Thermo-elastic behavior of grossular garnet at high pressures and temperatures

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ABSTRACT

The thermo-elastic behavior of synthetic single crystals of grossular garnet (CaAl2Si3O12) has been studied in situ as a function of pressure and temperature separately. The same data collection protocol has been adopted to collect both the pressure-volume ($P-V$) and temperature-volume ($T-V$) data sets to make the measurements consistent with one another. The consistency between the two data sets allows simultaneous fitting to a single pressure-volume-temperature Equation of State (EoS), which was performed with a new fitting utility implemented in the latest version of the program EoSFit7c. The new utility performs fully weighted simultaneous fits of the pressure-volume EoS combined with any $P-V$ EoS. Simultaneous refinement of our $P-V$ data combined with that of $K^T$ as a function of $T$ allowed us to produce a single $P-V-T-K^T$ equation of state with the following coefficients:

$$V_0 = 1664.46(5) \text{ Å}^3, K_{10} = 166.57(17) \text{ GPa and } K^T = 4.96(7) a_{300 \text{K}, \text{lab}} = 2.09(2) \times 10^{-5} \text{ K}^{-1}$$

with a refined Einstein temperature ($\theta_1$) of 512 K for a Holland-Powell-type thermal pressure model and a Tait third-order EoS. Additionally, thermodynamic properties of grossular have been calculated for the first time from crystal Helmholtz and Gibbs energies, including the contribution from phonons, using density functional theory within the framework of the quasi-harmonic approximation.

Keywords: Grossular, high-pressure, high-temperature, diffraction, bulk modulus, $P-V-T-K^T$ fit, EosFit

INTRODUCTION

Stable over a wide range of pressure and temperature conditions, garnets are among the most abundant phases in the Earth’s upper mantle and transition zone. Yet coherent and homogeneous Equation of State (EoS) coefficients to reliably describe their behavior at simultaneous high pressures and high temperatures still have to be determined with high accuracy and precision. Recent papers have shown the importance of a robust and valid description of the elastic behavior of the most abundant mineral phases for the accurate calculation of host-inclusion entrapment pressures that in turn allow the growth conditions in the Earth to be inferred (e.g., Angel et al. 2014, 2015a, 2015b; Ashley et al. 2015; Milani et al. 2015). However, the determination of a full set of elastic coefficients of a mineral is always challenging because of the limitations in performing simultaneous high-pressure ($P$) and high-temperature ($T$) experiments on one side and because of the lack of consistent measurements performed separately at high $P$ and high $T$. Therefore, a reliable description of the elastic behavior of minerals at high $P-T$ with a single set of EoS coefficients can be extremely challenging.

Pressure-volume EoS is well developed and capable of reproducing the isothermal volume or density changes of materials to within the experimental uncertainties. A natural approach to describing the $P-V-T$ behavior of a material is therefore to describe how the volume ($V_{0T}$), bulk moduli ($K_{0T}$), and its pressure derivatives ($K'_{0T}$) change with increasing temperature (at room pressure), and then use these parameters to calculate the isothermal compression at the temperature of interest. A potential limitation of this approach is that while the variation of $K_{0T}$ with $T$ can be measured, the variation of $K'_{0T}$ with $T$ has been measured very rarely, although it is obvious that it should increase slightly with increasing temperature. As Helffrich and Connolly (2009) pointed out, the common assumption that $K_{0T}$ does not change

† Notation: subscripts on $K$ (e.g., $K_{0T}$) indicate the reference pressure and temperature to which the bulk modulus is referred; superscripts $S$ or $T$ (e.g., $K^S$ or $K^T$) stand for adiabatic or isothermal quantities.