Effects of water on P-V-T equation of state of pyrope

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Abstract

High-pressure single-crystal / powder synchrotron X-ray diffraction was carried out on a hydrous pure magnesium pyrope ($\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) containing 900 ppmw H_2O , synthesized at 4.0 GPa and 1300 K. The pressure-volume (P - V) single-crystal data from room pressure to 9.81 GPa at ambient temperature were fitted by a third-order Birch-Murnaghan equation of state (BM-EoS) yielding a unit-cell volume of $V_0 = 1505.14 \pm 0.38 \text{ \AA}^3$, an isothermal bulk modulus of $K_0 = 160 \pm 3 \text{ GPa}$ and its pressure derivative $K'_0 = 5.2 \pm 0.4$. When fixing $K'_0 = 4.0$, the data yielded $V_0 = 1504.58 \pm 0.32 \text{ \AA}^3$ and $K_0 = 166 \pm 2 \text{ GPa}$. The pressure-volume-temperature (P - V - T) EoS of the synthetic hydrous pyrope was also measured at temperatures up to 900 K and pressures up to 16.75 GPa, using a diamond anvil cell in conjunction with *in situ* synchrotron angle-dispersive powder X-ray diffraction. The P - V data at room temperature and in a pressure range of 0.0001-14.81 GPa were then analyzed by a third-order BM-EoS and yielded $V_0 = 1505.35 \pm 0.25 \text{ \AA}^3$, $K_0 = 161 \pm 2 \text{ GPa}$, $K'_0 = 5.0 \pm 0.3$. With K'_0 fixed to 4.0, we also obtained $V_0 = 1505.04 \pm 0.29 \text{ \AA}^3$ and $K_0 = 167 \pm 1 \text{ GPa}$. Consequently, we fitted the P - V - T data with the high-temperature third-order BM-EoS approach and obtained the thermoelastic parameters of $V_0 = 1505.4 \pm 0.3 \text{ \AA}^3$, $K_0 = 162 \pm 1 \text{ GPa}$, $K'_0 = 4.9 \pm 0.2$, the temperature derivative of the bulk modulus $(\partial K_0 / \partial T)_P = -0.018 \pm 0.004 \text{ GPa K}^{-1}$, and the thermal expansion

coefficient at ambient conditions $\alpha_0 = (3.2 \pm 0.1) \times 10^{-5} \text{ K}^{-1}$. These properties were consistent with the thermal pressure EoS analysis. These new results on hydrous pyrope were also compared with previous studies of anhydrous pyrope. The main effect of hydration on pyrope is to decrease K_0 and increase K'_0 by increasing the vacancies or unoccupied volume in the structure. The entire dataset enabled us to examine the thermoelastic properties of important mantle garnets and this data has further applications for modeling the P-T conditions in the upper mantle of the Earth's interior using deep mineral assemblages.

Keywords: Hydrous pyrope; Equation of state; High temperature and pressure; X-ray diffraction; Diamond anvil cell

1. Introduction

Silicate garnets are nesosilicates with the general formula $\text{X}_3\text{Y}_2(\text{SiO}_4)_3$, where the eight-coordinated dodecahedral X sites are usually occupied by divalent cations (typically Mg, Fe, Mn, or Ca) and the six-coordinated octahedral Y sites by trivalent cations (typically Al, Fe, or Cr). These octahedral/tetrahedral sites form a three-dimensional corner-sharing network which defines interstitial dodecahedral divalent metal sites with eight-fold coordination (Smyth et al. 2000). Garnets are widespread minerals in the upper mantle and transition zone of Earth, comprising of up to 40 % of the pyrolite composition volume and up to 70 % of the eclogitic composition (Akaogi and Akimoto 1977; Anderson and Bass 1984; Irifune and Ringwood 1987; Ita and Stixrude 1992; Dymshits et al., 2014). Garnets are also important components of the subducted oceanic crust (Irifune and Ringwood 1993; Karato et al. 1995) as stable phases in a wide range of pressures and temperatures, and play a fundamental role in many high-pressure and high-temperature petrologic processes (Deer et al. 1992; Pavese et al. 2001). As the principal mineral end member of the garnet group, pyrope ($\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) is widely accepted as playing an important role in understanding the properties of the upper mantle and transition zone (Withers et al. 1998; Mookherjee and Karato 2010). Garnet lherzolite models of the upper mantle can contain a pyrope volume about 15% (Gwanmesia et al. 2006). Pyrope forms a complete solid solution with MgSiO_3 -majorite (Gasparik 2000), another garnet found in the upper mantle and transition zone of the Earth. Natural garnets from eclogite xenoliths are usually pyrope-rich (Lu and Keppler

1997). Therefore, accurate knowledge of the thermoelastic properties of pyrope is directly relevant for deducing appropriate compositional models, seismic tomographic images, and the velocity and density profiles of the Earth's interior (e.g. Duffy and Anderson 1989; Flanagan and Shearer 1999; Weidner and Wang 2000).

The nominally anhydrous mineral phases in the Earth's upper mantle and transition zone (410-660 km depth) may serve as a large internal reservoir of water which has profound implications for Earth's evolution as a water planet (Ohtani 2005; Beran and Libowitzky 2006; Tenner et al. 2009). Water plays important roles in the phase transformation kinetics in the Earth's interior, which affects the mantle dynamics (e.g., Kubo et al. 1998). Trace amounts of dissolved hydrogen defects in nominally anhydrous mantle phases influence the physical properties of mantle materials, such as rheology (e.g., Karato 2006), elasticity (e.g., Jacobsen 2006), electrical conductivity (e.g., Karato 1990; Huang et al. 2005), and shear strength (e.g., Chen et al. 1998; Mei and Kohlstedt 2000; Jung and Karato 2001; Kavner 2003). Much effort has been made estimating the water storage capacity of nominally anhydrous mineral phases to determine factors controlling water incorporation into the structure (e.g., Mackwell and Kohlstedt 1990; Rossman and Aines 1991; Kohlstedt et al. 1996; Rossman 1996; Lu and Keppler 1997; Withers et al. 1998; Smyth et al. 2003, 2007; Skogby 2006; Mookherjee and Karato 2010; Tenner et al. 2012). In the context of water storage at high pressures, garnet is a particularly important phase because grossular ($\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) is known to be capable of dissolving up to 20.80 wt.% H_2O (Passaglia and Rinaldi 1984; O'Neill et al. 1993) and significant water content has been found in pyrope garnet from xenoliths (Bell and Rossman 1992). Water content in garnet also can be used to place constraints on water fugacities (Aines and Rossman 1984). Trace element zoning in garnet may be used to investigate the P-T paths in metamorphic rocks (Hickmott et al. 1987; Hickmott 1989). Hydrogen zonation in garnet may be an important source of information about the metamorphic processes that occur during crystal growth (Hickmott 1989). Since garnet increases in abundance from about 5% volume at a 150 km depth to around 30% at a 650 km depth (Ringwood 1991), it is important to know whether this phase can dissolve large amounts of water throughout its compositional and P-T stability range. Previous studies have revealed that hydroxyl occurrence in nominally anhydrous mantle phases is closely related to cation vacancy defects (e.g., Stalder et al. 2005; Skogby 2006). Moreover, water may be incorporated in garnets as OH^- defects associated with

