1 **Revision 2**

2 ***P-V-T* equation of state of Ca$_3$Cr$_2$Si$_3$O$_{12}$ uvarovite garnet by using a diamond**
3 **anvil cell and *in situ* synchrotron X-ray diffraction**

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15 Abstract: The pressure-volume-temperature (*P-V-T*) equation of state (EoS) of synthetic uvarovite
16 has been measured at high temperatures up to 900 K and high pressures up to 16.20 GPa, by using
17 *in situ* angle-dispersive X-ray diffraction and diamond anvil cell. Analysis of room-temperature
18 *P-V* data to a third-order Birch-Murnaghan EoS yielded: V_0=1736.9±0.5Å^3, K_0=162±2 GPa and
19 K'_0=4.5±0.3. With K'_0 fixed to 4.0, we obtained: V_0=1736.5±0.3 Å^3 and K_0=164±1 GPa. Fitting of
20 our *P-V-T* data by means of the high-temperature third order Birch-Murnaghan equations of state,
21 given the thermoelastic parameters: V_0=1736.8±0.8 Å^3, K_0=162±3 GPa, K'_0=4.3±0.4,
22 $(\partial K/\partial T)_P$=-0.021±0.004 GPaK^{-1} and α_0=(2.72±0.14)×10^{-5} K^{-1}. We compared our elastic parameters
23 to the results from the previous studies for uvarovite. From the comparison of these fittings, we
24 propose to constrain the bulk modulus and its pressure derivative to K_0=162 GPa and K'_0=4.0-4.5
25 for uvarovite. Present results were also compared with previously studies for other ugrandite
26 garnets-grossular and andradite, indicated that the compression mechanism of uvarovite might be
27 similar with grossular and andradite. Furthermore, a systematic relationship, K_0(GPa)=
28 398.1(7)-0.136(8)V_0(Å^3) with a correlation coefficient R^2 of 0.9999, has been established based on
29 these isostructural analogues. Combining these results with previous studies for pyralspite
30 garnets-pyrope, almandine and spessartine, the compositional dependence of the thermoelastic
31 parameters (bulk modulus, thermal expansion and the temperature derivative of the bulk modulus)
32 were discussed.

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34 *Keywords : Uvarovite; Equation of state; High pressure and High temperature; X-ray diffraction; Diamond anvil*

35 *cell*

36 **INTRODUCTION**

37   Silicate garnets are considered important rock-forming minerals of the Earth's interior existing
38 in the upper mantle and transition zone, comprising up to 40 % by volume of the pyrolite
39 composition and up to 70 % of eclogitic composition (Akaogi and Akimoto 1977; Anderson and

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40   Bass 1984; Irifune and Ringwood 1987; Ita and Stixrude 1992; Dymshits et al. 2014). They occur

41   as stable phases in a wide range of pressures, temperatures and chemical environments, and play a

42   fundamental role in high pressure and high temperature petrogenetic processes (Deer et al. 1992;

43   Pavese et al. 2001). Garnets are also important components of subducted oceanic crust, and it is

44   suggested that garnet-rich subducted crust can be gravitationally trapped in the lowermost part of

45   transition zone (Irifune and Ringwood 1993; Karato et al. 1995). In addition, former experiments

46   at high pressure and high temperature on garnets showed that post-garnet transitions occur at

47   pressure and temperature conditions relatively close to the ones of the 660 km depth discontinuity

48   (Irifune et al. 1996; Akaogi et al. 1998; Gréaux et al. 2011). Therefore, understanding the

49   thermoelastic properties of garnets is essential to infer appropriate compositional models and

50   regional seismic profiles of the Earth's interior (Duffy and Anderson 1989; Weidner and Wang

51   2000).

52   The minerals of the garnet group are divided into two series, pyralspite and ugrandite.

53   Uvarovite is a chromium-bearing ugrandite garnet group species with the formula $Ca_3Cr_2Si_3O_{12}$,

54   and is thus distinguished from both grossularite ($Ca_3Al_2Si_3O_{12}$) and andradite ($Ca_3Fe_2Si_3O_{12}$).

55   Uvarovite is one of the rarest of the garnet group minerals, but nonetheless prevalent in many

56   terrains and geologic settings (Green and Falloon 1998; O'Neill and Palme 1998; Chopelas 2005;

57   Klemme et al. 2005), and its thermoelastic behavior at high pressure and high temperature will

58   shed light on other ugrandite garnets, as well as pyralspite garnets. It can form a complete solid

59   solution series with grossular and andradite in the Earth's interior (Huckenholz and Knittel 1976).

60   Uvarovite has generally been found associated with serpentinite, chromite, metamorphic

61   limestones, and skarn ore-bodies; it has formed from contact metamorphic processes or

62   hydrothermal processes (Challis et al. 1995; Graham et al. 1996; Proenza et al. 1999). In addition,

63   as the Earth's mantle usually contains much more Cr than the Earth's crust (Green and Falloon

64   1998; O'Neill and Palme 1998), uvarovite is also an important mineral end-member component of

65   most mantle garnets (Klemme et al. 2005). However, it is still among the least investigated garnets

66   in the previous studies. In particular, experimental determinations on the thermoelatic and

67   thermodynamic properties of uvarovite at the high pressure/high temperature condition are few

68   (Klemme et al. 2005). Most previous experimental studies focused on the elasticity of uvarovite at

69   high pressure and room temperature (Bass 1986; Leger et al. 1990; Wang and Ji 2001; Diella et al.

70   2004). Leger et al. (1990) measured the *P-V* equation of state of synthetic uvarovite at high

71   pressure using a diamond anvil cell instrument with synchrotron radiation X-ray diffraction.

72   Afterwards, Diella et al. (2004) examined the elastic parameters of natural uvarovite garnet at high

73   pressure by synchrotron radiation X-ray diffraction by means of a diamond anvil cell.

74   To date, the thermoelastic properties of garnets including grossular and andradite have been

75   extensively studied using both the multianvil apparatus and the diamond anvil cell (Gréaux and

76   Yamada 2014; Zou et al. 2012; Gréaux et al. 2011; Fan et al. 2009; Gwanmesia et al. 2006, 2009;

77   Nishihara et al. 2005; Pavese et al. 2001; Wang et al. 1998; Yagi et al. 1987). However, up to now,

78   all of the studies on uvarovite have been limited to either at high pressure and room temperature or

79   at high temperature and ambient pressure. There are no reports in the literature about the

80   thermoelasticity of uvarovite at simultaneously high pressure and high temperature. Therefore, in

81   this study, we have investigated the *P-V-T* relations of a synthetic end-member uvarovite garnet at

82   high pressure and high temperature, using a diamond anvil cell combined with *in situ* synchrotron

83   radiation angle-dispersive X-ray diffraction. The thermoelastic property of uvarovite garnet was

84   obtained by the fitting of the present *P-V-T* data to the high temperature Birch-Murnaghan (HTBM)

85   EoS and thermal pressure EoS. Our results were also discussed with respect to previous reports of

86   thermoelastic properties of other silicate garnets.

