Bridgmanite-like crystal structure in the novel Ti-rich phase synthesized at transition zone condition

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ABSTRACT

A new Ti-bearing bridgmanite-like phase with a three-fold commensurate superstructure of the ideal MgSiO3-perovskite structure was observed in a [Mg5/6Al1/6][Si1/2Ti1/3Al1/6]O3 crystal synthesized in the model system Mg3Al2Si3O12–MgTiO3 at 20 GPa and 1600 °C. The compound was found to be orthorhombic, space group Pnma, with lattice parameters $a = 14.767(3)$, $b = 6.958(1)$, $c = 4.812(1)$ Å, $V = 494.4(2)$ Å$^3$, which represents a 3$a$ × $b$ × $c$ superstructure of the typical Pnma perovskite structure. The structure was refined to $R = 0.024$ using 846 independent reflections. The superstructure mainly arises from the ordering of titanium in one of the octahedral positions. Crystal-chemical details of the different polyhedra in the superstructure are discussed in comparison to pure MgSiO3. This is the first documented superstructure of a bridgmanite phase, and Ti-rich bridgmanite in the lower mantle arising from local Ti-enrichments may exhibit different physical properties and elemental partitioning behavior from Ti-poor, peridotitic bridgmanite. The study also shows that large amounts of Ti can stabilize bridgmanite-like compounds at considerably lower pressure than lower mantle conditions.

KEYWORDS: bridgmanite, titanium, lower mantle, crystal structure, microprobe analysis, synthesis

INTRODUCTION

Normal mantle peridotite contains ~0.2 wt% TiO2 (e.g. McDonough and Sun 1995). However, Ti-rich lithologies may occur in the mantle as a result of oceanic crust subduction.
Mid-ocean ridge basalt has about 1.5 wt% TiO₂, whereas ocean island basalt may contain about twice that amount (e.g. Wilson 1989). Experiments show that the solubility of titanium in subduction zone fluids is very low (e.g. Audetat and Keppler 2005; Tropper and Manning 2005), so that during slab dehydration TiO₂ should be retained in subducting crust and transported eventually into the lower mantle.

According to experimental data (e.g. Walter et al. 2004; Liebske et al. 2005), bridgmanite in primitive mantle peridotite will contain about 0.2–0.3 wt% TiO₂. This estimate is consistent with inclusions in diamonds that have been interpreted to represent samples of peridotitic bridgmanite (e.g. Harte 2010). However, some composite inclusions in diamonds have been interpreted as the products of retrograde unmixing of former bridgmanite formed in subducted oceanic crust, and these have much higher TiO₂ contents ranging between about 4 and 7 wt% TiO₂ (Walter et al. 2011; Thomson et al. 2014; Zedgenizov et al. 2015).

Low-degree melts formed either in subducted crust or in the mantle as a consequence of volatile enrichment (e.g. CO₂ or water) are also expected to contain several weight percent levels of TiO₂ (e.g. Thomson et al. 2016), and reaction of these melts with surrounding mantle may produce local enrichments in TiO₂. For example, inclusions in diamonds interpreted to represent former Ca-rich perovskite can contain more than 50 mol% of CaTiO₃ component (Brenker et al. 2005; Walter et al. 2008) and these have been interpreted to represent reaction between low-degree melts and mantle peridotite in the transition zone (Walter et al. 2008; Armstrong et al. 2012; Thomson et al. 2016). A similar process in the lower mantle would also be expected to leave TiO₂ enriched domains, with implications for the crystal chemistry, thermo-elastic properties and structure of bridgmanite.

In order to understand the potential role of Ti-rich bridgmanite in the deep mantle, we must first quantify the affect of Ti incorporation on the bridgmanite structure. To this end, we performed experiments on a Ti-rich MgSiO₃-bridgmanite composition in the model system pyrope (Prp–Mg₃Al₂Si₃O₁₂) – geikielite (Gkl–MgTiO₃) at 20 GPa and 1600 °C. Here we present the results of a structural study based on X-ray diffraction data from a bridgmanite-like single crystal with the highest Ti content ever reported. We find that the ordering of titanium in the structure is responsible for the occurrence of a three-fold superstructure.

