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ABSTRACT

The thermo-elastic behaviour of synthetic single crystals of grossular garnet ($Ca_3Al_2Si_3O_{12}$) 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*) datasets in order to make the measurements consistent with one another. The consistency between the two datasets 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 *P-V-T and P-K-T* data using a thermal pressure Equation of State combined with any PV EoS. Simultaneous refinement of our *P-V-T* 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) Å^3, K_{T0} = 166.57(17) GPa and $K`$ = 4.96(7) $\alpha_{(300K, 1bar)}$ = 2.09(2)*10^{-5} K^{-1} with a refined Einstein temperature (θ_E) of 512K for a Holland-Powell-type thermal pressure model and a Tait 3rd-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 fit, EosFit

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52   **1. INTRODUCTION**

53   Stable over a wide range of pressure and temperature conditions, garnets are among the most

54   abundant phases in the Earth's upper mantle and transition zone. Yet coherent and homogeneous

55   equation of state coefficients to reliably describe their behaviour at simultaneous high pressures and

56   temperatures still have to be determined with sufficient accuracy and precision. Recent papers have

57   shown the importance of a robust and valid description of the elastic behaviour of the most

58   abundant mineral phases for the accurate calculation of host-inclusion entrapment pressures that in

59   turn allow the growth conditions in the Earth to be inferred (e.g. Angel et al. 2014, 2015a, 2015b;

60   Ashley et al. 2015; Milani et al. 2015). However, the determination of a full set of elastic

61   coefficients of a mineral is always challenging because of the limitations in performing

62   simultaneous high-pressure (P) and temperature (T) experiments on one side and because of the

63   lack of consistent measurements performed separately at high-P and high-T. Therefore, a reliable

64   description of the elastic behaviour of minerals at high-P,T with a single set of Equation of State

65   (EoS) coefficients can be extremely challenging.

66   Pressure-volume EoS are well-developed and are capable of reproducing the isothermal

67   volume or density changes of materials to within the experimental uncertainties. A natural approach

68   to describing the P-V-T behaviour of a material is therefore to describe how the volume (V_{0T}), bulk

69   moduli (K_{0T}[1]) and its pressure derivatives (K_{0T}') change with increasing temperature (at room

70   pressure), and then use these parameters to calculate the isothermal compression at the temperature

71   of interest. A potential limitation of this approach is that while the variation of K_{0T} with T can be

72   measured, the variation of K_{0T}' with T has been measured very rarely, although it is obvious that it

73   should increase slightly with increasing temperature. As Helffrich and Connolly (2009) pointed out,

74   the common assumption that K_{0T}' does not change with temperature in combination with the

75   approximation that $\partial K_{0T}/\partial T$ is constant, often leads to the prediction of non-physical negative

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[1] Notation: subscripts on K (e.g. $K_{P,T}$) 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.

76   thermal expansion coefficients at reasonably modest pressures for a large number of materials. An

77   alternative approach is to employ the idea of thermal pressure (e.g. Anderson 1995). Then the total

78   pressure (P) at a given V and T can be expressed as the sum of two terms:

79    $$P(V,T) = P(V,T_{ref}) + Pth(T)$$

80   The function $P(V,T_{ref})$ is the isothermal equation of state for material at the reference temperature,

81   up to the volume at P and T_{ref}. As shown in the Figure 1, if $T > T_{ref}$, then $P(V,T_{ref}) < P(V,T)$. The

82   thermal-pressure $Pth(T)$ is the pressure that would be created by increasing the temperature from

83   T_{ref} to T at constant volume, which is the isochor of the material passing through the final P,T point

84   of interest. As shown in Figure 1, the concept of thermal pressure is therefore essentially a way of

85   calculating $P(V,T)$ along a different path in P-T space. We can consider that the isothermal

86   compression part that gives us $P(V,T_{ref})$ is well-defined. The slope of the isochor is given by

87    $\left(\dfrac{\partial P}{\partial T}\right)_V = \dfrac{\alpha}{\beta} = \alpha K^T$ (where α is the volume thermal expansion and β is the compressibility of the

88   material) so the thermal pressure is $Pth = \int_{Tref}^{T} (\alpha K^T)_V \, dT$. In order to use a thermal-pressure EoS one

89   then has to know, or to make an assumption, about how the product αK^T varies along the isochor.

90   For many materials and P,T ranges of interest (e.g. Figure 1) the temperatures are in the region of

91   the Debye temperature, so the isochor is linear and thus αK_T is a constant. In this case

92    $Pth \sim (\alpha K^T)_V (T - Tref)$.