charge balancing or oxidation-reduction reactions, or it may substitute Si in the hydrogarnet substitution (Lu and Keppler 1997; Withers et al. 1998; Mookherjee and Karato 2010). Therefore, the hydrous component in garnet has important geological implications for the Earth's mantle, and it is critical to understand the state of water and its role in the structure of garnets in the Earth's interior.

To date, the elasticity of pyrope has been extensively studied using both multi-anvil apparatus and the diamond anvil cell (e.g., Hazen and Finger 1978; Sato et al. 1978; Levien et al. 1979; Leitner et al. 1980; Leger et al. 1990; Conrad et al. 1999; Zhang et al. 1998; Chen et al. 1999; Wang and Ji 2001; Sinogeikin and Bass 2000, 2002; Li et al. 2011). Up to now, most of the pyrope studies have been limited to either high pressure and room temperature or ambient pressure and high temperature, however, there have been few studies that focus on the thermoelastic properties of pyrope (Bonczar and Graham 1977; Wang et al. 1998; Sinogeikin and Bass 2002; Gwanmesia et al. 2006; Zou et al. 2012; Lu et al. 2013; Du et al. 2015). Furthermore, to our knowledge, there are no reports about the thermoelasticity of hydrous pyrope at simultaneously high pressure and high temperature, which hinders the accurate determination of appropriate compositional models and density profiles of the Earth's upper mantle.

Here, we investigated the pressure-volume-temperature (P - V - T) relations of a synthetic hydrous pyrope at high pressure and high temperature up to 17 GPa and 900 K, using a diamond anvil cell combined with *in situ* synchrotron radiation angle-dispersive X-ray diffraction. The thermoelastic properties of the hydrous pyrope were obtained by fitting the present P - V - T data to the high-temperature Birch-Murnaghan (HTBM) EoS and thermal pressure EoS. We also discuss our results with respect to previous reports of the thermoelastic properties of anhydrous pyrope, and evaluate the high pressure-temperature and hydrogen effects on pyrope to aid the current understanding of Earth's deep upper-mantle mineralogical models.

2. Sample and Experimental methods

2.1. Sample

The synthesis of hydrous pyrope was carried out using a multi-anvil pressure apparatus (YJ-3000T), at the Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, China.

Details of this experimental set-up are described elsewhere by Xie et al. (1993). The pressurization system of this press consisted of six WC anvils, with their tips truncated to $23.5 \times 23.5 \text{ mm}^2$, which were simultaneously pushed by six hydraulic rams to generate high pressure in the experimental assembly (Fan et al. 2013). The pressure in the sample chamber was calibrated using a quartz-coesite phase transition and the high-pressure melting curve of copper, with a pressure measurement error margin of less than 1.5%. The temperature in the sample chamber was measured using a Pt-Pt₉₀Rh₁₀ thermocouple, with an uncertainty value less than 5 K (Xie et al. 1993, 2002). The starting materials used in the synthesizing experiments were stoichiometric amounts of high purity magnesium oxide (MgO), aluminum oxide (Al₂O₃) and silica (SiO₂). The mixture was then melted at 1700 K which produced a homogeneous glass after quenching. The homogeneous glass was crushed and ground into a fine powder in acetone and then encapsulated in platinum capsules with 10 wt.% of deionised water. The synthesis was carried out at 4.0 GPa and 1300 K with a run duration of 48 h, and perfectly clear and inclusion-free single crystals of pyrope were picked from the charge. The ambient X-ray diffraction data were collected using a D/Max-2200 X-ray diffractometer with graphite crystal monochromator and Cu K α radiation. The ambient powder X-ray spectrum of pyrope was indexed according to the standard spectra (JCPDS 87-1093), confirming that the structure of the synthetic pyrope was cubic, and belonged to the $Ia\bar{3}d$ space group. The electron probe microanalysis further confirmed that the synthetic sample was a single phase with the composition as follows (in wt%): MgO, 29.9(3); Al₂O₃, 24.9(2); SiO₂, 44.7(2), which can be also written in term of formula unit as Mg_{3.01}Al_{2.00}Si_{3.01}O₁₂.

Several crystals were mounted individually in epoxy resin so that doubly-polished crystal slabs could be prepared. After polishing, the crystal slabs were extracted from the resin and cleaned using CCl₄. An electronic micrometer with a 1 μm precision was used to measure the sample thickness, which ranged between 300 and 500 μm . A Nicolet 5700 FTIR spectrometer coupled with a microscope was used to analyze the OH contents of X-ray-oriented, faceted single crystals using a KBr beam-splitter and a liquid-nitrogen cooled MCT-A detector. Measurements were performed through optically clean, inclusion-free, and crack-free areas under a continuous dry air flush. Where samples were large enough, we employed a focused 100 μm spot size on the crystal surface through redundant aperturing. Smaller apertures were used to analyze areas down to $40 \times 40 \text{ }\mu\text{m}$. Our synthesized pyropes have an asymmetric peak in the absorption spectrum centered at

3630 cm⁻¹ (Fig. 1), which corresponds exactly to those in the OH spectra of synthetic pyropes of previous studies (Geigei et al., 1991; Withers et al., 1998). The water contents were computed from integrated absorbances using the calibration of Bell et al. (1995) for pyrope, which showed that the water content of this hydrous pyrope sample was about 900 ppmw.

