Equation of state and crystal structure of a new germanate post-titanite phase

FABRIZIO NESTOLA,1,2,* PÉTER NÉMETH,3,4 ROSS J. ANGEL,5 AND PETER R. BUSECK4,6

1Dipartimento di Geoscienze, Università di Padova, Via Giotto 1, I-35137, Padova, Italy
2CNR-IGG, Sezione di Padova, Via Giotto 1, I-35137, Padova, Italy
3Chemical Research Center of the Hungarian Academy of Sciences, Pusztaszéki út 59-67, H-1025, Budapest, Hungary
4School of Earth and Space Exploration, Arizona State University, Tempe, Arizona 85287-1404, U.S.A.
5Virginia Tech Crystallography Laboratory, Department of Geosciences, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, U.S.A.
6Department of Chemistry/Biochemistry, Arizona State University, Tempe, Arizona 85287-1604, U.S.A.

ABSTRACT

The compressibility and crystal structure of a recently discovered post-titanite phase of CaGe$_2$O$_5$ was investigated by single-crystal X-ray diffraction to 8.6 GPa at room temperature in a diamond-anvil cell. Unit-cell parameters decrease non-linearly with increasing pressure and do not show any discontinuity in the pressure range investigated. The unit-cell volume decreases by about 4.6% to 8.6 GPa. The $P$-$V$ data were fit using a third-order Birch-Murnaghan equation of state giving the following coefficients: $V_0 = 345.65(4)$ Å$^3$, $K_0 = 159(1)$ GPa, and $K'_0 = 5.0(3)$. A parameterized form of the same equation of state was used to obtain the axial moduli for $a$, $b$, and $c$. The room-pressure ratios of axial compressibility are 2.64:1.00:1.42, indicating strong compression anisotropy, with $b$ the stiffest direction and $a$ the most compressible one. The crystal-structure data confirm that no change in symmetry occurs at high-pressure. Most of the compression to 8.6 GPa is accommodated by the CaO$_6$ and GeO$_4$ polyhedra, with reductions in volume of 5.6 and 4.6%, respectively. The analysis of the individual bond-lengths with pressure is discussed to explain the observed strong axial anisotropy. A comparison with the closely related crystal structure of andalusite shows that the post-titanite phase is less compressible by about 10%. A further comparison with other titanite phases studied at high-pressures allows us to obtain a qualitative model capable of predicting their bulk moduli when unit-cell volume at ambient conditions is known.

**Keywords:** Post-titanite, single crystal, high pressure, X-ray diffraction

INTRODUCTION

Many germanates show phase transformations similar to those of silicates but at lower pressures (e.g., Ross and Navrotsky 1988). Therefore, analogous germanates provide important information on the behavior of silicate minerals in the Earth’s mantle, which may not be quenchable or readily studied within their $P$-$T$ stability field. Recent discoveries include a new polymorph of CaGe$_2$O$_5$ with space group $Pbam$, which has a density at ambient conditions that is 5% greater than its low-pressure polymorph, which has a triclinically distorted titanite structure. The new phase, found to be stable above about 8 GPa and 1270 K, has been called post-titanite CaGe$_2$O$_5$, and its crystal structure was determined at ambient conditions (Németh et al. 2007). The discovery at high pressure of new phases, such as post-titanite CaGe$_2$O$_5$, clearly indicates that even if the chemistry of the mantle is well known, we cannot yet be confident that we have found all of the possible polymorphs that could occur under extreme conditions of temperature and pressure typical of Earth’s mantle.

* E-mail: fabrizio.nestola@unipd.it

The aim of the current study was to determine the compressional and crystal-structure behavior of post-titanite CaGe$_2$O$_5$ using single-crystal X-ray diffraction. We discuss our results in comparison to andalusite, which is a closely related silicate structure, and to different titanite phases.

EXPERIMENTAL METHODS

A colorless single crystal of post-titanite CaGe$_2$O$_5$ from the study of Németh et al. (2007) was selected for high-pressure X-ray diffraction. An untwinned crystal measuring 150 × 75 × 45 μm was loaded in an ETH-type diamond cell (Miletich et al. 2000) using a T301 steel gasket, pre-indentated to 90 μm with a hole of 250 μm diameter. A mixture of methanol:ethanol with a 4:1 ratio was used as a hydrostatic pressure-transmitting medium, and a crystal of quartz was loaded in the DAC together with the post-titanite sample as an internal pressure standard (Angel et al. 1997). Unit-cell parameters (Table 1) were determined at 10 different pressures up to about 8.6 GPa and room temperature on a Huber four-circle diffractometer (non-monochromatized MoKα radiation) using eight-position centering of 16 Bragg reflections according to the procedure of King and Finger (1979). Centering procedures and vector-least-square refinement of unit-cell constants were performed using the SINGLE04 software (Angel et al. 2000) according to the protocols of Ralph and Finger (1982) and Angel et al. (1997). Unit-cell parameters measured in this work (Table 1) at room pressure are within 2–3 standard deviations of Németh et al. (2007); the differences are entirely attributable to differences in laboratory calibrations.