93   A number of other assumptions or models of the behaviour of the material can be made,

94   including the Debye and similar models which make assumptions about the vibrational and hence

95   thermal behaviour of materials. Holland and Powell (2011) noted that the form of αK^T against

96   temperature should have the shape of a heat capacity function and developed an approximation for

97   the integral of αK^T that involves an Einstein function, as follows:

$$Pth = \alpha_0 K_{00} \left(\frac{\theta_E}{\xi_0} \right) \left(\frac{1}{\exp\left(\theta_E / T\right) - 1} - \frac{1}{\exp\left(\theta_E / T_{ref}\right) - 1} \right)$$

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99   with ξ_0 being the same as in the thermal expansion equation of Kroll et al. (2012). This thermal-

100   pressure model has the physically-correct properties that the product αK^T becomes constant at high

101   temperatures while it decreases to zero at low temperatures. This means that both the bulk modulus

102   K_{0T} and the thermal expansion become constant at low temperatures, and both have an

103   approximately linear variation with temperature above θ_E. The exact expressions for thermal

104   expansion and bulk modulus as a function of temperature depend on the choice of isothermal

105   equation of state, but at T_{ref} and zero pressure $\alpha = \alpha_0$ (Holland and Powell 2011). In this study we

106   used the Holland and Powell (2011) model of thermal pressure in combination with the Tait

107   isothermal EoS (so as to maintain compatibility with Thermocalc, Holland and Powell 2011) to

108   determine the EoS of grossular ($Ca_3Al_2Si_3O_{12}$) garnet. We show that the thermal pressure approach

109   allows the full P-V-T EoS to be determined by fitting simultaneously measurements of the volume

110   and bulk modulus over a range of temperature but only at room pressure. Additional separate

111   measurements of the volume compression curve at high-P can be used to provide either an

112   independent test of the EoS parameters, or be used to further constrain them in simultaneous global

113   fits of all available data. This approach has the advantage of not requiring data from simultaneous

114   high-P, high-T measurements which remain challenging with respect to both the control and

115   accurate measurement of P and T, and with respect to the precision in volume measurements. A

116   comparison with previous literature data (e.g. Skinner 1956; Isaak et al. 1992; Thieblot et al. 1998;

117   Kono et al. 2010; Gwanmesia et al. 2014; Du et al. 2015 etc..) is provided together with a further

118   crosscheck of our experimental data against the results obtained by density functional theory (DFT)

119   ab-initio simulation. Thermodynamic properties of grossular have been calculated for the first time

120   from crystal Helmholtz and Gibbs energies, including the contribution from phonons, using density

121   functional theory within the framework of the quasi-harmonic approximation.

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2. METHODS

2.1 Sample synthesis and characterization

Synthetic single crystals of pure end-member grossular (Gr_{100}) garnets were synthesized at high pressures with a multi-anvil apparatus at the Bayerisches Geoinstitut. Stoichiometric mixtures of CaO (prepared by decarbonation of $CaCO_3$), $Al(OH)_3$ and SiO_2 were packed into platinum capsules of 3.5 mm length and 2 mm diameter. Samples were synthesized at 6 GPa and 1300°C. The experimental sample was heated in 23 mins and the temperature was kept at 1300°C for 40 mins. Each multi-anvil experiment was performed with Cr-doped MgO octahedra of 18 mm edge length combined with tungsten carbide cubes of 11 mm truncation-edge lengths. For all the experiments a graphite heater was employed. Experiments were quenched by cutting the electrical power supply to the furnace. Single-crystals of up to ca. 100 μm in diameter were recovered from the capsules. The compositions of the crystals have been determined by electron microprobe at the University of Padova using a Cameca CAMEBAX-micro operating at 15 nA and 15 kV with standards of andradite for Si, spinel for Al and diopside for Ca. Results from the chemical analyses are reported in Table 1. Two crystals (with size ca. 80 x 30 x 30 μm) were selected for the X-ray diffraction study based on the absence of twinning and visible inclusions and on the quality of their diffraction peak profiles (FWHM not greater than 0.15°).

2.2 Thermal expansion behaviour by single crystal X-ray diffraction experiments

The high-temperature single-crystal X-ray diffraction experiments were performed at the University of Pavia with a HUBER four-circle point detector diffractometer operating at 50 kV and 30 mA (Mo*Kα* radiation) and equipped with a 0.8 mm short collimator and automated with the SINGLE software (Angel and Finger 2011). This diffractometer is equipped with a newly designed

148   micro-furnace controlled by a Eurotherm temperature regulator (Alvaro et al. 2015). For the high-T

149   experiments, one single crystal of grossular was placed inside a thin-walled quartz vial (0.3 mm

150   inner diameter and 26 mm long) and held in position by means of quartz wool. The vial was then