2.2. Room temperature and high pressure single-crystal X-ray diffraction experiment

Before loading into the diamond anvil cell, the pyrope crystal was examined in air. The refined unit-cell parameters constrained to cubic symmetry are reported in Table 1. The *in situ* room-temperature and high-pressure synchrotron single-crystal X-ray diffraction experiments were carried out at the BL15U1 beamline using angle-dispersive diffraction with diamond-anvil cells at the Shanghai Synchrotron Radiation Facility (SSRF). A symmetric-type diamond anvil cell equipped with 500 μm diamond culets was used for pressure generation. A gasket made of stainless steel foil (type T301) with pre-indented thickness of $\sim 55 \mu\text{m}$ and a center hole of 200 μm in diameter served as the sample chamber. The 4:1 methanol-ethanol mixture was used as a pressure transmitting medium, which is hydrostatic up to 10 GPa as demonstrated by Piermarini et al. (1973) and Angel et al. (2007). A ruby chip was loaded as a pressure calibrant together with the hydrous pyrope sample (about $50 \times 50 \times 25 \mu\text{m}$) in the sample chamber. Ruby fluorescence spectra were collected before and after each collection of X-ray diffraction data, and the positions of the R1 and R2 peaks were determined by fitting them with Lorentzian functions. The pressure was calculated from the fitted R1 and R2 peak positions using the method of Mao et al. (1978). Diffraction images were collected using MAR-165 charge coupled device (CCD) detector, placed at a distance of approximately 180mm to the sample. The detector geometry parameters were calibrated using a CeO₂ diffraction standard. The X-ray beam was monochromatized to a wavelength of 0.6199Å and focused down to $2 \times 3 \mu\text{m}^2$ area. Diffraction data were collected while the diamond anvil cell rotated around the vertical axis of the instrument (ω -axis) from -12 to +12°, with a typical exposure time of 0.5s/deg. Diffraction images were analyzed using the GSE_ADA/RSV software package (Dera et al. 2013). Then, the unit-cell parameters of hydrous pyrope were calculated by a least squares technique using Unitcell software (Holland and Redfern 1997). Each diffraction pattern has at least 30 good single crystal diffraction spots. Except the single crystal diffraction spots of diamond, all the other single crystal diffraction spots could be successfully indexed using the cubic symmetry of pyrope. In the calculation, at least 11 sample

diffraction spots were used to refine the unit-cell parameters: (400), (420), (332), (422), (431), (521), (611), (620), (444), (640), and (642).

2.3. High-temperature and high-pressure powder X-ray diffraction experiment

High-temperature and high-pressure experiments were carried out by using a modified Merrill–Bassett type diamond-anvil cell. The culet-size of the diamonds, sample chamber of the gaskets and the pressure transmitting medium were the same as those in the single crystal diffraction experiment. The hydrous pyrope powders were slightly pressed between two opposing diamond anvils to form an approximately 25 μm thick disk, and a piece of the sample about 100 μm in diameter was loaded into the sample chamber. The cell pressure was determined using the equation of state of gold (pressure marker) as proposed by Fei et al. (2007). Heating was conducted using a resistance-heating system, and the temperature was measured using a Pt₉₀Rh₁₀-Pt₁₀₀ thermocouple attached to the pavilion of the diamond anvil. We first compressed the sample up to 10 GPa and then increased the temperature up to 900 K. Heating was maintained at 900 K for about 15 minutes in order to minimize the effect of any stress that could develop during cold compression. Following this, the temperature was lowered down to 300 K in 200 K steps. At each P-T condition, an X-ray diffraction pattern was collected after the experiment temperature was maintained for ~600 s. The typical exposure time for collecting the diffraction patterns of the sample and the pressure marker was 600 s. Details of the experimental setup and cell assembly are described in Fan et al. (2010).

In situ high temperature and high pressure powder X-ray diffraction experiments were conducted at the 4W2 beamline of the Beijing Synchrotron Radiation Facility (BSRF). An image plate detector (MAR-345) was used to collect diffraction patterns. The wavelength of the monochromatic X-ray beam was 0.6199 Å and calibrated by scanning through the Mo metal K-absorption edge. The X-ray beam was focused to a beam size of 20×30 μm^2 full-width at half maximum (FWHM) by a pair of Kirkpatrick-Baez mirrors. The tilting and rotation of the detector relative to the incident X-ray beam was calibrated using cerium dioxide (CeO₂) powder as the X-ray diffraction standard. The sample-detector distance was calculated from the powder CeO₂ diffraction pattern at ambient conditions. The collected diffraction patterns were integrated to generate the conventional one-dimensional diffraction profiles using Fit2D (Hammersley et al. 1996). Figure 2 shows a typical fitting of the full X-ray diffraction pattern of hydrous pyrope at

10.79 GPa and 900 K. Analyses of all the patterns were carried out using the full profile-fitting technique implemented in the EXPGUI/GSAS software package (Larson and Von Dreele 2000; Toby 2001). The refinement of the peak positions and extraction of the cell parameters were achieved by reducing full diffraction patterns following the Le Bail method (Le Bail et al. 1988). Precision of the volume determination for hydrous pyrope was estimated from the full spectrum fitting (Le Bail refinement) of X-ray diffraction profiles.

3. Results and Discussion

The unit-cell parameters of hydrous pyrope refined from single-crystal and powder X-ray diffraction are summarized in Table 1 and 2, respectively. The room temperature and high pressure single-crystal X-ray diffraction data were fitted to the third-order BM-EoS to derive bulk modulus (K_0) and its pressure derivative (K'_0) of hydrous pyrope. For the high temperature and high pressure powder X-ray diffraction data, first we fitted the compression P - V data at the 300 K isotherm to the BM-EoS for comparison, and then applied the high-temperature BM-EoS and thermal pressure EoS approach to derive the thermoelastic parameters from the measured P - V - T data.