87   **SAMPLE AND EXPERIMENT**

88   The uvarovite sample was synthesized using a multi-anvil pressure apparatus (YJ-3000T), at the

89   Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, China. Details of this

90   experimental setup have been described elsewhere by Xie et al. (1993). The pressurization system

91   of this press consists of six WC anvils, with their tips truncated as 23.5×23.5 mm^2, which are

92   simultaneously pushed by six hydraulic rams so that high pressure is generated in the experimental

93   assembly (Fan et al. 2013). The pressure in the sample chamber was calibrated by using

94   quartz-coesite phase transition and the high-pressure melting curve of copper, with the error

95   involved in pressure measurement being less than 1.5%. The temperature in the sample chamber

96   was calibrated by means of Pt-Pt$_{90}$Rh$_{10}$ thermocouple, with the error involved in temperature

97   measurement being less than 5 K (Xie et al. 1993, 2002). The starting materials used in the

98   synthesizing experiments were stoichiometric amounts of high purity calcium carbonate ($CaCO_3$),

99   chromium oxide (Cr_2O_3), aluminum oxide (Al_2O_3) and silica (SiO_2). These mixtures were

100 pretreated at 1200 K in a platinum dish for 12 h to decarbonate. The mixture was then melted at

101 1700 K which produced, after quenching, a homogeneous glass. The homogeneous glass was

102 crushed into a fine powder using acetone and then encapsulated in Platinum tubes. The

103 synthesizing conditions were 2.5 GPa, 1400 K, and 24 h to form a single phase. The ambient

104 X-ray diffraction data were collected using a D/Max-2200 X-ray diffractometer with graphite

105 crystal monochromator and Cu Kα radiation. The ambient X-ray spectrum of uvarovite was

106 indexed according to the standard spectra (JCPDS 82-1914), confirming that the structure of the

107 synthetic uvarovite is cubic, and belongs to the *Ia3d* space group. Its composition was confirmed

108 by using electron microprobe analysis (EPMA-1600).

109 High pressure and high temperature experiments were carried out by using a modified

110 Merrill–Bassett type diamond-anvil cell (DAC). A pair of 500 μm culet-size diamond anvil was

111 used. Gaskets made from stainless steel foil (type T301), pre-indented to a thickness of ~50 μm

112 and then drilled to a diameter of 200 μm, served as the sample chamber. The uvarovite sample

113 powders were slightly pressed between two opposing diamond anvils to form an approximately 25

114 μm thick disk, and a piece of uvarovite sample about 100 μm in diameter was loaded into the

115 sample chamber. The cell pressure was determined using the equation of state of gold (pressure

116 marker). The pressure transmitting medium was a 16:3:1 mixture ethanol-methanol-water. Heating

117 was carried out by using a resistance-heating system, and the temperature was measured by a

118 Pt$_{90}$Rh$_{10}$-Pt$_{100}$ thermocouple, which was attached to the pavilion of the diamond.

119 Figure 1 shows the pressure-temperature (*P-T*) path of the present high pressure and high

120 temperature experiments, up to 16 GPa and 900 K. We first compressed the sample up to 10 GPa

121 and then increased the temperature up to 900 K. Heating was maintained at 900 K for several

122 minutes in order to minimize the effect of non-hydrostatic stress that could develop upon cold

123 compression. Each *in situ* X-ray diffraction patterns was collected after heating, during cooling

124 down to 300 K, by 200 K steps. Subsequently, the pressure was decreased to ~ 5 GPa at room

125 temperature. This experimental procedure was repeated for cycles (1)→(6) at the

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126   pressure-temperature conditions up to 16 GPa and 900 K. The spectrums were selected after the
127   experiment temperature was kept for ~600 s. Typical exposure times for collecting diffraction
128   patterns of the sample and the pressure marker were 600 s. Details of the experimental setup and
129   cell assembly were described in Fan et al. (2010).
130   *In situ* high pressure and high temperature angle-dispersive X-ray diffraction experiments were
131   conducted at the 4W2 beamline of the Beijing Synchrotron Radiation Facility (BSRF). An image
132   plate detector (MAR-345) was used to collect diffraction patterns. The wavelength of the
133   monochromatic X-ray beam was 0.6199 Å calibrated by scanning through the Mo metal
134   *K*-absorption edge. The X-ray beam was focused to a beam size of 20×30 μm^2 full-width at half
135   maximum (FWHM) by a pair of Kirkpatrick-Baez mirrors. The tilting and rotation of the detector
136   relative to the incident X‑ray beam were calibrated using cerium dioxide (CeO_2) powder as the
137   X-ray diffraction standard. The sample-detector distance was calculated from the powder CeO_2
138   diffraction pattern at ambient conditions. The diffraction patterns were integrated to generate the
139   conventional one-dimensional profiles using the Fit2D program (Hammersley 1996). Analyzes of
140   all the patterns were carried out by means of the full profile-fitting technique implemented in the
141   EXPGUI/GSAS software package (Larson and Von Dreele 2000; Toby 2001). Refinement of peak
142   positions and extraction of cell parameters were achieved by reducing full diffraction patterns
143   following the Le Bail method (Le Bail et al. 1988). Precision upon the volume for uvarovite was
144   estimated from the full spectrum fitting (Le Bail refinement) of X-ray diffraction profiles. X-ray
145   diffraction patterns for the uvarovite sample collected at the present experiment pressure and
146   temperature conditions showed that no phase transformation were observed throughout these
147   experiments. Figure 2 shows a typical fitting of the full X-ray diffraction pattern at 15.33 GPa and
148   900 K for uvarovite.

149   **RESULT AND DISCUSSION**

150   Unit-cell volumes of uvarovite at various pressures and temperatures conditions are shown in
151   Table 1. The results of conventional x-ray diffraction collected at ambient condition gives the
152   unit-cell volume V_0=1736.94±0.54 Å^3 for uvarovite in this study, which is in good agreement with
153   the results reported by Carda et al. (1994) (i.e., V_0 = 1736.87 Å^3). To derive thermoelastic
154   parameters from the measured *P-V-T* data, we first fitted the compression *P-V* data at the 300 K
155   isotherm to the Birch-Murnaghan equation of state (EoS), and then applied other commonly
156   employed methods, the High-Temperature Brich-Murnaghan (HTBM) EoS and thermal pressure
157   EoS approach.