151   mounted on a metal goniometer head on the diffractometer. During the high-temperature

152   experiments the effects of the crystal offsets and the diffractometer aberrations were compensated

153   by using the eight-position centring method (King and Finger 1979) before starting the high-T

154   measurement. The unit-cell parameters (Table 2 and Figure 2) were determined at 23 different

155   temperatures from room-T up to 1020 K using only 4-position centring because of the spatial

156   restrictions described in Alvaro et al. (2015). A further 7 measurements were then made on cooling

157   back to room temperature. Each individual measurement took about 12 hours, and the high-

158   temperature experiment lasted for a total of 14 days. Unconstrained unit-cell parameters confirmed

159   the cubic symmetry within 1 e.s.d. Therefore, only constrained unit-cell parameters obtained by

160   vector least-squares fit (Ralph and Finger 1982) are reported in Table 2. Unit-cell parameters

161   determined on the heating and cooling cycles are indistinguishable.

162   The low-temperature single-crystal X-ray diffraction experiment was performed on the very

163   same crystal used for the high-T experiment still mounted inside its quartz vial. The experiment was

164   carried out at the Institut für Mineralogie und Kristallographie at the University of Wien using a

165   Stoe StadiVari diffractometer equipped with an Incoatec IμS microsource (Mo-target, with multi-

166   layer mirror optics, operating at 50kV and 0.1mA) and a Pilatus 300K area detector. Low

167   temperatures were achieved using an Oxford Cryojet system that allows measurements to be

168   performed between 100 and 500 K. Full intensity data collections up to 110° 2θ (with a coverage of

169   99% and redundancy higher than 4) were performed at 10 different temperatures from room-T down

170   to 100 K. Correction of the crystal offsets from the goniometer center were made by first

171   performing a short data collection and adjusting the crystal position to make the frame scale factors

172   flat. Unconstrained unit-cell parameters confirmed the cubic symmetry within 1 e.s.d.; therefore,

173   only constrained unit-cell parameters are reported in Table 2 and Figure 2 together with those

174   obtained at high-*T*.

175

176   *2.3 Compressibility behaviour by single crystal X-ray diffraction experiments*

177   High-pressure single-crystal X-ray diffraction experiments for the grossular garnet were

178   carried out with a Huber four-circle diffractometer at the Bayerisches Geoinstitut. The

179   diffractometer operates at 50 kV and 40 mA (MoKα radiation), is equipped with a point detector

180   and is automated by SINGLE software (Angel and Finger 2011). The sample was loaded in a ETH-

181   type diamond-anvil cell (DAC, Miletich et al. 2000) using a steel gasket, pre-indented to 100 μm

182   thickness and with a hole diameter of 250 μm. Methanol:ethanol mixture 4:1 was used as pressure

183   transmitting medium, which remains hydrostatic up to about ~ 9.5 GPa (Angel et al. 2007; Klotz et

184   al. 2009). A single crystal of quartz was loaded in the DAC together with the sample and used as a

185   pressure standard (Angel et al. 1997). During the centring procedure, the effects of crystal offsets

186   and diffractometer aberrations were eliminated from the refined peak position by the eight-position

187   centring method (King and Finger 1979). Unconstrained unit-cell parameters were obtained by

188   vector least-squares fit (Ralph and Finger 1982) on not less than 20 reflections up to 2θ = 29°. The

189   symmetry-unconstrained unit-cell edges show deviations smaller than 1 e.s.d. from the constrained

190   ones thus confirming the cubic symmetry within 1 e.s.d.. Therefore, only the constrained unit-cell

191   parameters have been reported in Table 3 and Figure 3.

192

193   *2.4 Fitting of the pressure-volume-temperature-modulus data using EoSFit7c*

194   All fits described in this manuscript have been performed with the EosFit7c program (Angel

195   et al. 2014). Previous versions of this program were able to fit isothermal EoS, thermal expansion

196   models and the thermal-pressure EoS of Holland and Powell (2011) to *P-V*, *V-T* or *P-V-T* data, by

197   the method of least-squares. We have now extended the capabilities of EosFit-7c to also fit all of

198   these forms of EoS to bulk and linear moduli, either alone or in combination with volume or unit-

199   cell parameter data. Fits are performed by weighted non-linear least squares to minimise the

200   residuals P_{obs}-P_{calc}, using the effective variance method (Orear 1982) to convert the experimental

201   uncertainties in volume and bulk moduli, pressure and temperature of each datum into an effective

202   uncertainty in P (Angel 2000). Input bulk moduli can be either adiabatic (K^S) or isothermal values

203   (K^T), but in either case they must be Reuss values, corresponding to the response of the material

204   under hydrostatic pressure. The Voigt and Reuss bulk moduli of a material quantify its volume

205   response to the application of uniform strain and uniform stress (hydrostatic pressure) respectively.