**Experimental**

**Synthesis**

The starting material was made by mixing pure oxides of MgO, SiO₂, Al₂O₃ and TiO₂ in stoichiometric proportions to make the composition pyrope (Prp–Mg₃Al₂Si₃O₁₂) – geikielite (Gkl–MgTiO₃) Prp₃₀Gkl₇₀ (mol.%). The experiment that produced run product 1608-70 was...
carried out at $P = 20$ GPa and $T = 1600 \, ^\circ C$ using a 1000-t Kawai-type multi-anvil apparatus installed at the Ehime University (Matsuyama, Japan). Samples were compressed by eight cubic tungsten carbide anvils with 4-mm truncation edge lengths, and using pyrophyllite as a gasketing material. High temperature was achieved using a cylindrical LaCrO$_3$ heater, and temperature was measured with a W$_{97}$Re$_3$–W$_{75}$Re$_{25}$ thermocouple. The sample was loaded into a platinum capsule and was isolated from the heater by an MgO insulator (Sirotkina et al. 2015). The approximate sample volume after the experiment was 1.0 mm$^3$. Sample pressure was calibrated at room temperature using the semiconductor–metal transitions of Bi, ZnS and GaAs (Irifune et al. 2004). The effect of temperature on pressure was further corrected using the α–β and β–γ phase transitions of olivine (Katsura and Ito 1989; Yamada et al. 2004). Ti-bearing bridgmanite-like phase was the modally dominant phase in the run product, and was accompanied by a minor amount of periclase and rutile (Fig. 1), in keeping with the reaction:

\[ 7\text{MgTiO}_3 (\text{giekelite}) + 3\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12} (\text{pyrope}) \rightarrow 3\text{Mg}_5\text{Al}_2\text{Ti}_2\text{Si}_3\text{O}_{18} (\text{Ti-Brd}) + \text{TiO}_2 (\text{rutile}) + \text{MgO} (\text{periclase}). \]

**Data collection and crystal-structure solution and refinement**

A small crystal ($38 \times 52 \times 55 \, \mu m$), hand-picked under a reflected light microscope from the run product 1608-70 (Fig. 1), was preliminarily examined with a Bruker-Enraf MACH3 single-crystal diffractometer using graphite-monochromatized MoKα radiation. The measured orthorhombic cell parameters are: $a_s = 14.767(3)$, $b_s = 6.958(1)$, $c_s = 4.812(1)$ Å, which represents a $3a_b \times b_b \times c_b$ superstructure of the typical $Pnma$ perovskite structure with $a_b = 4.9$, $b_b = 6.9$, $c_b = 4.8$ Å (the subscripts “s” and “b” mean superstructure and basic structure, respectively). Next, data were collected with an Oxford Diffraction Xcalibur 3 diffractometer (X-ray MoKα radiation, $\lambda = 0.71073$ Å) fitted with a Sapphire 2 CCD detector (with 130 s exposure time per frame). Intensity integration and standard Lorentz-polarization corrections were done with the CrysAlis RED (Oxford Diffraction 2006) software package. The program ABSPACK of the CrysAlis RED package (Oxford Diffraction 2006) was used for the absorption correction. The $R_{int}$ (Laue group $mmm$) decreased from 0.076 to 0.032 after the absorption correction. A careful inspection of the frames (and of the reconstructed precession photographs) collected in the present study did not reveal any reflection streaks and/or structural disorder. The reflections were quite sharp and not ‘structured’.

Taking into account (i) the results obtained by the analysis of reflection conditions ($0kl$: $k+l = 2n$, $hk0$: $h = 2n$; $h00$: $h = 2n$, $0k0$: $k = 2n$; $00l$: $l = 2n$), (ii) the distribution of $|E|$ values that strongly indicated the presence of an inversion centre ($|E^2 - 1| = 0.990$), and (iii) the fact that the maximal klassengleiche subgroup of the space group $Pnma$ (with an enlarged three-fold unit cell) is still $Pnma$, attempts to solve the crystal structure were made in this space
group. The Mg atom site of the \textit{Pnma} bridgmanite structure (Wyckoff position 4c) splits into three new 4c positions (MgA, MgB, and MgC), whereas the Si atom site (Wyckoff position 4b) splits into two 4b and 8d positions. The full-matrix least-squares program SHELXL-97 (Sheldrick 2008), working on $F^2$, was used for the refinement of the structure. Site-scattering values were refined at the Mg and octahedral sites using scattering curves for neutral species (Ibers and Hamilton 1974) as follows: Mg vs. [ ] and Ti vs. [ ]. The O sites (refined as O vs. [ ]) were found fully occupied, and the occupancy factors were then fixed to 1.00. Two Mg sites (i.e., MgA and MgB) showed a site scattering of 12 electrons and were thought to be fully occupied by Mg and fixed accordingly (in agreement with the observed bond distances – see below), whereas the MgC site showed a mean electron number of 12.4, thus indicating the presence of a small amount of a heavier element than Mg. From the analysis of the site geometry, we attributed a Mg$_{0.50}$Al$_{0.50}$ population (electron number of 12.5) to this site. One of the octahedral sites (4b site) was found fully occupied by Ti, whereas the second octahedral site showed a mean electron number of 13.9, thus indicating the presence of a small amount of a lighter element than Si. Taking into account the chemical composition of the crystal, the crystal-chemical details and the already site-assigned elements, we attribute a Si$_{0.75}$Al$_{0.25}$ population (electron number of 13.8) to this site. The refinement of the site occupancy with the restrictions described above, produced an overall stoichiometry of Mg$_8$(Mg$_{2.5}$Al$_{0.5}$)[Ti$_4$(Si$_{6.5}$Al$_{0.5}$)]O$_{36}$, which, with $Z = 4$ and grouping together the same atomic species, can be written as (Mg$_{2.5}$Al$_{0.5}$)[Ti(Si$_{1.5}$Al$_{0.5}$)]O$_9$. If we write the formula on the basis of three oxygen atoms, it is [Mg$_{0.83}$Al$_{0.17}$][Si$_{0.50}$Ti$_{0.33}$Al$_{0.17}$]O$_3$, or [Mg$_{5/6}$Al$_{1/6}$][Si$_{1/2}$Ti$_{1/3}$Al$_{1/6}$]O$_3$.

