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 threefold commensurate superstructure of the ideal MgSiO3-perovskite structure was observed in a [Mg3/6Al1/6][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) Å3, which represents a 3a × 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., Audétat 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.

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-geikielite (Prp–Gkl; Mg3Al2Si3O12–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 threefold superstructure.

EXPERIMENTAL METHODS

Synthesis

The starting material was made by mixing pure oxides of MgO, SiO2, Al2O3, and TiO2 in stoichiometric proportions to make the composition pyrope–geikielite (Prp–Gkl; Mg3Al2Si3O12–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 threefold superstructure.