158   **Pressure-volume data at room temperature**

159   Birch-Murnaghan equation of state
160
161   The pressure-volume (*P-V*) relations have been determined by fitting the present
162   room-temperature data to a third order Birch-Murnaghan (III-BM) EoS, which is represented as
163   follows:

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

4

165   where V_0, K_0, K'_0 are the unit-cell volume, isothermal bulk modulus and its pressure derivative at

166   ambient condition, respectively. Analyses of Eq. (1) with all parameters free yield V_0=1736.9±0.5

167   Å^3, K_0=162±2 GPa, K'_0=4.5±0.3 for uvarovite. With K'_0 fixed at 4, the fitting results yield

168   V_0=1736.5±0.3 Å^3 and K_0=164±1GPa, respectively. Figure 3 shows the volume compression (V/V_0)

169   of uvarovite as a function of pressure (P) and derived equation of state, and compared with the

170   previous study by Diella et al. (2004).

171   We used a methanol-ethanol-water mixture with 16:3:1 for the pressure medium in this study,

172   which freezes above 10 GPa, and the hydrostatic circumstance of sample chamber will be

173   influenced. However, the sample chamber in this study has been heated up to 900 K at pressure

174   higher than 10 GPa for the relaxation of the deviatoric stress. Although the effect of deviatoric

175   stress on the unit-cell volume measurements should be small, we still need to assess the impact of

176   non-hydrostatic compression to bulk modulus in this study. In this study, the bulk modulus and its

177   pressure derivative obtained from the hydrostatic conditions (up to 10 GPa, room temperature),

178   K_0=162±3 GPa, K'_0=4.4±0.5, which is very consistent with the results of fitting all the

179   room-temperature data that lead to K_0=162±2 GPa, K'_0=4.5±0.3.

180   Figure 4 shows the volume Eulerian finite strain ($f_E = [(V_0/V)^{2/3}-1]$) versus "normalized

181   pressure" ($F_E = P/[3f_E(2f_E + 1)^{5/2}]$) plot ($F_E$-$f_E$ plot, (Angel 2000)) of uvarovite in this study. The

182   weighted linear regression through the data points yields the intercept value, $F_E(0)$ = 162(2) GPa

183   for uvarovite, which shows an excellent agreement with the isothermal bulk modulus obtained by

184   the III-BM-EoS. Furthermore, it is clear from Figure 4 that the normalized pressure as a function

185   of the Eulerian strain at 300 K has a positive slope, which is consistent with a value of K'_0 slightly

186   larger than 4 (Angel 2000), showing that the III-BM-EoS is a reasonable description of the P-V

187   data in this study.

188

189   Vinet equation of state

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191   We also analyzed the P-V data using the Vinet EoS (Vinet et al. 1986; 1987). The Vinet EoS

192   was derived from an "universal equation" for solids and results in:

193                $P(V)=3K_0 y^{-2}(1-y)\exp[\eta_0(1-y)]$ (2)

194   where $y=x^{1/3}$, $x=V/V_0$ and $\eta_0=(3/2)(K'_0-1)$. Analyses of Eq. (2) with all parameters free yield

195   V_0=1736.9±0.6 Å^3, K_0=161±3 GPa, K'_0=4.4±0.3 for uvarovite, which are reasonably consistent

196   with those derived by the fitting to BM EoS, given V_0=1736.9±0.5 Å^3, K_0=162±2 GPa,

197   K'_0=4.5±0.3 (Table 2). In addition, with K'_0 fixed at 4, the fitting results yield V_0=1736.4±0.4 Å^3

198   and K_0=164±1GPa, respectively, which are also extremely consistent with the results of BM EoS,

199   given V_0=1736.5±0.3 Å^3 and K_0=164±1GPa, respectively.

200   **Pressure-volume-temperature data and thermoelastic parameters**

201   High-Temperature Birch-Murnaghan equation of state

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203   The P-V-T data (Table 1) were used to determine the thermoelastic properties of uvarovite up to

204   ~16 GPa and 900 K. The third order P-V-T Birch-Murnaghan equation of state was applied to our

205   high pressure and high temperature data in the form as follows:

5

206 $\quad P=(3/2) K_{T0} [(V_{T0}/V)^{7/3} - (V_{T0}/V)^{5/3}] \times \{1+(3/4)(K'_{T0} - 4)[(V_{T0}/V)^{2/3} - 1]\}$ $\quad$ (3)

207 In this equation, the thermal dependences of the zero-pressure volume V_{T0} and bulk modulus K_{T0}

208 at different isotherms are expressed using the following equations:

209 $$V_{T0} = V_0 \exp \int_{300}^{T} \alpha_T dT$$
$\quad$ (4)

210

$$K_{T0}=K_0+(\partial K_{T0}/\partial T)_P \times (T-300)$$ $\quad$ (5)

211 where V_0 is the volume at room pressure and temperature, and the temperature derivative for the

212 unit-cell volume V_{T0} can be estimated by a function of the thermal expansion at ambient pressure

213 α_T (Eq. 4). The thermal dependence of the bulk modulus K_{T0} is expressed by a linear function of

214 temperatures, temperature derivative $(\partial K_{T0}/\partial T)_P$ and K_0 (Eq. 5).

215 $\quad$ The thermoelastic parameters α_T, $(\partial K_T/\partial T)_P$, K_0 and K'_0 obtained for uvarovite in this study are

216 showed in Table 3. Fitting of the present P-V-T data to the HTBM EoS yields: V_0=1736.8±0.8 Å^3,

217 K_0=162±3 GPa, K'_0=4.3±0.4, $(\partial K/\partial T)_P$=-0.021±0.004 GPaK^{-1} and α_0=(2.72±0.14)×10^{-5} K^{-1}. With

218 K'_0 fixed at 4, the fitting results yield V_0=1736.6±0.6 Å^3, K_0=164±1 GPa, $(\partial K/\partial T)_P$=-0.018±0.004

219 GPaK^{-1} and α_0=(2.69±0.12)×10^{-5} K^{-1}, respectively. We also fixed K'_0 to 4.5 which given by P-V

220 data in this study, and obtained V_0=1737.0±0.6 Å^3, K_0=161±1 GPa, $(\partial K/\partial T)_P$=-0.022±0.004

221 GPaK^{-1} and α_0=(2.76±0.13)×10^{-5} K^{-1}, respectively. The bulk modulus K_0 and K'_0 determined here

222 are within uncertainties, consistent with the values derived from fitting of our P-V data at 300 K.

223 The values of $(\partial K_T/\partial T)_P$ and V_0 within uncertainties are almost unaffected by the choice of K'_0. In

224 addition, the α_0 becomes larger with increasing K'_0 but the difference fall within uncertainties.

225 However, the K_0 slightly deviate because of the strong correlation between K_0 and K'_0. These are

226 very similar to the experimental results of Gréaux and Yamada (2014) for spessartine, and Zou et

227 al. (2012) and Lu et al. (2013) for pyrope, which also showed that the thermal parameter

228 $(\partial K_T/\partial T)_P$ was almost unaffected by the variations of K'_0, whereas the value of K_0 deviate

229 significantly because of the strong correlation between K_0 and K'_0. The measured cell volumes are

230 plotted in Figure 5 as a function of pressure together with the isotherms calculated using the

231 thermoelastic parameters derived from the current fits, showing a good agreement between the fit

232 and the measured P-V-T data.