Successive cycles were run introducing anisotropic temperature factors for all the atoms leading to $R1 = 0.024$ for 846 observed reflections [$F_o > 4\sigma(F_o)$] and $R1 = 0.029$ for all 2312 independent reflections and 80 parameters. Bond distances are reported in Table 1, whereas fractional atomic coordinates, atomic displacement parameters and the list of the observed and calculated structure factors are in the CIF$^1$.

**Chemical composition**

A preliminary chemical analysis using energy dispersive spectrometry, performed on the same crystal fragment used for the structural study as well as on other fragments from the same run product, did not indicate the presence of elements ($Z > 9$) other than Ti, Al, Mg and Si. The chemical composition was then determined using wavelength dispersive analysis (WDS) by means of a Jeol JXA-8600 electron microprobe. We used 40 s as counting time. The matrix correction was performed with the Bence and Albee (1968) program as modified

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$^1$ For a copy of CIF, document item ……., contact the Business Office of the Mineralogical Society of America.
by Albee and Ray (1970). The standards employed were forsterite (Mg, Si), synthetic Al₂SiO₅ (Al), and synthetic TiO₂ (Ti). The crystal used for the X-ray study was found to be homogeneous within the analytical uncertainty. The average chemical composition (six analyses on different spots) is (wt %): MgO 31.03(12); SiO₂ 28.14(18); TiO₂ 25.20(10); Al₂O₃ 15.80(11); total 100.17(18); corresponding, on the basis of 3 oxygen atoms, to [Mg₀.₈₂₄(₈)Si₀.₅₀₁(₉)Ti₀.₃₃₈(₇)Al₀.₃₃₂(₈)]O₃.

RESULTS AND DISCUSSION

On the whole, the crystal structure of the Ti-rich bridgmanite-like phase (Fig. 2) is topologically similar to that of MgSiO₃ bridgmanite. The three-fold commensurate superstructure is mainly due to the ordering of titanium in one of the octahedral sites. The mean bond distances observed for the two pure Mg-polyhedra (2.219 and 2.222 Å, for MgA and MgB, respectively) are very close to that observed in pure MgSiO₃ (2.205 Å; Dobson and Jacobsen 2004). On the contrary, the shorter mean bond distance observed for MgC (2.152 Å) is in agreement with the presence of Al replacing Mg. The octahedral site fully occupied by Ti shows a mean bond distance of 1.924 Å, which is slightly shorter than the <Ti-O> distance observed in rutile (1.958 Å; Swope et al. 1995) and in CaTiO₃ perovskite (1.953 Å; Yamanaka et al. 2002). The (Si₀.₇₅Al₀.₂₅) octahedron exhibits a mean bond distance of 1.766 Å, which is slightly larger than that observed in stishovite (1.757 Å; Hill et al. 1983) in agreement with the presence of Al replacing Si. The proposed cation distribution is in agreement with the bond valence analysis carried out using the parameters reported by Brese and O’Keeffe (1991), i.e. MgA = 2.19, MgB = 2.06, MgC = 2.47, Ti = 4.29, Si = 4.05, O₁ = 2.09, O₂ = 2.28, O₃ = 1.95, O₄ = 2.14, O₅ = 2.19, and O₆ = 2.15 v.u.

