

## LETTER

A new high-pressure  $\text{CaGe}_2\text{O}_5$  polymorph with 5- and 6-coordinated germaniumPÉTER NÉMETH,<sup>1,2,\*</sup> KURT LEINENWEBER,<sup>2</sup> THOMAS L. GROV,<sup>2</sup> AND PETER R. BUSECK<sup>1,2</sup><sup>1</sup>School of Earth and Space Exploration, Arizona State University, Tempe, Arizona 85287-1404, U.S.A.<sup>2</sup>Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287-1604, U.S.A.

## ABSTRACT

We discovered a new  $\text{CaGe}_2\text{O}_5$  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,  $V = 345.2(1)$  Å<sup>3</sup>, and  $Z = 4$ . The new phase, which we call post-titanite  $\text{CaGe}_2\text{O}_5$ , is the high-pressure polymorph of titanite  $\text{CaGe}_2\text{O}_5$ . 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  $\text{CaSi}_2\text{O}_5$  could be expected to form at high-pressure conditions and thus might exist in Earth's mantle.

**Keywords:**  $\text{CaGe}_2\text{O}_5$  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  $\text{CaGe}_2\text{O}_5$  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 ( $\text{CaTiSiO}_5$ ).  $\text{CaSi}_2\text{O}_5$ , 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  $\text{CaGe}_2\text{O}_5$ . This phase has 5- and 6-coordinated Ge. Because it is the HP polymorph of titanite  $\text{CaGe}_2\text{O}_5$ , we call it post-titanite  $\text{CaGe}_2\text{O}_5$ . 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  $\text{CaGe}_2\text{O}_5$  formed by reacting  $\text{CaCO}_3$  and  $\text{GeO}_2$  in a Pt crucible at 1593 K for 5 hours. The presence of  $\text{CaGe}_2\text{O}_5$  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  $\text{MgO}$  + 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%  $\text{Ca(OH)}_2$  and excess  $\text{GeO}_2$  powder to the starting materials of some HP runs (Table 1). The  $\text{Ca(OH)}_2$  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  $\text{CaGe}_2\text{O}_5$  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  $\text{CaGe}_2\text{O}_5$ 

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  $\text{CaGe}_2\text{O}_5$  is based on a network of 5- and 6-coordinated Ge polyhedra (Fig. 1a). Chains of  $\text{GeO}_6$  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  $\text{CaGe}_2\text{O}_5$ 

Titanite  $\text{CaGe}_2\text{O}_5$  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  $\text{Ca(OH)}_2$

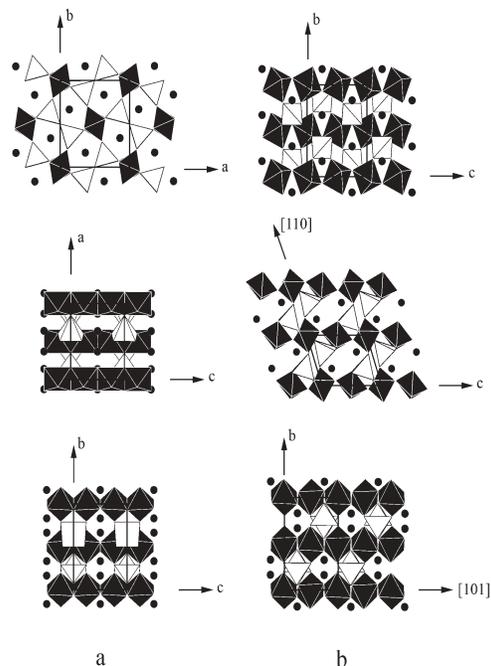
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group  $\bar{C}1$ , Malcherek and Bosenick 2004) at ambient temperature. At 714 K a transformation to a high-temperature modification occurs. Above this temperature titanite  $\text{CaGe}_2\text{O}_5$  is monoclinic ( $a = 6.5699$ ,  $b = 8.8212$ ,  $c = 6.8845$  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  $\text{CaGe}_2\text{O}_5$  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  $\text{CaGe}_2\text{O}_5$  titanites are similar. A comparison to the monoclinic titanite serves to show the unique features of the post-titanite  $\text{CaGe}_2\text{O}_5$ . The volume difference at ambient pressure and temperature between the post-titanite and titanite  $\text{CaGe}_2\text{O}_5$  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  $\text{CaGe}_2\text{O}_5$  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  $\text{CaGe}_2\text{O}_5$ , but the connection is via corner sharing rather than the edge-sharing that occurs in post-titanite  $\text{CaGe}_2\text{O}_5$  (Fig. 1a).