233 $\quad$ Likewise, we also need to assess the impact of non-hydrostatic compression to thermoelastic

234 parameters in this study. Fitting of the P-V-T data at pressures below ~ 10 GPa to the HTBM EoS

235 yields: V_0=1736.4±0.9 Å^3, K_0=164±4 GPa, K'_0=3.9±0.6, $(\partial K/\partial T)_P$=-0.020±0.006 GPaK^{-1} and

236 α_0=(2.65±0.22)×10^{-5} K^{-1}. With K'_0 fixed at 4, the fitting results yield V_0=1736.8±0.7 Å^3, K_0=163±2

237 GPa, $(\partial K/\partial T)_P$=-0.018±0.006 GPaK^{-1} and α_0=(2.68±0.17)×10^{-5} K^{-1}, respectively. These values are

238 very consistent with the results of fitting all the P-V-T data that lead to V_0=1736.8±0.8 Å^3,

239 K_0=162±3 GPa, K'_0=4.3±0.4, $(\partial K/\partial T)_P$=-0.021±0.004 GPaK^{-1} and α_0=(2.72±0.14)×10^{-5} K^{-1}. This

240 also indicates that the impact of non-hydrostatic compression to thermoelastic parameters is very

241 limited in this study.

242 $\quad$ As discussed by some authors (Funamori et al. 1996; Nishihara et al. 2004; Trots et al. 2013;

243 Zhuravlev et al. 2013), the choice of pressure scale maybe affects the thermoelastic parameters

244 derived from P-V-T experiments. The pressure scale of Au by Fei et al. (2007) is based on the

245 measured thermoelastic properties of Au at high pressure and high temperature, while the Au

246 pressure scale by Dorogokupets and Dewaele (2007) is based on the expanded

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247   Mie–Grüneisen–Debye approach. We also calculated the thermoelastic parameters of uvarovite by

248   using pressure values based on Dorogokupets and Dewaele (2007) (given in Table 3). The value of

249   α_0 is a little bit lowered from 2.69×10^{-5} K^{-1} for Fei et al. (2007) scale to 2.60×10^{-5} K^{-1} using

250   Dorogokupets and Dewaele (2007) scale for $K'_0=4.0$, while the other parameters are relatively

251   unaffected by the change of scale.

252

253   Thermal pressure equation of state

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255   We also analyzed the P-V-T data using the thermal pressure approach (e.g., Anderson, 1995,

256   1999; Jackson and Rigden, 1996). The thermal pressure ΔP_{th} was obtained by subtracting the

257   pressure at volume V and at room temperature (derived from Eq. (1)) from the pressure measured

258   at the same V and at temperature T.

259
$$\Delta P_{th} = P(V,T) - P(V,300) = \left[\alpha K_T + \left(\frac{\partial K_T}{\partial T} \right)_V \ln\left(\frac{V_0}{V} \right) \right] \times (T - 300) \qquad (6)$$

260   Figs. 6 and 7 show thermal pressure of uvarovite against temperature and unit-cell volume,

261   respectively. It is seen that thermal pressure of uvarovite varies linearly with temperature and

262   almost independent of volume. A fit of the data in this study yields $K_0=162\pm2$ GPa, $K'_0=4.5\pm0.6$,

263   and $\alpha_0=(2.68\pm0.18) \times 10^{-5}$ K^{-1}, which are reasonably consistent with those derived by the fitting to

264   HTBM EoS (Table 3). Within the uncertainty of the fit $(\partial K_T/\partial T)_V$ value is roughly zero, indicating

265   that the thermal pressure is independent of volume, which is the same with the conclusions of

266   Wang et al. (1998) who also found that the thermal pressure in garnet shows linear variation with

267   T up to 1200 K independent of compression (V/V_0), concluding that $(\partial K_T/\partial T)_V$ is very close to zero.

268   The same conclusions have been drawn for some other silicate minerals, such as olivine (Guyot et

269   al. 1996), $CaSiO_3$ perovskite (Wang et al. 1996) and ringwoodite (Nishihara et al. 2004). By using

270   the thermodynamic relation: $(\partial K_T/\partial T)_P = (\partial K_T/\partial T)_V - \alpha K_T K'_T$, we can obtain $(\partial K_T/\partial T)_P = -0.020(3)$

271    $GPaK^{-1}$. This result is also in good agreement with current analysis using HTBM EoS (Table 3).

272   **Comparison with other silicate garnets**

273   The current results compared with previous studies for uvarovite are also shown in Table 2. The

274   bulk modulus in this study is in good agreement with previous studies for uvarovite within

275   uncertainties (Bass 1986; Leger et al. 1990; Wang and Ji 2001; Diella et al. 2004). Bass (1986)

276   used Brillouin spectroscopy to study a single crystal of synthetic uvarovite, and reported a very

277   consistent result ($K_0=162$ GPa) with this study. Subsequently, Leger et al. (1990) investigated the

278   behavior of synthetic uvarovite at high pressure and also reported a very similar K'_0 of 4.7 with

279   this study ($K'_0=4.7$) using the bulk modulus value obtained by Brillouin method (Bass 1986).

280   Wang and Ji (2001) measured the elastic properties of a natural uvarovite by ultrasonic method

281   and given $K_0=164.8\pm0.2$ GPa, $K'_0=4.7\pm0.9$, which are also very consistent to this study together

282   with Bass (1986) and Leger et al. (1990) within their uncertainties. However, in the case of Diella

283   et al. (2004), their K_0 value of 160 GPa is associated with a higher K'_0 of 5.8. As shown in Figure

284   2, at low-pressure our P-V relation agrees well with Diella et al. (2004). However, they carried out

285   experiments up to 12 GPa, and then deviations with our data arise above ~12 GPa because of their

286   high K'_0 value. Indeed, as shown in Table 2, Diella et al. (2004)'s unit-cell volume is smaller than

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287   our study, which is related to their use of natural uvarovite, which contains substantial amounts of
288   Al in the Cr-site. Different techniques employed and sample quality may have influence on the
289   value of K'_0 (Huang and Chen 2014). From the comparison of this study with previous results, we
290   propose to constrain the bulk modulus and its pressure derivative to K_0=162 GPa and K'_0=4.0-4.5
291   for uvarovite.