The unit-cell of the Ti-rich bridgmanite-like phase is: a = 14.767(3), b = 6.958(1), c = 4.812(1) Å. If we consider a/3 (in order to easily compare the average unit cell of the superstructure and the normal bridgmanite structure), we get the value of 4.922 Å. Then, by converting the Pnma setting in the conventionally reported Pbnm space group of bridgmanite, we get (for Ti-Brd): a = 4.812, b = 4.922, c = 6.958 Å, V = 164.8 Å³. Several interesting crystal-chemical parameters can be calculated, as the tilt among octahedra. The simplest method of estimating tilt angles between octahedra in Pbnm perovskites is from the unit-cell parameters. Provided the octahedra remain regular, the tilt angle can be related to a single rotation about the [111] pseudocubic axis, designated as Φ, and given by the relation: Φ = cos⁻¹(\sqrt{2a²/bc}) (e.g. O’Keeffe et al. 1979). In the case of Ti-Brd, neglecting the fact that we are now considering an average Pbnm structure and not ideal polyhedra, the value is 17.02°. If we plot our datum in the diagram proposed by Sinmyo et al. (2014) and consider a x-value...
(\(\text{Fe+Al}\) = 0.34 a.p.f.u., the Ti-bridgmanite-like phase (filled red circle in Fig. 3) falls close to the trend of (Mg,Fe)\(\text{SiO}_3\) perovskites. However, in this diagram Ti is not considered. If we consider the influence of Ti similar to that of trivalent cations in perovskites, the x-value in Figure 3 is 0.67 a.p.f.u and the behavior would be intermediate (empty red circle in Fig. 3) between those observed for the series (Mg,Fe)\(\text{SiO}_3\) and those in (Mg,Fe)(Si,Al)\(\text{O}_3\) perovskites. Even more interesting, if we consider the overall mean of the volumes of the Mg\(\text{O}_{12}\) polyhedra \(\{\text{MgA 37.40 Å}^3; \text{MgB 35.63 Å}^3; \text{MgC (which hosts Al) 33.31 Å}^3\}\), 35.45 Å\(^3\), and the overall mean of the two octahedral-site volumes [one hosting Ti (9.36 Å\(^3\)) and one hosting Si\(_{0.75}\)Al\(_{0.25}\) (7.20 Å\(^3\)])], taking into account the different multiplicity of the two sites, we get 7.92 Å\(^3\). The ratio of the two volumes, \(V_X/V_Y\), is 4.476. Then, if we calculate the overall polyhedral tilting \(\Phi\) defined as \(1 - \cos^2\theta m\cos\theta z\) (Thomas 1996), we get 0.0873, perfectly in line with the predicted trend. We note that \(V_X/V_Y\) = 4.477 and \(\Phi\) = 0.0872 are nearly identical to those for pure Mg\(\text{SiO}_3\) (Dobson and Jacobsen 2004). However, this is not surprising, considering that in Ti-Brd there is a smaller \(\langle V_X\rangle\) compared to Mg\(\text{SiO}_3\) because of the presence of Al replacing Mg at the MgC site. However, the MgA and the MgB sites are more expanded with respect to the Mg site in Mg\(\text{SiO}_3\), thus resulting in a higher average value (i.e., \(\langle V_X\rangle\) = 35.45 Å\(^3\) compared to 34.38 Å\(^3\) in Mg\(\text{SiO}_3\)). Furthermore, in Ti-Brd we have one octahedral site fully occupied by Ti\(^{4+}\), which is larger than Al\(^{3+}\). This gives rise to an overall \(\langle V_Y\rangle\) of 7.92 Å\(^3\), which is slightly higher than that observed for the octahedral Si in Mg\(\text{SiO}_3\) (7.68 Å\(^3\)). As a consequence, the ratio between the X and Y volumes in Ti-Brd and pure Mg\(\text{SiO}_3\) is almost identical. It is very likely that the cation ordering responsible for the occurrence of the superstructure is thermodynamically favored (with respect to a disordered structure) to reduce lattice strains.

The (Al,Ti)–for–(Mg,Si) substitution also induces a strong distortion of the octahedral site quantifiable with an increase of the octahedral angle variance \(\sigma^2\) (Robinson et al. 1971) from 1.56 in pure Mg\(\text{SiO}_3\) (Dobson and Jacobsen 2004) to an average weighted value of 37.02 in Ti-Brd (\(\sigma^2_{\text{Ti site}}\) = 29.13 and \(\sigma^2_{\text{(Si,Al) site}}\) = 40.97). A slight increase of distortion with respect to pure Mg\(\text{SiO}_3\) was also noticed in Al-bearing (Kojitani et al. 2007) and Cr-bearing (Bindi et al. 2014) bridgmanite.