3.1. Room-Temperature Birch-Murnaghan equation of state (BM-EoS)

The pressure-volume (P - V) data from the single-crystal (Table 1) and powder sample (Table 2) were fitted to a third order BM-EoS:

$$P = (3/2) K_0 [(V_0/V)^{7/3} - (V_0/V)^{5/3}] \times \{1 + (3/4)(K'_0 - 4)[(V_0/V)^{2/3} - 1]\} \quad (1)$$

where V_0 , K_0 , and K'_0 are the unit-cell volume, isothermal bulk modulus and its pressure derivative at ambient conditions, respectively. The fitting without any constraints yielded $V_0 = 1505.14 \pm 0.38 \text{ \AA}^3$, $K_0 = 160 \pm 3 \text{ GPa}$, $K'_0 = 5.2 \pm 0.4$ for the single-crystal sample and $V_0 = 1505.35 \pm 0.25 \text{ \AA}^3$, $K_0 = 161 \pm 2 \text{ GPa}$, $K'_0 = 5.0 \pm 0.3$ for the powder sample. With fixed K'_0 at 4 (*i.e.* the second order BM-EoS), the fitting yielded $V_0 = 1504.58 \pm 0.32 \text{ \AA}^3$ and $K_0 = 166 \pm 2 \text{ GPa}$ for the single-crystal and $V_0 = 1505.04 \pm 0.29 \text{ \AA}^3$ and $K_0 = 167 \pm 1 \text{ GPa}$ for the powder. The single-crystal and powder data show excellent agreement with each other. Fitting the combined data yielded: $V_0 = 1505.02 \pm 0.23 \text{ \AA}^3$, $K_0 = 161 \pm 2 \text{ GPa}$, $K'_0 = 5.2 \pm 0.3$ (without any constraints) and $V_0 = 1504.33 \pm 0.31 \text{ \AA}^3$, and $K_0 = 167 \pm 1 \text{ GPa}$ (with fixed $K'_0 = 4$). Figure 3 shows the volume compression (V/V_0) of hydrous pyrope

as a function of pressure (P) and the derived equation of state from the combined data (without any constraints).

The second order BM-EoS yielded a significant larger K_0 than the third order BM-EoS. Figure 4 shows the volume Eulerian finite strain ($f_E = [(V_0/V)^{2/3} - 1]$) versus the “normalized pressure” ($F_E = P/[3f_E(2f_E + 1)^{5/2}]$) plot (*i.e.* F_E - f_E plot, (Angel 2000)) of hydrous pyrope in this study. The weighted linear regression through the data points yielded the hydrous pyrope intercept value, $F_E(0) = 161 \pm 2$ GPa, which shows excellent agreement with the isothermal bulk modulus obtained by the third-order BM-EoS (161 ± 2 GPa). Furthermore, it is clear from Figure 4 that the normalized pressure as a function of the Eulerian strain at 300 K has a positive slope, which is consistent with a value of K'_0 slightly larger than 4 (Angel 2000) shows that the third-order BM-EoS is a reasonable description of the P - V data in this study.

We used a methanol-ethanol mixture with a ratio of 4:1 for the pressure medium in this study. This medium solidifies at a pressure above 10 GPa, and therefore the hydrostatic pressure environment in the sample chamber may be influenced (Piermarini et al. 1973; Angel et al. 2007). However, the sample chamber in this study was heated up to 900 K at pressures higher than 10 GPa for the relaxation of the deviatoric stress. The effect of deviatoric stress on the unit-cell volume measurements should be minimal, and this is confirmed by fitting the experimental data under hydrostatic conditions (below 10 GPa) which yields a very similar result ($K_0 = 162 \pm 3$ GPa, $K'_0 = 4.9 \pm 0.5$) to the whole pressure range fitting.

3.2. High-Temperature Birch-Murnaghan equation of state

The P - V - T data (Table 2) from powder X-ray diffraction experiments were used to determine the thermoelastic properties of hydrous pyrope up to ~17 GPa and 900 K. The high temperature third order BM-EoS was applied to our high pressure and high temperature data in the following form:

$$P = (3/2) K_{T0} [(V_{T0}/V)^{7/3} - (V_{T0}/V)^{5/3}] \times \{1 + (3/4)(K'_{T0} - 4)[(V_{T0}/V)^{2/3} - 1]\} \quad (2)$$

In this equation, the thermal dependences of the zero-pressure volume (V_{T0}) and the bulk modulus (K_{T0}) at different temperatures are expressed using the following equations:

$$V_{T0} = V_0 \exp \int_{300}^T \alpha_T dT \quad (3)$$

$$K_{T0} = K_0 + (\partial K_0 / \partial T)_P \times (T - 300) \quad (4)$$

where α_T is the thermal expansion at ambient pressure and $(\partial K_0/\partial T)_P$ is the temperature derivative of K_0 at constant P.

The thermoelastic parameters α_0 , $(\partial K_0/\partial T)_P$, and K_0 of the hydrous pyrope obtained in this study are showed in Table 4 and Figure 5. Fitting our P - V - T data to the high temperature BM EoS yielded $V_0 = 1505.38 \pm 0.27 \text{ \AA}^3$, $K_0 = 162 \pm 1 \text{ GPa}$, $K'_0 = 4.9 \pm 0.2$, $(\partial K_0/\partial T)_P = -0.018 \pm 0.004 \text{ GPa K}^{-1}$ and $\alpha_0 = (3.2 \pm 0.1) \times 10^{-5} \text{ K}^{-1}$. With K'_0 fixed to 4.0, we also obtained $V_0 = 1505.22 \pm 0.28 \text{ \AA}^3$, $K_0 = 168 \pm 1 \text{ GPa}$, $(\partial K_0/\partial T)_P = -0.017 \pm 0.005 \text{ GPa K}^{-1}$ and $\alpha_0 = (3.06 \pm 0.09) \times 10^{-5} \text{ K}^{-1}$ for hydrous pyrope. The K_0 values determined here are consistent with those derived from our P - V data fitting at 300 K within accepted uncertainties. We also calculated the temperature derivative of the bulk modulus extracted from each isotherm, and obtained $(\partial K_0/\partial T)_P = -0.018 \pm 0.005 \text{ GPa K}^{-1}$ for hydrous pyrope, which is very consistent with the results from the whole set of P - V - T data available in this study ($(\partial K_0/\partial T)_P = -0.018 \pm 0.004 \text{ GPa K}^{-1}$) within their uncertainties.