206   When uniform stress is applied to a cubic material, it undergoes isotropic (i.e. uniform) strain.

207   Therefore, the Voigt and Reuss bulk moduli of a cubic material are identical. We remind the reader

208   that this is not true for materials of lower symmetry and therefore the use of Voigt values, or Voigt-

209   Reuss-Hill averages, in Equations of state of crystals with symmetry lower than cubic is

210   inconsistent with the theory underlying equations of state under hydrostatic conditions, and will

211   lead to incorrect results (e.g. Angel et al. 2009).

212   If the input moduli to EosFit7c are isothermal, no further conversion is made, and the

213   observational equations for such data in the least-squares are simply the expression for the bulk

214   modulus in terms of pressure for each EoS. These expressions are direct for invertible EoS such as

215   the Murnaghan or Tait EoS (Freund and Ingalls 1989; Holland and Powell 2011; Angel et al. 2014).

216   For non-invertible EoS the procedure used is to calculate the compression ratio V/V_{00} corresponding

217   to the observed K and then use the P-V expression of the EoS to calculate the corresponding

218   pressure. If adiabatic moduli are provided as input data, they are converted to isothermal values by

219    $K^S = (1 + \alpha_V \gamma T) K^T$ where the value of thermal expansion (α_V) is taken from the current EoS at the

220   pressure and temperature of interest. The Grüneisen parameter γ can be expressed in terms of

221   measurable quantities, for example $\gamma = \dfrac{\alpha_V K^S}{C_p} = \dfrac{\alpha_V K^T}{C_V}$. However, since heat capacity data is not

222   available at elevated pressures, in EosFit7c we use the simple approximation (Anderson 1996) that

223    $\gamma(P,T) = \gamma_0 \left(\dfrac{V(P,T)}{V_0} \right)^q$, with the value of q close to 1 for 'normal' solids under modest P,T

224   conditions. Only Boehler and Ramakrishnan (1980) and Boehler (1982) appear to have attempted to

225   measure the value of q, showing that it scales with volume. This means that the Grüneisen

226   parameter scales with volume, increasing with increasing temperature and decreasing upon

227   compression, which when considered as a measure of the pressure-dependence of the frequencies of

228   vibrational modes, is reasonable. This will break down when the material becomes very

229   anharmonic, near to structural phase transitions, but should not be a problem for materials such as

230   the grossular garnet in this study. The value of γ_0 (i.e. γ value at the reference conditions) and of q

231   can be set by the user in Eosfit7c.

232   For linear moduli that describe the variation of the unit-cell parameters with pressure as

233     $M_i^T = -a_i \dfrac{\partial P}{\partial a_i}$, the procedure is analogous to that used for linear dimensions in EosFit7 (Angel et

234   al., 2014). Internally the linear moduli are converted to volume-like bulk moduli as $K_i = \dfrac{M_i}{3}$ and

235   treated with volume EoS. For the conversion of adiabatic to linear moduli, we use the relationship

236   between isothermal and adiabatic compressibilities $\beta_i^T = \beta_i^S + \dfrac{\alpha_i \alpha_V T}{C_p}$ which can be derived from

237   the fundamental relationship between isothermal and adiabatic elastic compliances

238     $s_{ijkl}^T = s_{ijkl}^S + \dfrac{\alpha_{ij} \alpha_{kl} T}{C_p}$ with the C_p in units of Jm^{-3}K^{-1} (Nye 1985). The substitution $\dfrac{\gamma}{K^S} = \dfrac{\alpha_V}{C_p}$ gives

239     $\beta_i^T = \beta_i^S + \dfrac{\alpha_i \gamma T}{K^S} = \beta_i^S \left(1 + \dfrac{\alpha_i \gamma T \beta_V^S}{\beta_i^S}\right)$ which can be rewritten in terms of moduli as

240     $M_i^S = \left(1 + \alpha_i \gamma T \dfrac{M_i^S}{K^S}\right) M_i^T$. It is important to notice that for cubic materials $\alpha_i = \alpha_V/3$ and $\dfrac{M_i^S}{K^S} = 3$

241   so that only for cubic materials this can be written as $M^S = (1 + \alpha_v \gamma T) M^T$ which is the same

242   relation as for the bulk moduli.

243

244   *2.5 Ab-initio DFT (Density Functional Theory)*

245   Ab-initio calculations have been performed in order to crosscheck our experimental results at

246   simultaneous high-*P* and *T*. Thermodynamic properties of grossular have been calculated from

247   crystal Helmholtz and Gibbs energies, including the contribution from phonons, using density

248   functional theory (DFT) within the framework of the quasi-harmonic approximation (QHA).

