Thermal equation of state of CaGeO₃ perovskite

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ABSTRACT

Pressure-volume-temperature data have been obtained for CaGeO₃ perovskite up to 9.6 GPa and 1100 K using a cubic anvil, DIA-type high-pressure apparatus in conjunction with synchrotron X-ray diffraction. The data were analyzed using Birch-Murnaghan equation of state and thermal pressure approach with the bulk modulus at ambient pressure, Kₐ₀, and its pressure derivative, K'ₐ₀, constrained by previous measurements. A fit of the unit-cell volume data to the high-temperature Birch-Murnaghan (HTBM) equation of state gives (∂K/∂T)p = −0.025 ± 0.015 GPa/K, a = 1.047 ± 0.356 × 10⁻¹/K, and b = 3.282 ± 0.735 × 10⁻⁸/K² for the thermal expansion α expressed by a + bT. The thermal pressure approach yields αK = 4.04 ± 0.37 × 10⁻¹ GPa/K and (∂²P/∂T²)p = 6.17 ± 1.28 × 10⁻⁸ GPa/K². The energy dispersive X-ray diffraction data reveal no indication of a structural phase transition over the P-T range of the current experiment. A systematic relationship, Kₐ₀ = 6720/V(molar) − 13.07 GPa, has been established based on these isostructural analogues, which predicts Kₐ₀ = 261(15) for MgSiO₃ perovskite and 225(8) for CaSiO₃ perovskite, respectively.

Keywords: CaGeO₃ perovskite, equation of state, thermal pressure, high pressure and high temperature, X-ray diffraction

INTRODUCTION

Calcium germanate (CaGeO₃) has served as an excellent analog for MgSiO₃ because both structures exhibit the same sequence of phase transformations from a pyroxenoid wollastonite structure (space group PT, Nagai and Yamanaka 1997) to a tetragonal garnet phase (space group I₄₁/a; Nakatsuka et al. 2005) and subsequently to an orthorhombic perovskite phase (space group Pbnm; Sasaki et al. 1983). However, the phase transformations occur at much lower pressures in the germanate than in the corresponding isostructural silicate (Ringwood and Seabrook 1963; Ringwood and Major 1967; Susaki et al. 1985; Ross et al. 1986). A high-pressure EXAFS study of orthorhombic CaGeO₃ perovskite suggested that the structure became less distorted with increasing pressure with the possibility of a phase transition to a tetragonal perovskite structure at about 12.5 GPa (Andrault and Poirier 1991). A subsequent far-infrared study by Lu and Hofmeister (1994), however, found no evidence of such phase transition up to 24.4 GPa. Ross and Angel (1999) studied the compressibility of CaGeO₃ perovskite single crystal using diamond-anvil cell at pressures up to 8.6 GPa at ambient temperature, from which constraints on the bulk modulus (Kₐ₀ = 194.0 ± 2.1 GPa) and its pressure derivative (K'ₐ₀ = 6.1 ± 0.5) were obtained. Recently, Liu and Li (2007) determined the ambient-pressure adiabatic bulk (Kₐ₀) and shear (Gₐ₀) moduli and their pressure derivatives Kₐ₀ = 194.6(11) GPa, Gₐ₀ = 109.5(5) GPa, K'ₐ₀ = 6.4(2), G'ₐ₀ = 1.7(1) from an ultrasonic study up to 10 GPa. No phase transitions have been observed in both the single-crystal compression study and the in-situ ultrasonic measurements at the pressures below 10 GPa. At high temperatures, Liu et al. (1991) suggested that the metastable CaGeO₃ perovskite undergoes a pseudotetragonal modification of an orthorhombic perovskite structure near 520 K at ambient pressure. However, Durben et al. (1991) did not find any symmetry-breaking structural transformations or soft-mode behavior between room temperature and 923 K from Raman scattering measurements. Up to now, all of the studies on CaGeO₃ perovskite have been limited to either at high pressure and room temperature or at high temperature and ambient pressure. No thermoelastic equation of state (EoS) result has been reported for CaGeO₃ perovskite.

Unit-cell volume (V) measurements under simultaneous high pressure-temperature (P-T) conditions in large-volume presses using intense synchrotron X-ray have been one of the most useful ways to establish reliable thermal EoS for solids (e.g., Wang et al. 1996, 1998; Nishihara et al. 2004; Liu and Li 2006). In this paper, we report the results from in situ measurements of the unit-cell volumes of CaGeO₃ perovskite at simultaneous high P-T conditions to 9.6 GPa and 1100 K. The parameters of the thermal EoS are obtained by fitting the P-V-T data using the third-order Birch-Murnaghan EoS and the thermal pressure approach.

SAMPLE AND EXPERIMENTS

The CaGeO₃ perovskite polycrystalline sample in this study was synthesized at 8 GPa and 1273 K for 1 h in a 1000-ton uniaxial split-cylinder apparatus (USCA-1000, Li et al. 1996) from wollastonite-CaGeO₃ powder (Liu et al. 1991). In the synthesizing experiment, a special P-T path was designed to preserve the integrity of the sample and to relax the intergranular stresses as discussed by Gwannamie and Liebermann (1992). The crystallographic structure of the specimen recovered at ambient conditions was confirmed to be a pure perovskite phase by comparison...