Likewise, fitting the P - V - T data at pressures below $\sim 10 \text{ GPa}$ to the high temperature BM-EoS yielded $V_0 = 1505.33 \pm 0.31 \text{ \AA}^3$, $K_0 = 163 \pm 2 \text{ GPa}$, $K'_0 = 5.1 \pm 0.4$, $(\partial K_0/\partial T)_P = -0.020 \pm 0.006 \text{ GPa K}^{-1}$ and $\alpha_0 = (3.3 \pm 0.2) \times 10^{-5} \text{ K}^{-1}$. These values are very consistent with the results of fitting all the P - V - T data that lead to $V_0 = 1505.38 \pm 0.27 \text{ \AA}^3$, $K_0 = 162 \pm 1 \text{ GPa}$, $K'_0 = 4.9 \pm 0.2$, $(\partial K_0/\partial T)_P = -0.018 \pm 0.004 \text{ GPa K}^{-1}$ and $\alpha_0 = (3.2 \pm 0.1) \times 10^{-5} \text{ K}^{-1}$ within their uncertainties.

3.3. Thermal pressure equation of state

We also analyzed the P - V - T data using a thermal pressure approach (e.g., Anderson 1995; Jackson and Rigden 1996). The thermal pressure (ΔP_{th}) was obtained by subtracting the pressure at volume (V) and at room temperature (derived from Eq. (1)) from the pressure measured at the same V and at temperature (T).

$$\Delta P_{th} = P(V, T) - P(V, 300) = \left[\alpha K_T + \left(\frac{\partial K_T}{\partial T} \right)_V \ln \left(\frac{V_0}{V} \right) \right] \times (T - 300) \quad (6)$$

Figs. 6 and 7 show the thermal pressure of hydrous pyrope against temperature and the unit-cell volume, respectively. The show that the thermal pressure of hydrous pyrope varies linearly with temperature and is almost independent of volume. A fit of the data in this study yielded $K_0 = 160 \pm 2 \text{ GPa}$, $K'_0 = 4.8 \pm 0.4$, and $\alpha_0 = (2.9 \pm 0.2) \times 10^{-5} \text{ K}^{-1}$, which is reasonably consistent with those derived by HTBM EoS fitting (Table 4). Within the uncertainty of the fit, the $(\partial K_T/\partial T)_V$ value is roughly zero, indicating that the thermal pressure is independent of volume. Wang et al. (1998) also found

that the thermal pressure in garnet shows linear variation with T up to 1200 K independent of compression (V/V_0), concluding that the $(\partial K_T/\partial T)_V$ is very close to zero. The same conclusion has been drawn for many other silicate minerals, such as olivine (Guyot et al. 1996), CaSiO_3 perovskite (Wang et al. 1996) and ringwoodite (Nishihara et al. 2004). By using the thermodynamic relation: $(\partial K_T/\partial T)_P = (\partial K_T/\partial T)_V - \alpha K_T K'_T$, we obtained $(\partial K_0/\partial T)_P = -0.021(3) \text{ GPaK}^{-1}$ which is in good agreement with current analysis using HTBM EoS (Table 4).

3.4. Comparison with previous studies of anhydrous pyrope

Our hydrous pyrope results compared with previous studies for anhydrous pyrope are also shown in Table 3. Numerous studies on elastic properties of anhydrous pyrope have been investigated by some authors. Table 3 summarizes the K_0 and K'_0 for anhydrous pyrope determined by various experimental techniques, including X-ray diffraction, ultrasonic interferometry and Brillouin scattering spectroscopy (Hazen and Finger 1978; Sato et al. 1978; Levien et al. 1979; Leitner et al. 1980; Leger et al. 1990; Conrad et al. 1999; Zhang et al. 1998; Chen et al. 1999; Wang and Ji 2001; Sinogeikin and Bass 2000, 2002; Li et al. 2011; Du et al. 2015). Levien et al. (1979) measured the unit-cell parameters of pyrope in a diamond anvil cell at pressures up to 5 GPa using a single crystal X-ray diffraction method, and obtained the bulk modulus $K_0 = 175(1) \text{ GPa}$ and $K'_0 = 4.5(5)$. Leitner et al. (1980) determined the elastic moduli of a synthetic single crystal of pyrope using Brillouin spectroscopy, and reported $K_0 = 175(1) \text{ GPa}$. Subsequently, Leger et al. (1990) used this K_0 value and using powder X-ray diffraction to report $K'_0 = 3.4$ for pure synthetic pyrope. Zhang et al. (1998) also investigated the equation of state and crystal structure of pyrope under hydrostatic conditions up to 33 GPa using single crystal X-ray diffraction, and obtained $K_0 = 171(2) \text{ GPa}$ and $K'_0 = 4.4(2)$. In addition, Conrad et al. (1999) conducted high-pressure Brillouin scattering experiments on near end-member single crystal pyrope at pressures up to 10 GPa in a diamond-anvil cell with a methanol-ethanol-water pressure medium, and calculated K_0 and K'_0 as 171.3 GPa and 3.22, respectively. Sinogeikin and Bass (2000) also measured the single-crystal elastic properties of synthetic pyrope up to 20 GPa using a Brillouin scattering method, and reported that the K_0 and K'_0 were 169.4(20) GPa and 4.1(3), respectively. In contrast, studies using synthetic polycrystalline specimens and ultrasonic interferometry in a 1000 ton split-cylinder multi-anvil apparatus (Chen et al. 1999) yielded $K_0 = 171(2)$ and $K'_0 = 5.3(4)$, the largest value of K'_0 in the previous studies for anhydrous pyrope.

Recently, Du et al. (2015) also measured the unit-cell parameters of synthetic pyrope up to 10 GPa using synchrotron X-ray powder diffraction, and yielded $K_0 = 169.2 (2)$ by fixing K'_0 at 4.4 which taken from Zhang et al. (1998). From the results of these previous studies, the anhydrous pyrope bulk modulus and its pressure derivative are within the ranges of $K_0 = 170$ -175 GPa and $K'_0 = 3.2$ -5.3. However, we obtained the bulk modulus and its pressure derivative as $K_0 = 161$ GPa and $K'_0 = 5.0$ for the hydrous pyrope (about 900 ppmw) in this study. The K_0 value of our hydrous pyrope was around 5-7 % smaller than the anhydrous pyrope from previous studies, but its K'_0 value was slightly larger. This phenomenon is similar to the effects of water on the elastic properties of olivine, reducing K_0 and increasing K'_0 (Smyth et al. 2005; Jacobsen 2006) although unchanged K'_0 for hydrous olivine was also proposed (Chen et al. 2011).