249   Periodic DFT calculations were performed with the plane-wave VASP package (Kresse and

250   Furthmüller 1996) within GGA approximation, with projector-augmented waves (PAW, Blöchl

251   1994) and the PBEsol functional (Perdew et al. 2008). A plane-wave cutoff of 520 eV (1.3 x default

252   VASP value) was used as recommended in the VASP package. Energy convergence was tested for

253   two k-meshes 2x2x2 and 4x4x4. Since the denser mesh did not lead to any significant reduction in

254   energy (ΔE<0.001 eV) the 2x2x2 mesh was used both for unit cell optimization and subsequent

255   calculation of interatomic forces. The cell was optimized at 17 pressure points within the range [-8

256   to 8GPa] with step of 1 GPa. The threshold for electronic and ionic convergence was set to 10^{-8} and

257   10^{-6} eV, respectively. The atomic forces were converged to 10^{-5} eV/Å. Phonon frequencies at

258   constant cell volumes were calculated in program PHONOPY (Togo and Tanaka 2015) which takes

259   advantage of the direct method of Parlinsky et al. (1997). The force constants used to construct the

260   dynamical matrices (input for PHONOPY) were calculated in the VASP package using density

261   functional perturbation theory (DFPT, Baroni et al. 2001) and taking into account symmetries of the

262   conventional body-centered cell of the garnet, containing 160 atoms. The results obtained with

263   DFT-GGA commonly overestimate cell volume values of ionic solids by up to 9.5% with respect to

264   experimental results while PBEsol functional brings the discrepancy down to 2% (Perdew et al.

265   2008). In our case, the DFT calculations yielded volume values of 1664.6 Å^3 (static DFT), 1681.9

266   Å^3 (zero-point vibration included) and 1687.3 Å^3 (T=290 K) which agree with experimental values

267   of 1664.3 Å at room *P* and *T*, (0.0001 GPa and 300 K) within 0.0 %, 1.1% and 1.4% respectively.

268   This volume overestimation amounts to about -2 GPa, on the pressure scale, with respect to the

269   experimental datum.

270

271   **3. RESULTS**

272   *3.1 Temperature-volume data*

273   The room-*PT* unit-cell volumes (V_{00}) of grossular as determined in this study, agree with one

274   another to better than 1 e.s.d. thus confirming the reliability of the unit-cell lattice determination

275   with different instruments and measurement protocols. Therefore, we combined the high-*T*

276   measurements together with those at low-*T* in a single dataset without any normalization or re-

277   scaling. The evolution of the unit-cell volume with temperature is reported in Figure 2 and Table 2

278   where the low-*T* and the high-*T* data are reported together. A continuous increase of the unit-cell

279   volume is observed as a function of temperature with no evidence of any irreversible change in the

280   crystal occurred up to the maximum temperature reached in this study. Data collected both with

281   increasing and decreasing temperature overlap within experimental error, thus indicating good

282   experimental reproducibility. The temperature-volume data for the entire range of *T* studied were fit

283   using the software EoSFit7c (Angel et al. 2014) using a Kroll-type EoS (Kroll et al. 2012) allowing

284   for refinement of the Einstein temperature (θ_E) but not refining K′ value that was kept fixed to 5

285   (i.e. the value from compressibility data, see the following sections). The thermal expansion

286   coefficients obtained were $\alpha_{(298K,\ 1bar)}$ = 2.08(2)*10^{-5} K^{-1}, V_{00} = 1664.45(7) Å^3 with θ_E= 515(20) K.

287   We compared our *T-V* for grossular with those from Isaak (1992) determined by dilatometry. Isaak

288   et al. (1992) measured physical expansions, and converted such values to volume expansions

289   Yv(obs). Conversion of Isaak et al. (1992) data (taken from their Table 2) to unit-cell volumes has

290   been performed according to $V = V_0\left(1 + Y_V obs\right)$. In order to ensure that our measurements and those

291   by Isaak et al. (1992) were on the same volume scale we used our V_{00} at the same reference

292   temperature of 293K used by Isaak et al. (1992). A plot of the two datasets (see Figure 2) shows

293   that they agree within their mutual uncertainties.

294

295   *3.2 Temperature-volume-bulk modulus data*

296   Isaak et al. (1992) also determined the adiabatic bulk modulus of grossular by RUS

297   measurements and then used measured heat capacity data and their own thermal expansion data to

298   also calculate the isothermal bulk modulus at each measurement temperature by means of

299    $K^S = (1 + \alpha_V \gamma T) K^T$, using the value of the Grüneisen parameter $\gamma = \dfrac{\alpha_V K^S}{C_p}$. The reliability of the

300   heat capacity (C_p) data by Isaak et al. (1992) has been confirmed by comparison with the more

301   recent data by Bosenick et al. (1996) (see Figure 4). The C_p values determined by Isaak et al. (1992)

302   fall well within the scatter of the data determined by Bosenick et al. (1996) and are also in good

303   agreement with those we have obtained from the DFT calculations.

