, 105, 25955–25968.
- Stebbins, J.F. and McMillan, P. (1989) Five- and six-coordinated Si in $\text{K}_2\text{Si}_4\text{O}_9$ glass quenched from 1.9 GPa and 1200 °C. *American Mineralogist*, 74, 965–968.
- Stebbins, J.F. and Poe, B. (1999) Pentacoordinate silicon in high-pressure crystalline and glassy phases of calcium disilicate (CaSi_2O_5). *Geophysical Research Letters*, 26, 2521–2523.
- Walker, D. (1991) Lubrication, gasketing, and precision in multianvil experiments. *American Mineralogist*, 76, 1092–1100.
- Xue, X., Stebbins, J.F., Kanzaki, M., McMillan, P.F., and Poe, B. (1991) Pressure-induced silicon coordination and tetrahedral structural changes in alkali oxide-silica melts up to 12 GPa: NMR, Raman, and infrared spectroscopy. *American Mineralogist*, 76, 8–26.

TABLE 5. Selected interatomic distances (in Å) and bond valences for CaGe_2O_5 calculated using the program Eutax (M. O'Keeffe, personal communication)

Atom 1	Atom 2	Distance	Bond valence
Ge1	-O1	1.884(2)	0.694
	-O1	1.884(2)	0.694
	-O3	1.873(3)	0.714
	-O3	1.873(2)	0.714
	-O4	1.938(2)	0.599
Ge2	-O4	1.938(2)	0.599
	-O1	1.826(2)	0.811
	-O1	1.826(2)	0.811
	-O2	1.868(2)	0.729
	-O2	1.865(2)	0.729
Ca	-O4	1.825(2)	0.812
	-O1	2.434(2)	0.283
	-O1	2.434(2)	0.283
	-O1	2.534(2)	0.216
	-O1	2.534(2)	0.216
	-O2	2.380(2)	0.328
	-O2	2.380(2)	0.328
	-O3	2.377(2)	0.330
	-O3	2.310(2)	0.396

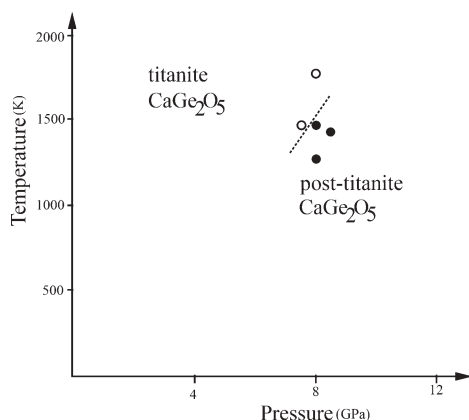


FIGURE 2. Phase relationships of CaGe_2O_5 from the experimental data of Table 1. Filled and open circles represent samples of post-titanite CaGe_2O_5 and titanite CaGe_2O_5 , respectively. The proposed phase boundary between them is plotted as a dashed line.