292   Another interesting question is how single crystal vs powder X-ray diffraction methods might
293   influence the elastic/thermoelastic parameters of uvarovite garnet. Rath et al. (2003) investigated
294   the compression behavior of natural uvarovite at high pressure using single-crystal X-ray
295   diffraction and given K_0=168±5 GPa. In comparison to the results of powder X-ray diffraction
296   experiments (K_0=162 GPa), the bulk modulus of uvarovite from single-crystal X-ray diffraction
297   experiments is a little bit higher than powder X-ray diffraction experiments. However, if consider
298   the uncertainty, they are also consistent each other within their uncertainties. By far, there are not
299   related reports about the thermoelastic properties of uvarovite garnet using single-crystal X-ray
300   diffraction method, what's more, the single-crystal X-ray diffraction experiments of garnet at high
301   pressure and high temperature is also very limited (Lu et al. 2013). But, Lu et al (2013) measured
302   the single-crystal elasticity of natural Fe-bearing pyrope using *in situ* Brillouin spectroscopy and
303   X-ray diffraction at simultaneous high P-T conditions for the first time, and given the temperature
304   derivative of the bulk modulus for pyrope $(\partial K_T/\partial T)_P$ =-0.023±0.002 GPaK^{-1}, which is very
305   consistent to the results from Zou et al. (2012) $((\partial K_T/\partial T)_P$ =-0.024±0.013 GPaK^{-1}) and Wang et al.
306   (1998) $((\partial K_T/\partial T)_P$ =-0.020±0.003 GPaK^{-1}) using powder X-ray diffraction method within their
307   uncertainties. So, there has no important influence on the thermoelastic parameters of pyrope
308   using different X-ray diffraction methods (single crystal vs powder). In addition, considering the
309   temperature derivative of the bulk modulus for uvarovite is very similar with the results of pyrope
310   (Table 3), we deduce that the influence on the thermoelastic parameters of uvarovite using
311   different X-ray diffraction methods (single crystal vs powder) maybe also very limited. In order to
312   confirm it, further examinations through high P-T single-crystal X-ray diffraction experiments on
313   the uvarovite garnet are needed.

314   Elastic properties of other ugrandite garnets-grossular and andradite have been investigated by
315   some authors. Table 2 summarized the bulk moduli and their pressure derivatives for uvarovite
316   together with grossular and andradite determined by various experimental techniques. As shown in
317   Table 2, experimental studies have indicated that the K_0 values of uvarovite from the literatures is
318   about 162 GPa within their uncertainties. However, the K_0 values for andradite and grossular from
319   the literatures exhibit slight discrepancies with each other, ranging from 157 to 162 GPa, and 166
320   to 172 GPa, respectively. From Table 2, we can find that the grossular has the highest
321   incompressibility of the ugrandite garnets; in contrast, the andradite has the lowest
322   incompressibility of the ugrandite garnets, and the incompressibility of uvarovite is between them.
323   The high pressure behavior of ugrandite garnets could be explained on the basis of the crystal
324   structure of silicate garnets: The garnet group is composed of minerals of the general formula
325   $X_3Y_2Z_3O_{12}$. The X-site is 8-coordinated (dodecahedra), the Y-site is 6-coordinated (octahedra) and
326   the Z-site is 4-coordinated (tetrahedra). Milman et al. (2001) showed that the bulk modulus of
327   garnet is strongly affected by the bulk modulus of the dodecahedra, but Dymshits et al. (2014)
328   concluded that not only the dodecahedral sites, but also the behavior of the garnet framework and
329   relative sizes of the 8- and 6-coordinated cations, control garnet compression. So, if we compared
330   the effective ionic radius of cations in the octahedral sites of ugrandite garnets cited here, the

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331 effective ionic radius of $Fe^{3+}(VI)$ (0.645 Å) for andradite is larger than $Cr^{3+}(VI)$ (0.615 Å) for

332 uvarovite and $Al^{3+}(VI)$ (0.535 Å) for grossular (Shannon 1976). Correspondingly, the mean bond

333 length of $Fe^{3+}(VI)$-O in andradite (2.019 Å) (Antao 2013) is larger than the mean bond lengths of

334 $Cr^{3+}(VI)$-O in uvarovite (1.984 Å) (Wildner and Andrut 2001) and $Al^{3+}(VI)$-O in grossular (1.926

335 Å) (Geiger and Armbruster 1997). The bond strength of $Fe^{3+}(VI)$-O in andradite may be weaker

336 than the corresponding bonds in uvarovite and grossular due to the larger bond lengths,

337 accordingly, andradite has a larger compressibility and smaller isothermal bulk modulus (Zhang J

338 1999; Milman et al. 2001; Liu et al. 2008).

339   Table 2 also lists the available bulk moduli (K_0) and unit-cell volumes (V_0) of the ugrandite

340 garnets, which are important for mantle mineralogy. These K_0-V_0 data are also plotted in Figure 5.

341 The inverse relationship between bulk modulus K_0 and unit-cell volume V_0 has been widely used

342 for predicting bulk moduli of mantle minerals crystallizing in similar structures (Anderson and

343 Anderson 1970; Zhang J 1999; Liu et al. 2008; Xiao et al. 2013). It can be expressed as

344 K_0V_0=constant. To build reliable trends among ugrandite garnets within isostructural groups, it is

345 important to examine the systematic relationships among mantle silicate ugrandite garnets. As can

346 be seen in Figure 8, the three ugrandite garnets exhibit an excellent linear relationship between

347 their unit-cell volumes and bulk moduli. The linear fitting gives a formula as K_0(GPa)=

348 $398.1(7)-0.136(8)V_0$(Å^3) with a correlation coefficient R^2 of 0.9999. Obviously, the K_0-V_0 linear

349 function is better than the inverse relationship to predict the bulk modulus of the ugrandite garnets

350 over a wide range of volume and composition. This indicates that there are similar factors

351 governing the compression behaviors in these ugrandite garnets.

352   The results about the pressure derivative of bulk modulus in this study are also summarized in

353 Table 2 and compared with data for grossular and andradite garnets from previous studies. From

354 the results, we conclude that K'_0 for uvarovite garnets from the room-temperature III-BM EoS fit

355 (K'_0=4.5) and high-temperature III-BM EoS fit (K'_0=4.3) are entirely identical within the fitting

356 error in this study. They are also very similar to the pressure derivative of bulk modulus for

357 synthetic grossular (K'_0=4.42) by Kono et al. (2010) and synthetic andradite (K'_0=4.4) by Zhang et

358 al. (1999). Furthermore, the values of the pressure derivative of bulk modulus for uvarovite

359 garnets in this study are also in excellent agreement with other silicate garnets for which it was

360 proposed that K'_0 is close to 4.0 (Zhang et al. 1999; Stixrude and Lithgow-Bertelloni 2005;

361 Gwanmesia et al. 2006; Kono et al., 2010; Gréaux et al. 2011; Zou et al. 2012; Lu et al. 2013;

362 Huang and Chen 2014). On the other hand, our pressure derivative of K'_0=4.5(3) cannot agree with

363 that of K'_0=1.89(1.72) proposed by Pavese et al. (2001) for natural andradite and K'_0=6.2(5)

364 proposed by Pavese et al. (2001) for natural grossular. Different sample quality may have

365 influence on the determination of K'_0 (Huang and Chen 2014). But studies with laser induced

366 phonon spectroscopy (Brillouin scattering) on garnets at high pressures generally result in K'_0~4.0

367 (Sinogeikin and Bass 2000; Lu et al. 2013; Dymshits et al. 2014), which is considered to be

368 accurate, because it is from direct measurements of elastic moduli at high pressure conditions

369 (Nishihara et al. 2004, 2005).