Wang et al. (1998) measured the P - V - T relations of pyrope garnet at pressure and temperature conditions up to 11 GPa and 1163 K with energy-dispersive synchrotron X-ray diffraction in a cubic-anvil, DIA-6 type apparatus. By fixing $K'_0 = 5$, they obtained $K_0 = 170(2)$ GPa, $(\partial K_0 / \partial T)_P = -0.020(3)$ GPaK⁻¹, and $\alpha_0 = 2.58 (28) \times 10^{-5}$ K⁻¹. Sinogeikin and Bass (2002) presented the single-crystal elasticity of pure synthetic pyrope at temperatures up to 800°C using Brillouin light scattering spectroscopy in a ceramic high-temperature cell, indicating $K_0 = 169(2)$ GPa and $(\partial K_0 / \partial T)_P = -0.019(3)$ GPaK⁻¹. Gwanmesia et al. (2006) determined the acoustic wave velocities of synthetic polycrystalline pyrope up to 9 GPa and 1000°C by ultrasonic interferometry combined with energy-dispersive synchrotron X-ray diffraction in a cubic-anvil DIA-type apparatus, and obtained $K_0 = 172(2)$ GPa and $(\partial K_0 / \partial T)_P = -0.026(4)$ GPaK⁻¹ by fixing $K'_0 = 3.9$. Recently, Zou et al. (2012) measured the thermoelastic properties of synthetic pyrope garnet at higher pressure and temperature conditions (up to 19 GPa and 1700 K) using *in situ* energy-dispersive synchrotron X-ray diffraction combined with a Kawai-type multi-anvil apparatus, and concluded that $K_0 = 167(3)$ GPa, $(\partial K_0 / \partial T)_P = -0.021(9)$ GPaK⁻¹, and $\alpha_0 = 2.89 (33) \times 10^{-5}$ K⁻¹ for fixed $K'_0 = 4.6$. Du et al. (2015) also investigated the thermo-compression of a series of synthetic garnets with the pyrope, grossular, and intermediate compositions up to about 900 K and to 10 GPa using synchrotron X-ray powder diffraction with a diamond anvil cell, and obtained $\alpha_0 = 2.74 (5) \times 10^{-5}$ K⁻¹ for end-member pyrope. The results of previous studies indicate that the temperature derivative of anhydrous pyrope bulk modulus $((\partial K_0 / \partial T)_P)$ ranges from -0.019 GPaK⁻¹ to -0.026 GPaK⁻¹, and the coefficients of thermal expansion (α_0) range from 2.58×10^{-5} K⁻¹ to 2.89×10^{-5} K⁻¹.

However, we obtained $(\partial K_0/\partial T)_P = -0.018(4) \text{ GPaK}^{-1}$ and $\alpha_0 = 3.2(1) \times 10^{-5} \text{ K}^{-1}$ for hydrous pyrope (about 900 ppmw) in this study. The $(\partial K/\partial T)_P$ value of the hydrous pyrope in this study is in agreement with anhydrous pyrope, whereas the α_0 value of the hydrous pyrope is slightly larger than anhydrous pyrope. Lu et al. (2013) measured the single-crystal elasticity of natural Fe-bearing pyrope using *in situ* Brillouin spectroscopy and X-ray diffraction at high-pressure and temperature conditions up to 20 GPa and 750 K in an externally-heated diamond anvil cell, and found $(\partial K_0/\partial T)_P = -0.023(2) \text{ GPaK}^{-1}$ for Fe-bearing pyrope, which is very consistent with the results from Wang et al. (1998) ($(\partial K_0/\partial T)_P = -0.020(3) \text{ GPaK}^{-1}$) and Zou et al. (2012) ($(\partial K_0/\partial T)_P = -0.021(9) \text{ GPaK}^{-1}$) for pure pyrope using a synchrotron X-ray diffraction method within their uncertainties. Therefore, based on the existing data, we believe that the temperature derivative of the pyrope bulk modulus may not be significantly affected by its iron and hydrogen content; however, hydrogen can slightly raise the thermal expansion coefficient of pyrope.

4. Geophysical Implications

Earth's mantle mostly consists of nominally anhydrous minerals, such as olivine, pyroxenes, garnet, and their high-pressure equivalents (Williams and Hemley 2001). Although these minerals do not contain OH groups in their formulas, they can dissolve traces of OH as point defects (Hirschmann 2006). Investigations of natural samples suggest that these minerals may represent a major reservoir of water in the Earth (e.g. Rossman and Smyth 1990; Skogby et al. 1990; Smyth et al. 1991; Bell and Rossman 1992a, 1992b; Rossman 1996; Bell et al. 2003). Pyrope occurs commonly in nature both as a metamorphic mineral and as a high-pressure phase, which is stable under upper mantle conditions (Leitner et al. 1980), and it is probably also important in the mantle-transition zone (420-670 km) depth phases (Duffy and Anderson 1989). Furthermore, previous studies also predicted that pyrope could incorporate significant amounts of water as hydroxyl (e.g. Bell and Rossman 1992b; Bell et al. 1995; Beran and Libowitzky 2006). Therefore, using the newly-determined thermoelastic properties of hydrous pyrope in our present study, we calculated the density profiles of the major upper-mantle minerals.

We used high-temperature BM-EoS to calculate the densities of the following constituent minerals at conditions corresponding to the upper mantle: olivine ($(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$) (Liu and Li

2006), orthopyroxene (MgSiO_3) (Shinmei et al. 1999), clinopyroxene (omphacite- $\text{Di}_{63}\text{Jd}_{37}$; $\text{Di}=\text{Ca}(\text{Mg,Fe})\text{Si}_2\text{O}_6$, $\text{Jd}=\text{NaAlSi}_2\text{O}_6$) (Nishihara et al. 2003), anhydrous pyrope ($\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) (Zou et al. 2012), and hydrous pyrope ($\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) (this study). As shown in previous studies, orthopyroxene with the space group *Pbca* transforms to high-pressure *C2/c* clinoenstatite at the relevant pressure and temperature conditions of the upper mantle (e.g. Shinmei et al. 1999; Bromiley G and Bromiley F 2006; Yu and Wentzcovitch 2009; Finkelstein et al. 2015). Therefore we used the thermoelastic parameters determined for *C2/c* clinoenstatite by Shinmei et al. (1999) in our calculations. In addition, the effect of iron incorporation on the elastic/thermoelastic properties of pyrope was studied experimentally (e.g. Lu et al. 2013; Huang and Chen 2014), and indicated that incorporation of a small amount of iron (about 25 %) in pyrope increases the pressure derivative of the bulk modulus by 7%, but has a negligible effect on other thermoelastic parameters (Lu et al. 2013). The upper-mantle garnet is mainly composed of pyrope with 6~23% iron substituting for magnesium (Richwood et al. 1968; Lee 2003), which has a smaller iron component than the iron-bearing pyrope sample used in the study by Lu et al. (2013). Thus in our calculations, we assumed that the incorporation of a small amount of iron (<25 %) has little effect on the thermoelastic properties of pyrope.