304   Using K and V data as a function of T it is obviously possible to refine V_{00}, α_0, θ_E and K_{00}. But

305   in addition it is possible and required to refine K' because this affects the results when using the

306   thermal pressure model as it appears in the isothermal EoS $P(V, T_{ref})$, and at room pressure

307    $P(V, T_{ref}) = -Pth(T)$. Simultaneous refinement of our T-V data and the T-K^S data from Isaak et al.

308   (1992) for grossular using γ_0=1.22 and q=0 (i.e. γ=$\gamma0$) yielded identical results as to those obtained

309   from fitting the T-V-K^T data (see Table 4[2]). This shows that the assumption that γ is constant is a

310   reasonable approximation for grossular. This observation is also in agreement with Isaak et al.

311   (1992) who calculated that γ drops by 0.1($\pm$ 0.05) over the temperature range from 300K to 1200K

312   and with our results from DFT calculations as shown in Figure 4 according to which γ drops to 1.24

313   at 650K and then it assumes constant values (e.g. changes of about 2 at the 3rd decimal place) above

314   650K.

315

316   *3.3 Pressure-volume data*

317   The unit-cell volume decreases smoothly with increasing pressure, as shown in Figure 3 and

318   reported in Table 2, up to the maximum hydrostatic pressure reached in this study of ~7.5 GPa.

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[2] The Equation of State coefficients reported in Table 4c representing the best fit of our data have been deposited as supplementary material in the form of .eos files (that can be read with EoSFit7c). They are also available directly from the authors.

319 Such pressure covers the stability pressure range for upper mantle garnets. Fit of the *P-V* data alone

320 using a 3rd order Tait EoS yielded the following coefficients: V_{00} = 1664.36(7) Å^3, K_{00} =

321 167.45(1.04) GPa and K_{00}` = 4.93(31) also reported in Table 4a. The goodness of the fit results was

322 confirmed by the low ΔP_{max} value (calculated as $|P_{obs} - P_{calc}|$) of 0.010 GPa. The equation of state

323 coefficients obtained with this method agree with those obtained by *T-V-K* fitting to better than 1

324 e.s.d. thus confirming the reliability of the results from the two fitting approaches.

325

326 *3.4 P-V-T-K and PVT Equation of State*

327   The remarkably good agreement between the lattice parameters as determined with different

328 experimental settings and that of the EoS coefficients obtained with different procedures allowed us

329 to perform a simultaneous refinement of the entire set of EoS coefficients by combining our

330 pressure-volume and temperature-volume data together with those of temperature-bulk modulus

331 (Isaak et al. 1992) into a single dataset. Fully weighted simultaneous fit of the *P-V-T-K* data has

332 been performed using a thermal pressure Equation of State with a 3rd order Tait EoS, allowing

333 simultaneous refinement of V_{00}, K_{00}, K_{00}', α_0 and θ_E. As expected, the resulting coefficients V_{00} =

334 1664.46(5) Å^3; K_{00}=166.57(17) GPa; K_{00}'=4.96(7); $\alpha_{(298K, 1bar)}$ = 2.09(2)*10^{-5} K^{-1}, with θ_E= 512(19)K

335 (γ_0=γ=1.22) agree within 2 σ to those from *P-V* and *T-V-K* separately (see Table 4). At this point it

336 is important to point out that the main difference between the *P-V-T-K* and *T-V-K* fits can be seen in

337 the description of the bulk moduli as a function of *T* (Figure 5a). It should be clear from Figure 5a

338 that while in the thermal regime between room-*T* and the maximum temperature reached with the

339 experiments the bulk moduli calculated from the *T-V-K* and *P-V-T-K* Equations of State agree

340 within mutual uncertainties, in the low-*T* regime much larger discrepancies are observed. These

341 discrepancies are due to the different values of θ_E in the two EoS.

342   Simultaneous refinement of the *P-V-T* data alone yielded the following coefficients V_{00} =

343 1664.44(6) Å^3; K_{00}=166.19(1.25) GPa; K_{00}'=5.14(40); $\alpha_{(298K, 1bar)}$ = 2.09(2)*10^{-5} K^{-1}, with θ_E= 512K

344 (not refined). Standard deviations on the bulk modulus (K_{0T}) and its first derivative (K') obtained

345 from the *P-V-T* fitting are 6-8 times larger than those from the *P-V-T-K* ones and, when considered,

346 the resulting coefficients from the *P-V-T* fit agree within 1 sigma with those obtained from the *P-V-*

347 *T-K* fits. The *P-V-T* results are not showed in Figure 5a for sake of clarity, however, the resulting

348 bulk moduli as a function of *T* agrees with the experimental data within 1 σ.