370   Table 3 and Figure 9 show a comparison of the temperature derivative of the bulk modulus for

371 uvarovite in this study to other ugrandite garnets-grossular and andradite, together with pyralspite

372 garnets-pyrope, spessartine and almandine. It is interesting to note that the temperature derivatives

373 of the bulk modulus in this study for uvarovite at any K'_0 are in excellent agreement with each

374 other and other ugrandite garnets-grossular and andradite within their experimental uncertainties

375   (Table 3 and Figure 9). Therefore, based on existing data, we believe the temperature derivative of

376   the bulk modulus of ugrandite garnets may not be significant affected by the composition. In

377   addition, the measurement in this study for synthetic uvarovite shows slightly lower the

378   temperature derivative of the bulk modulus than natural almandine by Fan et al. (2009) and natural

379   spessartine-almandine solid solutions ($Spe_{38}Alm_{62}$ and $Spe_{64}Alm_{36}$) by Fan et al. (2014) but the

380   difference fall within uncertainties. What is more, the temperature derivative of the bulk modulus

381   of this study for synthetic uvarovite are also in good agreement with the values of Zou et al. (2012)

382   and Wang et al. (1998) for synthetic pyrope within mutual uncertainties (Table 3). However, the

383   measurements of synthetic spessartine by Gréaux and Yamada (2014) yielded the $(\partial K/\partial T)_P$ values

384   to be -0.049 $GPaK^{-1}$ that are obviously higher than all of other silicate garnets. And Figure 9 also

385   shows the variation of bulk modulus with increasing temperature: spessartine softens faster than

386   other silicate garnets. The structural relaxation at high temperature of spessartine may be the

387   reason (Gréaux and Yamada 2014).

388   Table 3 also summarizes the thermal expansion of uvarovite in this study together with

389   grossular, andradite and pyralspite garnets-pyrope, spessartine and almandine. We can also note

390   that the thermal expansion of uvarovite in this study are in good agreement with other ugrandite

391   garnets-grossular and andradite within their experimental uncertainties (Table 3). In addition, the

392   thermal expansion of synthetic uvarovite in this study are also in excellent agreement with the

393   values of Zou et al. (2012) and Wang et al. (1998) for pyrope, Fan et al. (2009) for almandine,

394   Gréaux and Yamada (2014) for spessartine within mutual uncertainties (Table 3). In particularly,

395   the thermal expansion for uvarovite in this study is also very consistent with the values of Fan et al.

396   (2014) for spessartine-almandine solid solution within their uncertainties (Table 3). Therefore,

397   based on existing data, we believe the thermal expansion of silicate garnet may not be significant

398   affected by the composition, which is similar with the view of Nishihara et al. (2005) and Fan et al.

399   (2014) who considered that the thermal expansion coefficients on garnets show similar values

400   regardless of the garnet chemistry.

401   **IMPLICATIONS**

402   As experimentally confirmed, garnet occurs commonly in nature both as metamorphic mineral

403   and as a high pressure phase, stable under upper mantle conditions (Leitner et al. 1980), and are

404   probably also important phases in the mantle-transition zone (420-670 km) depth (Duffy and

405   Anderson 1989). A knowledge of the thermoelastic and thermodynamic properties of garnets is

406   therefore of great geophysical importance in the characterization of the thermal structure and

407   phase equilibria, and the construction of the upper mantle and transition zone composition models

408   of the Earth's interior (Duffy and Anderson 1989; Weidner and Wang 2000).

409   Cr-rich minerals are a common mineral phase in the Earth's mantle and crust (Cookenboo and

410   grutter 2010; Klemme 2004; liou et al. 2009; Stachel and Harris 1997; Van roermund 2009). In

411   particular, Cr-rich garnets (knorringite and uvarovite) are commonly found in the deep Earth, as

412   indicated by xenoliths in kimberlites and inclusions in diamonds (e.g., Nixon 1995; Stachel and

413   Harris 1997; Stachel et al. 1998; Bulanova et al. 2004). Furthermore, chromium concentration in

414   garnet increases with depth and is used in mantle barometry (Grütter et al. 2006). The presence of

415   Cr in the garnet lattice shifts significantly the spinel-garnet transformation-a major phase

416   boundary in the Earth's upper mantle-to pressures as high as 7 GPa (Klemme 2004). Pyrope and

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417 knorringite form a complete solid solution and garnets close to the pyrope 50-knorrigite 50
418 composition occur as inclusions in natural diamonds (Irifune et al. 1982). Therefore, the
419 thermoelastic and thermodynamic properties of Cr-bearing garnets (knorringite and uvarovite) at
420 high pressure and high temperature is essential to evaluate the phase relations and thermal
421 structure of the Earth's mantle. However, to date, meaningful thermal structure and phase relations
422 calculations in realistic mantle compositions cannot be performed, as thermoelastic and
423 thermodynamic data for many Cr-rich minerals (such as knorringite and uvarovite) are not as well
424 understood as one would wish (e.g., Asimov et al. 1995; Klemme 2004). In addition, the high
425 pressure phase relations and stability of knorringite are controversial (Ringwood 1977; Irifune et
426 al. 1982; Turkin et al. 1983; Klemme 2004; Zou and Irifune 2012). Furthermore, pure knorringite
427 garnet may be not a stable phase under the pressure and temperature conditions of upper mantle
428 and transition zone of deep-Earth (Zou and Irifune 2012), and high-precision thermoelastic and
429 thermodynamic data probably will never be available for this phase. However, our results show
430 that uvarovite is still stable at the present experiment pressure and temperature conditions which
431 are already close to the *P-T* conditions of upper mantle, so our results here may be used as analogs
432 to understanding the thermoelastic and thermodynamic properties of knorringite and Cr-bearing
433 garnets in the deep-Earth mantle. Moreover, the determination of thermoelastic property of
434 uvarovite ($Ca_3Cr_2Si_3O_{12}$) at high pressure and high temperature conditions in this study will also
435 shed light on the thermal structure and phase relations of the Earth's mantle. However, detailed
436 knowledges of the high pressure and high temperature phase relations and thermodynamic
437 parameters of the Cr-bearing garnets at the *P-T* conditions of the upper mantle and transition zone
438 will be needed to fully explore the thermodynamic stability of the deep-Earth mantle.
439   Additionally, the experimental study of silicate garnets end members at high pressure and high
440 temperature is also of great importance to constrain the compositional dependence of
441 thermoelastic properties in those minerals (Gréaux et al. 2011; Zou et al. 2012; Huang and Chen
442 2014). Such results are particularly valuable for the understanding of natural garnets' behavior at
443 high pressure and high temperature since they usually display relatively complex composition
444 (Gréaux and Yamada 2014). Based on the high pressure and high temperature angle-dispersive
445 X-ray diffraction experiments on uvarovite in this study and relevant literature data for grossular
446 and andradite, we conclude that the compression mechanism of uvarovite might be similar with
447 grossular and andradite. And the three ugrandite garnets exhibit an excellent linear relationship
448 between their unit-cell volumes and bulk moduli [$K_0(GPa)= 398.1(7)-0.136(8)V_0(Å^3)$, $R^2=0.9999$],
449 which is very important to examine the systematic relationships among mantle silicate ugrandite
450 garnets. On the one hand, the thermoelastic properties of uvarovite at high pressure and high
451 temperature in this study together with other studies for grossular and andradite will provide a
452 direct assessment of thermoelastic behavior of ugrandite garnets at simultaneous high pressure and
453 high temperature (Gréaux et al. 2011; Pavese et al. 2001). On the other hand, these new data set
454 thus allows us to place improved constraints on the compositional dependence of thermoelastic
455 parameters in the rocks of the upper mantle and transition zone (Jiang et al. 2004; Gwanmesia et al.
456 2009; Lu et al. 2013). Moreover, considering the abundance of garnets in the Earth's upper mantle
457 and transition zone, experimental studies on the thermoelasticity of garnets with a relevant
458 composition at upper-mantle pressure and temperature conditions have significantly implications
459 for understanding the chemical composition of the deep Earth (Bass and Anderson 1984; Duffy
460 and Anderson 1989; Cammarano et al. 2003; Li and Liebermann 2007), so these data also can be