Figure 8 shows the density-profiles of the constituent minerals for the Earth's upper mantle region between a 200 and 400 km depth along a normal continental geotherm (Katsura et al. 2010). The PREM density-profile (Dziewonski and Anderson 1981) is also shown in Fig. 9 for comparison. Compared with the modeled densities of anhydrous pyrope (Zou et al. 2012) at the P-T conditions of the upper mantle, our results show that the hydrogen effect on thermoelasticity of pyrope leads to a ~1% decrease in the density. In addition, the density profiles of olivine, orthopyroxene, and clinopyroxene are also modeled using existing results on their thermoelasticity parameters (Liu and Li 2006; Shinmei et al. 1999; Nishihara et al. 2003). The density profile of hydrous pyrope is ~6% higher than the PREM density profile, but closer to the PREM than the anhydrous pyrope density profile. Furthermore, the density profile of orthopyroxene is ~1.5% higher than the PREM density profile, whereas the density profiles of olivine and clinopyroxene are very close to the PREM density profile.

To better understand the density profiles and mineralogical models of the upper mantle, we also modeled the density profiles of two representative upper-mantle mineral assemblages, piclogite

and pyrolite, using the updated thermoelastic properties of hydrous pyrope for the Earth's upper mantle region between 200 and 400 km depth (Fig. 9). The pyrolite and piclogite models represent two global mineral compositions of the upper mantle that are commonly used for comparison between mineral physics results and global density profiles (Lu et al. 2013). The mineral assemblage in pyrolite model includes ~63% olivine, ~15% garnet, ~16% clinopyroxene, and ~6% orthopyroxene, whereas the piclogite model includes ~43% olivine, ~15% garnet, ~36% clinopyroxene, and ~6% orthopyroxene (Ita and Stixrude 1992). Here we made two assumptions: first, the chemical compositions of the constituent minerals do not change in this P-T range, which results in constant zero-pressure densities of the constituent minerals; and second, the volume proportions of the constituent minerals of piclogite and pyrolite models are constant. The results are shown in Fig. 9 and Fig. 10, and the PREM density profile is also shown in these figures for comparison. Fig. 9 shows that the piclogite and pyrolite models with hydrous pyrope match very well with each other, however, the modeled density profiles of both the piclogite and pyrolite models with hydrous pyrope are ~1.5% higher than the PREM density profile (Fig. 9). Fig. 10 shows the density profiles of pyrolite with hydrous pyrope and pyrolite with anhydrous pyrope at Earth's upper mantle region between a 200 and 400 km depth. The density profiles of both are higher than the PREM density profile, but the density profile of pyrolite with hydrous pyrope is slightly closer to the PREM density profile than pyrolite with anhydrous pyrope, which shows that hydrogen in pyrope can decrease the density of the pyrolite model towards the PREM. Furthermore, considering that the volume proportion of pyrope in the piclogite and pyrolite models is relatively small compared with olivine and pyroxene, incorporating water into the olivine and pyroxene of the upper mantle may make the density profiles of the pyrolite and piclogite models match the PREM density profile well. This once again proves that the nominally anhydrous mineral phases in the Earth's upper mantle (olivine, pyroxene, and garnet) can contain a significant amount of hydrogen. However, this still needs to be confirmed by measuring the thermoelasticity of all major hydrous upper mantle minerals at relevant P-T conditions in future experiments.

5. Conclusions

Incorporating 900 ppmw of water in pyrope crystal yields a reduction in its bulk modulus of 7%, a slight increase in its bulk modulus pressure derivative and thermal expansion coefficient, but little change in its bulk modulus temperature derivative. The presence of water in pyrope helps to reduce the densities of the pyrolite and piclogite models to better match the density profile of the PREM. Incorporating water in olivine and pyroxene is favorable for reconciling the discrepancy in the density profiles between the mineral physics models and the seismological model (PREM).

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Fig. 1 FTIR spectra of synthetic pyrope garnet for the wave-number range of 3300-3750cm⁻¹

Fig. 2 Le Bail profile fitting of the hydrous pyrope diffraction profiles at 13.21 GPa and 900 K. Observed spectra (black line), fitted spectra (red solid line), difference plot (blue solid line) and Bragg peak positions (tick marks) are shown. (Color online)

Fig. 3 Volume compression of hydrous pyrope at high pressure and room temperature from single-crystal X-ray diffraction experiments compared with the powder X-ray diffraction experiments in this study. The third-order BM EoS fitted with K_0 and K'_0 are 161 GPa and 5.0 for hydrous pyrope. The error bars of the data points are smaller than the symbols.

Fig. 4 Volume Eulerian strain-normalized pressure ($F_E f_E$) plot of hydrous pyrope. The solid line represents the linear fit through the data.

Fig. 5 Unit-cell volume of hydrous pyrope as a function of pressure and temperature. The solid lines represent the isothermal compression curve from fitting the HTBM EoS at 300, 500, 700, 900 K with the following parameters: $K_0=162\pm1$ GPa, $K'_0=4.9\pm0.2$, $(\partial K_0/\partial T)_P=-0.018\pm0.004$ GPaK⁻¹ and $\alpha_0=(3.19\pm0.10)\times10^{-5}$ K⁻¹. The error bars of the data points are smaller than the symbols.

Fig. 6 Thermal pressure of hydrous pyrope verses temperature. Solid circles are the hydrous pyrope data in this study. The solid line is the fitting results using a thermal pressure approach.

Fig. 7 Variations of thermal pressure with the unit-cell volume at various temperatures. The dashed lines correspond to the constant values of thermal pressure for a given temperature. The data indicates that $(\partial K_T/\partial T)_V$ is close to zero.