4. DISCUSSION

350 *4.1 Thermal expansion: comparison with literature data*

351   The measured room temperature-pressure volumes (V_{00}) reported in this study are in good

352 agreement with those previously reported in literature by several authors (see Table 4a and b). So

353 far, only few X-ray diffraction thermal expansion data are available for grossular garnet (e.g.

354 Skinner 1956; Bosenick and Geiger 1997; Thieblot et al. 1998; Du et al. 2015) and most of them

355 have been obtained by means of powder X-ray diffraction. Data from Du et al. (2015) and those by

356 Skinner (1956) have been re-fitted to their entire temperature range 296 K - 859 K (excluding two

357 outliers at 393 K and 477 K) and 284 K -980 K, respectively. On the other hand, data from Thieblot

358 et al. (1998) have been fitted from 300 K to 1453 K (i.e. well below the decomposition temperature)

359 excluding a few outliers at 607 K, 724 K, and 1241 K. The results of all the extrapolations at 300 K

360 are reported in Table 4b and shown Figure 2. As shown in Table 4b, there are considerable

361 differences between our data and those available in literature. These can be most likely ascribed to

362 the compositional differences between the various samples and/or to the uncertainties given by the

363 different experimental methods. For example, both Skinner (1956) and Thieblot et al. (1998) used

364 grossular-rich samples for their investigation. For sake of comparison, regardless the compositional

365 differences, these literature data have been re-fitted to Fei-type EoS (Fei 1995). Results from the

366 fitting are reported in Table 4b, and Figure 2.

367   As shown in Figure 2, our data for the low-*T* regime are in good agreement with those

368 reported by Bosenick and Geiger (1997) if their most scattered data (e.g. 195, 220 and 295 K) are

369 not considered.

370   The thermal expansion coefficients at 300 K from both Skinner (1956) and Du et al. (2015)

371 are smaller than those calculated from our fitting. The discrepancies between our dataset and that by

372 Skinner (1956) could be ascribed to the differences in composition as their sample referred to as a

373 'grossularite' has not been properly characterized. The thermal coefficient value obtained fitting the

374 data by Du et al. (2015) is not reliable as demonstrated by the negative thermal expansion at high-T

375 (regardless of the Equation of State model chosen). The same is true also for the data reported by

376 Thieblot et al. (1998), where the thermal expansion value decreases with increasing temperature.

377 Our datasets, ranging from 100 K to about 1000 K, allowed fitting of a Kroll-type EoS (Kroll et al.

378 2012), leading to a much more reliable description of the thermal behaviour of grossular. The

379 reliability of the Einstein temperatures used (θ_E=569(13) K) have been confirmed by comparison

380 with the saturation temperature (where $T_{sat} \approx \theta_E/2$) obtained from the fitting of the low-T data alone

381 (T_{sat}=270(6) K) using a Salje-type EoS (Salje et al. 1991). The agreement within 1 sigma is also

382 achieved when comparing with the θ_E from the P-V-T-K fit [θ_E=512(19) K, see Table 4c]

383

384 *4.2 Compressibility: comparison with literature data*

385   The elastic coefficients for grossular have been determined in several studies using different

386 methods (e.g. ultrasonic wave velocity, static compression experiments in diamond-anvil cell, ab-

387 initio calculations) as summarised in Table 4a. For purpose of comparison with the literature data,

388 the adiabatic bulk modulii (K^S) obtained by means of ultrasonic wave velocity techniques have been

389 converted to K^T.

390   DFT calculations of a P(V) curve, fitted by a third order Birch-Murnaghan EoS, provide a

391 value of 156 GPa for the bulk modulus K^T at 300K, and a K′ of 4.22. The *static* (no zero point and

392 thermal effects included) and the *athermal* (zero point corrected and a temperature of 0K) values

393 are respectively 163.9 and 160.1 GPa (K′ fixed at 4.22: the value we obtained at 300K). These

394 results are in line with the *standard* performances of DFT-GGA Hamiltonians like PBEsol, as they

395 generally underestimate bulk moduli by about 10 GPa at room temperature. Another DFT study

396 from the literature (Erba et al. 2014) provided a somewhat higher bulk modulus (171 GPa), but that

397 was a result from a static calculation with a hybrid HF/DFT (B3LYP) Hamiltonian which includes