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461   used to contribute to construction of compositional model of Earth's interior (Lu et al. 2013).

462   **ACKNOWLEDGMENTS**

470   **REFERENCES CITED**

471   Akaogi, M., and Akimoto, S. (1977) Pyroxene-garnet solid-solution equilibria in the systems

472        $Mg_4Si_4O_{12}$-$Mg_3Al_2Si_3O_{12}$ and $Fe_4Si_4O_{12}$-$Fe_3Al_2Si_3O_{12}$ at high pressures and temperatures.

473   Physics of the Earth and Planetary Interiors, 15, 90-106.

474   Akaogi, M., Ohmura, N., and Suzuki, T. (1998) High-pressure dissociation of $Fe_3Al_2Si_3O_{12}$ garnet:

475   phase boundary determined by phase equilibrium experiments and calorimetry. Physics of the

476   Earth and Planetary Interiors, 106, 103-113.

477   Anderson, D.L., and Anderson, O.L. (1970) The bulk modulus-volume relationship for oxides.

478   Journal of Geophysical Research, 75, 3494-3500.

479   Anderson, D.L., and Bass, J.D. (1984) Mineralogy and composition of the upper mantle.

480   Geophysical Research Letters, 11, 637-640.

481   Anderson, O.L. (1995) Equation of State of Solids for Geophysics and Ceramic Science. Oxford

482   University Press, New York, pp.243-274.

483   Angel, R. (2000) Equation of state. Reviews in Mineralogy and Geochemistry, 41, 35-60.

484   Antao, S.M. (2013) Three cubic phases intergrown in a birefringent andradite-grossular garnet and

485   their implications. Physics and Chemistry of Minerals, 40, 705-716.

486   Asimov, P.D., Hirschmann, M.M., Ghiorso, M.S., O'Hara, M.J., and Stolper, E.M. (1995) The

487   effect of pressure induced solid-solid phase transitions on decompression melting of the

488   mantle. Geochimica et Cosmochimica Acta, 59, 4489-4506.

489   Bass, J.D. (1986) Elasticity of uvarovite and andradite garnets. Journal of Geophysical Research,

490   91, 7505-7516.

491   Bass, J.D. (1989) Elasticity of grossular and spessartine garnets by Brillouin spectroscopy. Journal

492   of Geophysical Research, 94, 7621-7628.

493   Bass, J.D., and Anderson, D.L. (1984) Composition of the upper mantle: geophysical tests of two

494   petrological models. Geophysical Research Letters, 11, 229-232.

495   Bulanova, G.P., Muchemwa, E., Pearson, D.G., Griffin, B.J., Kelley, S.P., Klemme, S., and Smith,

496   C.B. (2004) Syngenetic inclusions in diamond from Sesekimberlite (Zimbabwe)-evidence for

497   metasomatic conditions of growth. Lithos, 77, 181-192.

498   Cammarano, F., Goes, S., Vacher, P., and Giardini, D. (2003) Inferring upper-mantle temperatures

499   from seismic velocities. Physics of the Earth and Planetary Interiors, 138, 197–222.

500   Challis, A., Grapes, R., and Palmer, K. (1995) Chromian muscovite, uvarovite, and zincian

501   chromite: Products of regional metasomatism in northwest Nelson, New Zealand. The

502   Canadian Mineralogist, 33, 1263-1284.

503 Chopelas, A. (2005) Single crystal Raman spectrum of uvarovite, $Ca_3Cr_2Si_3O_{12}$. Physics and

504   Chemistry of Minerals, 32, 525-530.

505 Deer, W.A., Howie, R.A., and Zussman, J. (1992) An introduction to the rockforming minerals.

506   John Wiley and Sons, New York.

507 Diella, V., Sani, A., Levy, D., and Pavese, A. (2004) High-pressure synchrotron X-ray diffraction

508   study of spessartine and uvarovite: a comparison between different equation of state models.

509   American Mineralogist, 89,371-376.

510 Duffy, T.S., and Anderson, D.L. (1989) Seismic velocity in mantle minerals and mineralogy of the

511   upper mantle. Journal of Geophysical Research, 94, 1895-1912.

512 Dymshits, A.M., Litasov, K.D., Shatskiy, A., Sharygin, I.S., Ohtani, E., Suzuki, A., Pokhilenko,

513   N.P., and Funakoshi, K. (2014) P-V-T equation of state of Na-majorite to 21 GPa and 1673 K.

514   Physics of the Earth and Planetary Interiors, 227, 68-75.

515 Fan, D.W., Ma, M.N., Wei, S.Y., Chen, Z.Q., and Xie, H.S. (2013) High Pressure Elastic Behavior

516   of Synthetic $Mg_3Y_2(SiO_4)_3$ Garnet up to 9GPa. Advances in Materials Science and

517   Engineering, 2013, 502702.

518 Fan, D.W., Xu, J.G., Ma, M.N., Wei, S.Y., Liu, J., and Xie, H.S. (2014) P-V-T equation of state of

519   spessartine-almandine solid solution measured using a diamond anvil cell and in situ

520   synchrotron X-ray diffraction. Submitted to Physics and Chemistry of Minerals.