### Isostructural compounds

Post-titanite  $\text{CaGe}_2\text{O}_5$  is isostructural with materials such as  $\text{BiMn}_2\text{O}_5$  (Niizeki and Wachi 1968) and rare earth alumin-



**FIGURE 1.** Structure models of two polymorphs of  $\text{CaGe}_2\text{O}_5$ . Black rectangular lines mark unit cells. (a) Post-titanite  $\text{CaGe}_2\text{O}_5$ ; black and white polyhedra are  $\text{GeO}_6$  octahedra and  $\text{GeO}_5$  pyramids, respectively. (b) Titanite  $\text{CaGe}_2\text{O}_5$ ; black and white polyhedra are  $\text{GeO}_6$  octahedra and  $\text{GeO}_4$  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 $\text{CaGe}_2\text{O}_5$

Our experimental data provide limited information about the stability field of post-titanite  $\text{CaGe}_2\text{O}_5$ . We recovered the post-

**TABLE 2.** Summary of X-ray diffraction data for post-titanite  $\text{CaGe}_2\text{O}_5$

<b>Crystal data</b>			
Color	Colorless	$V$ (Å <sup>3</sup> )	345.2(1)
Morphology	Platy	$Z$	4
Size (mm)	$0.27 \times 0.12 \times 0.03$	Stoichiometric formula	$\text{CaGe}_2\text{O}_5$
Cell setting	Orthorhombic	Formula weight $M_r$	265.26
Space group	$Pbam$	Calculated density	5.104 (g/cm <sup>3</sup> )
$a$ (Å)	7.306(2)	$F(000)$	496
$b$ (Å)	8.268(2)	Absorption coefficient $\mu$ (mm <sup>-1</sup> )	18.788
$c$ (Å)	5.714(1)	Temperature (K)	298(2)
<b>Data Collection</b>			
Radiation type	MoK $\alpha$	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	$\omega$ scan	Number of frames collected	1818
Cell measurement $\omega_{\min}$	3.57	Frame width ( $\omega$ )	0.3°
Cell measurement $\omega_{\max}$	27.49	Exposure time/frame	10 s
Number of measured reflections	3114		
<b>Refinement</b>			
Parameters Refined	45	$wR_{\text{all}}$	0.0445
$R_{\text{all}}$	0.0164	$wR_{\text{obs}}$	0.0443
$R_{\text{obs}}$	0.0159	Goodness of fit (S)	1.227

**TABLE 3.** Atomic coordinates, equivalent isotropic displacement parameters ( $U_{\text{iso}}$  in Å<sup>2</sup>), and bond valence sums calculated using the program Eutax (M. O'Keeffe, personal communication) for  $\text{CaGe}_2\text{O}_5$

Atom	$x$	$y$	$z$	$U_{\text{iso}}$	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 Å<sup>2</sup>) for  $\text{CaGe}_2\text{O}_5$

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  $\text{CaGe}_2\text{O}_5$  probably have a phase boundary with a positive  $dP/dT$  slope (Fig. 2).

### Post-titanite silicate in Earth's mantle?

$\text{CaSi}_2\text{O}_5$  is the silicate analog of  $\text{CaGe}_2\text{O}_5$ . Silicate with  $\text{CaSi}_2\text{O}_5$  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  $\text{CaSiO}_3$ , a mantle component, breaks down below 10–16 GPa and 1000–2800 K (Gasparik et al. 1994). Above 0.205 GPa,  $\text{CaSi}_2\text{O}_5$  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  $\text{CaSi}_2\text{O}_5$  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  $\text{CaSiO}_3$  perovskite and  $\text{CaSi}_2\text{O}_5$  titanite are unresolved (e.g., Shim et al. 2000). Therefore, a Ca-silicate with the post-titanite  $\text{CaGe}_2\text{O}_5$  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.

### ACKNOWLEDGMENTS

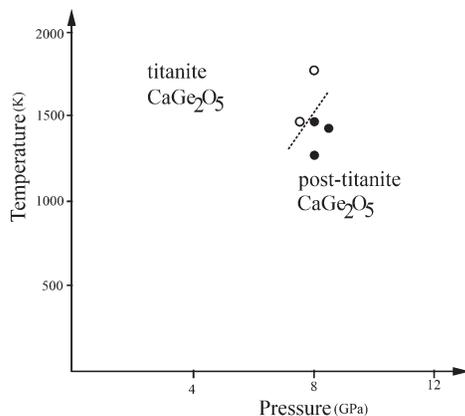
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**TABLE 5.** Selected interatomic distances (in Å) and bond valences for  $\text{CaGe}_2\text{O}_5$  calculated using the program Eutax (M. O'Keeffe, personal communication)

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  $\text{CaGe}_2\text{O}_5$  from the experimental data of Table 1. Filled and open circles represent samples of post-titanite  $\text{CaGe}_2\text{O}_5$  and titanite  $\text{CaGe}_2\text{O}_5$ , respectively. The proposed phase boundary between them is plotted as a dashed line.