398 an Hartree-Fock correction to the DFT-GGA electronic exchange functional. Indeed, such

399 correction proved to be crucial to compute bulk moduli (and vibrational frequencies) very close to

400 the experimental data (Prencipe et al. 2009, 2011, 2012, 2014), but it is computationally very costly

401 if a plane-wave basis set is used, as in the present case, and therefore it cannot be afforded. The

402 largest discrepancy in grossular bulk modulus value is with respect to the results obtained by Kawai

403 and Tsuchiya (2012) with a lattice dynamics approach together in combination with a LDA

404 functional. Furthermore, the first derivative of the bulk modulus (K′) which we could now reliably

405 refine clearly demonstrates that the correct value must be very close to 5 in agreement with some of

406 the previous studies (see Table 4a).

407

408 *4.3 Full elastic behaviour (P-V-T-K): comparison with literature data*

409   The new utility available in EoSFit7c allowed us to also apply the same method described in

410 the sections above (*P-V-T-K* fitting) to the available literature data obtained from independent

411 elastic measurements and *PVT* datasets (Kono et al. 2010; Gwanmesia et al. 2014). It is remarkable

412 the extra constraint given by the simultaneous weighted fit of the *K* data (see results in Table 4c)

413 which however applied to the literature dataset does not allow to obtain the same quality as for our

414 elastic coefficients due to the lack of data in the low-temperature regime. This combined with the

415 much lower accuracy and precision that in most cases arises by the limitation of the *P-V-T*

416 simultaneous measurements (i.e. pressure calibrant, pressure transmitting media etc.) give rise to

417 discrepancies such as those showed in Figure 5b. In this case the discrepancies in bulk modulus

418 values at high-*T* reach up to 4% (more than 6 GPa at 1400 K). In order to crosscheck the

419 measurements with the DFT results, we performed fitting of the DFT data in the temperature range

420 between 400 and 800K using a thermal pressure equation of state combined with a 3rd order Tait-

421 eos. For purpose of comparison with the other fits, bulk moduli values have been normalized to the

422   bulk moduli extrapolated at 0K from the P-V-T-K fit of the experimental data (Fig. 5a, red line).

423   The trend of the two fits agrees within 1σ thus confirming the reliability of our fitting results via P-

424   V-T-K fits even at the highest temperature where the DFT approach leads to the smallest deviations

425   from the experimental data.

426   **4. CONCLUSIONS AND IMPLICATIONS**

427   It is obvious that pressure-volume or temperature-volume measurements alone do not

428   provide strong constraints on the cross-terms in *P-T* space (e.g. $\partial K/\partial T$ or $\partial\alpha/\partial P$) which are

429   fundamental for the description of the elastic properties of a material at simultaneous high-*P* and

430   high-*T*. Limitation in experimental measurements and/or in the description of the pressure-volume-

431   temperature data (e.g. incorrect Equations of State, erroneous mis-use of Voigt, Reuss isothermal or

432   adiabatic bulk moduli) has often in the past lead to inaccurate unreliable or even completely wrong

433   results (e.g. negative thermal expansion, erroneous $\partial K/\partial T$ etc…) specially when the EoS are

434   subsequently extrapolated to high-*P,T*.

435   Pressure-volume EoS are well-developed and, if correctly used, are capable of reproducing

436   the isothermal volume or density changes of materials to within the experimental uncertainties.

437   Previous versions of the EoSFit program were able to fit isothermal EoS, thermal expansion models

438   and the thermal-pressure (Holland and Powell 2011) to *P-V*, *V-T* or *P-V-T* data, by the method of

439   least-squares. We have now extended the capabilities of EosFit7c to also fit all of these forms of

440   EoS to bulk and linear moduli, either alone or in combination with volume or unit-cell parameter

441   data. With this approach we can now provide a reliable description of the variation of *K'* with *T* thus

442   avoiding mistaken extrapolations leading to non-physical behaviour as often occurs for several

443   materials (Helffrich and Connolly 2009).

444   The consistency of the results obtained with this new fitting procedure has been shown by

445   comparison of results from using adiabatic and isothermal moduli. It has also been demonstrated the

446   importance of performing fitting with this procedure in terms of both accuracy and precision of the

447   thermoelastic coefficients when the *PT* cross-terms ($\partial K/\partial T$ or $\partial\alpha/\partial P$) are extrapolated in *PT* space

448 (see Figure 5b). Additionally, thermodynamic functions were calculated for grossular using DFT

449 approach within QHA. The obtained results are in fairly good agreement with experiment, when

450 allowing for the known short-comings of the functionals employed in the DFT.

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454 **Acknowledgment**

461
462 **REFERENCES**
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P-V-T-K fit on grossular

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