**IMPLICATIONS**

The new Ti-bridgmanite-like phase was synthesized at a transition zone pressure (20 GPa), even though it has a very similar crystal structure to the most abundant mineral in the lower mantle, Mg\(\text{SiO}_3\) bridgmanite, which becomes stable at about 24 GPa (Tschauner et al. 2014). This suggests that unlike Al (Kubo and Akaogi 2000), Ti-incorporation stabilizes the
bridgmanite-type structure to lower pressure, as is also the case for Ti-rich calcium perovskite (Kubo et al. 1997). Armstrong et al. (2012) investigated phase relations along the MgSiO$_3$-MgTiO$_3$ join and their data at ~25 GPa indicate a relatively modest solubility of MgTiO$_3$-component into bridgmanite (~10 mol%). Their results also indicate immiscibility with an MgTiO$_3$-rich phase. These authors observed an increase in MgTiO$_3$ solubility with pressure in bridgmanite, and their phase relations suggest closing of a miscibility gap between MgSiO$_3$-rich and MgTiO$_3$-rich phases by ~ 50 GPa. The new bridgmanite-like phase found here may represent the Ti-rich conjugate phase in this system.

It is not yet clear at what Ti-content this new Ti-bridgmanite-like phase stabilizes, or its minimum pressure stability, so it is difficult to assess its potential role in the mantle. The bulk Ti content is too low in mantle peridotite (~0.2%), and likely too low in subducted oceanic crust (~1–3%), to directly stabilize this new phase. However, inclusions in some superdeep natural diamonds provide evidence for Ti-rich domains at transition zone depths that are likely related to metasomatism by low-degree melts (e.g. Thomson et al. 2016). The new Ti-bridgmanite-like phase is potentially stable in such Ti-rich environments, where it could have important geochemical effects or act as a tracer for metasomatic processes. However, this phase has yet to be reported in natural diamonds. Further work is needed to determine the pressure-temperature-composition stability of this phase, and to determine its thermo-physical and chemical properties.

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FIGURE CAPTIONS

FIGURE 1. SEM-BSE image of idiomorphic Ti-bearing bridgmanite-like (Ti-Brd) crystals associated with rutile (Rt) and periclase (Per) in the run 1608-70 [P = 20 GPa, T = 1600 °C]. CamScan electronic microscope MV2300.

FIGURE 2. The structure of the Ti-bridgmanite-like phase down [010]. Mg sites are given as spheres (red: MgA and MgB; yellow: MgC). Octahedra refers to the Ti site (dark blue) and to the (Si,Al) site (light blue). The unit-cell and the orientation of the structure are outlined.

FIGURE 3. Variation in tilting angle $\Phi$ of different bridgmanites with cation composition (Fe+Al) in cations per formula unit. Solid squares MgSiO$_3$ and (Mg,Fe)SiO$_3$, black open circles (Mg,Fe)(Si,Al)O$_3$, black open triangles (Mg,Al)(Si,Al)O$_3$, black down triangles (Mg, Fe)SiO$_3$ with 100 % $\text{Fe}^{3+}/\Sigma\text{Fe}$. Filled and empty red circles refer to the Ti-bridgmanite-like phase. $\Phi$ was calculated from the unit-cell parameters of literature data as follows: Ito and Yamada (1982), Kudoh et al. (1990), Parise et al. (1990), Mao et al. (1991), McCammon et al. (1992), Wang et al. (1994), Fei et al. (1996), Fiquet et al. (1998), Jephcoat et al. (1999), Bolfan-Casanova (2000), Andrault et al. (2001), Dobson and Jacobsen (2004), Walter et al. (2004), Nishio-Hamane et al. (2005, 2008), Vanpeteghem et al. (2006), Saikia et al. (2009), Tange et al. (2009), Catalli et al. (2011), Boffa Ballaran et al. (2012), Hummer and Fei (2012) and Sinmyo et al. (2014).
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| Average Ti     | 29.13         | 1.0112        |
| Standard Deviation Ti | 9.36          |               |
| Average Si     | 40.97         | 1.0136        |
| Standard Deviation Si | 7.20         |               |
| Volume Ti      | 9.36          |               |
| Volume Si      | 7.20          |               |