Fig. 8 Calculated density profiles of constituent minerals in the upper mantle between 200 and 400 km. Anhydrous pyrope (black solid line), Hydrous pyrope (red solid line), Olivine (blue solid line), Opx (magenta solid line), Cpx (olive solid line). The PREM density profile is also shown (dashed line).

Fig. 9 Calculated density profiles of piclogite and pyrolite models. In these calculations, the zero-pressure densities and mineral proportions of the constituent minerals are assumed to be constant. The PREM density profile is also shown (dashed line).

Fig. 10 Calculated density profiles of pyrolite models with hydrous pyrope and with anhydrous pyrope. In these calculations, the zero-pressure densities and mineral proportions of the constituent minerals are assumed to be constant. The PREM density profile is also shown (dashed line).

Table 1 Unit cell parameters of hydrous pyrope from single-crystal X-ray diffraction data at high pressure and room temperature

P (GPa)	V ($\text{\AA}^3$)
0.0001	1505.24(8)
0.45(3)	1500.52(7)
1.32(11)	1492.75(8)
2.28(37)	1484.54(8)
3.44(28)	1474.38(9)
4.73(36)	1463.56(8)
5.62(47)	1457.87(10)
6.47(38)	1451.35(8)
7.59(43)	1442.13(10)
8.73(52)	1433.85(9)
9.81(48)	1427.22(10)

Numbers in parenthesis represent standard deviations.

Table 2 Unit cell parameters of hydrous pyrope from powder X-ray diffraction data at various pressure-temperature conditions

P (GPa)	T (K)	V ($\text{\AA}^3$)	P (GPa)	T (K)	V ($\text{\AA}^3$)
Compression before heating			9.38(58)	500	1438.79(83)
0.0	300	1505.53(64)	11.28(66)	500	1425.85(75)
1.46(22)	300	1492.13(76)	13.44(54)	500	1410.82(78)
5.59(51)	300	1457.56(86)	15.26(62)	500	1399.73(85)
7.85(37)	300	1441.26(82)	2.46(54)	700	1501.16(86)
9.64(48)	300	1428.62(85)	4.52(59)	700	1484.16(78)
Compression after heating			6.77(33)	700	1466.09(86)
0.12(1)	300	1504.28(92)	8.45(45)	700	1453.06(92)
2.52(32)	300	1482.26(85)	10.28(52)	700	1439.25(81)
4.11(47)	300	1469.09(84)	12.49(54)	700	1424.36(76)
6.63(57)	300	1449.75(74)	14.55(63)	700	1411.26(79)
8.83(63)	300	1434.26(87)	16.03(47)	700	1402.62(84)
10.65(58)	300	1422.08(84)	2.98(56)	900	1506.36(77)
12.15(55)	300	1411.87(88)	5.33(46)	900	1486.09(83)
13.66(28)	300	1402.09(75)	7.42(58)	900	1469.75(84)
14.81(37)	300	1395.10(92)	9.37(52)	900	1454.95(77)
1.55(15)	500	1500.13(86)	10.79(45)	900	1444.35(83)
3.28(24)	500	1484.66(83)	13.21(36)	900	1427.76(78)
5.44(33)	500	1467.09(87)	15.44(45)	900	1413.76(82)
7.56(45)	500	1450.83(76)	16.75(64)	900	1406.12(87)

Numbers in parenthesis represent standard deviations

Table 3 Bulk modulus and its pressure derivative of dry pyrope and hydrous pyrope

Sample	K_0 (GPa)	K'_0	V_0 (Å ³)	Methods	Reference
Hydrous Pyrope	167(1)	4.0 ^a	1505.04(29)	Powder-XRD	This study
Hydrous Pyrope	161(2)	5.0(3)	1505.35(25)	Powder-XRD	This study
Hydrous Pyrope	166(2)	4.0 ^a	1504.58(32)	Single crystal-XRD	This study
Hydrous Pyrope	160(3)	5.2(4)	1505.14(38)	Single crystal-XRD	This study
Dry Pyrope	172.8	3.8(1)	1503.87	Powder-XRD	Leger et al. (1990)
Dry Pyrope	169.2(2)	4.4 ^a	1503.2	Powder-XRD	Du et al. (2015)
Dry Pyrope	175(1)	4.5(5)	1503.4(5)	Single crystal-XRD	Levien et al. (1979)
Dry Pyrope	171(2)	4.4(2)	1502.9(3)	Single crystal-XRD	Zhang et al. (1998)
Dry Pyrope	171.32(2)	3.22	—	BLS	Conrad et al. (1999)
Dry Pyrope	171.2(20)	4.1(3)	—	BLS	Sinogeikin and Bass (2000)
Dry Pyrope	174.9(16)	4.7(3)	—	BLS	Jiang et al. (2004)
Dry Pyrope	171(2)	5.3(4)	—	UI	Chen et al. (1999)
Dry Pyrope	170.1(11)	4.9(6)	—	UI	Wang and Ji (2001)

XRD, X-ray diffraction; BS, Brillouin Light Scattering; UI, Ultrasonic interferometry

Numbers in parenthesis represent standard deviations

^a Fixed during fitting

Table 4 Thermoelastic parameters of hydrous pyrope using the HTBM equation of state compared with dry pyrope

Sample	$V_0(\text{\AA}^3)$	$K_0(\text{GPa})$	K'_0	$(\partial K/\partial T)_P (\text{GPaK}^{-1})$	$\alpha_0 (10^{-5}\text{K}^{-1})$	Reference
Dry pyrope	1503.1(5)	170(2)	5.0 ^a	-0.020(3)	2.58(28)	Wang et al. (1998)
Dry pyrope	—	169(2)	—	-0.019(3)	—	Sinogeikin and Bass (2002)
Dry pyrope	1502.5	172(4)	3.9 ^a	-0.026(2)	—	Gwanmesia et al. (2006)
Dry pyrope	1500.4(15)	167(3)	4.6 ^a	-0.021(9)	2.89(33)	Zou et al. (2012)
Dry pyrope	1502.8(4)	—	—	—	2.74(5)	Du et al. (2015)
Hydrous pyrope	1505.38(27)	162(1)	4.9(2)	-0.018(4)	3.19(10)	This study
Hydrous pyrope	1505.22(28)	168(1)	4.0 ^a	-0.017(5)	3.06(9)	This study

Numbers in parenthesis represent standard deviations

^a Fixed during fitting