521 Fan, D.W., Zhou, W.G., Liu, C.Q., Liu, Y.G., Wan, F., Xing, Y.S., Liu, J., Bai, L.G., and Xie, H.S.

522   (2009) The thermal equation of state of $(Fe_{0.86}Mg_{0.07}Mn_{0.07})_3Al_2Si_3O_{12}$ almandine.

523   Mineralogical Magazine, 73, 95-102.

524 Fan, D.W., Zhou, W.G., Wei, S.Y., Liu, Y.G., Ma, M.N., and Xie, H.S. (2010) A simple external

525   resistance heating diamond anvil cell and its application for synchrotron radiation x-ray

526   diffraction. Review of Scientific Instruments, 81, 053903.

527 Fei, Y.W., Ricolleau, A., Frank, M., Mibe, K., Shen, G.Y., and Prakapenka, V. (2007) Toward an

528   internally consistent pressure scale. Proceedings of the National Academy of Sciences, 104,

529   9182-9186.

530 Funamori, N., Yagi, T., Utsumi, W., Kondo, T., Uchida, T., Funamori, M. (1996) Simultaneous

531   high-P, high-T X-ray diffraction study of β-$(Mg, Fe)_2SiO_4$ to 26 GPa and 900 K. Journal of

532   Geophysical Research, 101, 8257-8269.

533 Geiger, C.A., and Armbruster, T. (1997) $Mn_3Al_2Si_3O_{12}$ spessartine and $Ca_3Al_2Si_3O_{12}$ grossular

534   garnet: Structural dynamic and thermodynamic properties. American Mineralogist, 82,

535   740-747.

536 Graham, I.T., Franklin, B.J., and Marshall, B. (1996) Chemistry and mineralogy of podiform

537   chromitite deposits, southern NSW, Australia: A guide to their origin and evolution.

538   Mineralogy and Petrology, 57, 129-150.

539 Gréaux, S., Kono, Y., Nishiyama, N., Kunimoto, T., Wada, K., and Irifune, T. (2011) P-V-T

540   equation of state of $Ca_3Al_2Si_3O_{12}$ grossular garnet. Physics and Chemistry of Minerals, 38,

541   85-94.

542 Gréaux, S., Nishiyama, N., Kono, Y., Gautron, L., Ohfuji, H., Kunimoto, T., Menguy, N., and

543   Irifune, T. (2011) Phase transformations of $Ca_3Al_2Si_3O_{12}$ grossular garnet to the depths of the

544   Earth's mantle transition zone. Physics of the Earth and Planetary Interiors, 185, 89-99.

13

545   Gréaux, S., and Yamada, A. (2014) P-V-T equation of state of $Mn_3Al_2Si_3O_{12}$ spessartine garnet.
546   Physics and Chemistry of Minerals, 41, 141-149.

547   Green, D.H., and Falloon, T.J. (1998) Pyrolite: A Ringwood concept and its current expression. In
548   Jackson, I., Ed., The Earth's mantle: Composition, structure and evolution, p. 311-380.
549   Cambridge University Press, Cambridge.

550   Grüttler, H., Latti, D., and Menzies, A. (2006) Cr-saturation in concentrate garnet compositions
551   from kimberlite and their use in mantle barometry. Journal of Petrology, 47, 801-820.

552   Guyot, F., Wang, Y., Gillet, P., and Ricard, Y. (1996) Quasiharmonic computations of
553   thermodynamic parameters of olivines at high pressure and high temperature: a comparison
554   with experiment data. Physics of the Earth and Planetary Interiors, 98, 17-29.

555   Gwanmesia, G.D., Wang, L., Triplett, R., and Liebermann, R.C. (2009) Pressure and temperature
556   dependence of the elasticity of pyrope-majorite [$Py_{60}Mj_{40}$ and $Py_{50}Mj_{50}$] garnet solid solution
557   measured by ultrasonic interferometry technique. Physics of the Earth and Planetary Interiors,
558   174, 105-112.

559   Gwanmesia, G.D., Zhang, J., Darling, K., Kung, J., Li, B., Wang, L., Neuville, D., and
560   Liebermann, R.C. (2006) Elasticity of polycrystalline pyrope $Mg_3Al_2Si_3O_{12}$ to 9 GPa and
561   1,000°C. Physics of the Earth and Planetary Interiors, 155, 179-190.

562   Hammersley, A.P., Svensson, S.O., Hanfland, M., Fitch, A.N., and Hausermann, D. (1996)
563   Two-dimensional detector software: from real detector to idealized image or two-theta scan.
564   High Pressure Research, 14, 235-248.

565   Huang, S., and Chen, J.H. (2014) Equation of state of pyrope–almandine solid solution measured
566   using a diamond anvil cell and *in situ* synchrotron X-ray diffraction. Physics of the Earth and
567   Planetary Interiors, 228, 88-91.

568   Huckenholz, H.G., and Knittel, D. (1975) Uvarovite: stability of uvarovite-grossular solid solution
569   at low pressure. Contributions to Mineralogy and Petrology, 49, 211-232.

570   Irifune, T., Koizumi, T., and Ando, J. (1996) An experimental study of the garnet-perovskite
571   transformation in the system $MgSiO_3$-$Mg_3Al_2Si_3O_{12}$. Physics of the Earth and Planetary
572   Interiors, 96, 147-157.

573   Irifune, T., and Ringwood, A.E. (1987) Phase transformations in a harzburgite composition to 26
574   GPa: implications for dynamical behaviour of the subducting slab. Earth and Planetary
575   Science Letters, 86, 365-376.

576   Irifune, T., and Ringwood, A.E. (1993) Phase transformation in subducted oceanic crust and
577   buoyancy relationships at depths of 600–800 km in the mantle. Earth and Planetary Science
578   Letters, 117, 101-110.

579   Irifune, T., Ohtani, E., and Kumazawa, M. (1982) Stability field of knorringite $Mg_3Cr_2Si_3O_{12}$ at
580   high pressure and high temperature and its implication to the occurrence of Cr-rich pyrope in
581   upper mantle. Physics of the Earth and Planetary Interiors, 27, 263-272.

582   Ita, J., and Stixrude, L. (1992) Petrology, elasticity, and composition of the mantle transition zone.
583   Journal of Geophysical Research, 97, 6849-6866.

584   Jackson, I., and Rigden, S.M. (1996) Analysis of P-V-T data: constraints on the thermoelastic
585   properties of high-pressure minerals. Physics of the Earth and Planetary Interiors, 96, 85-112.

586   Jiang, F.M., Speziale, S., and Duffy, T.S. (2004) Single-crystal elasticity of grossular- and
587   almandine-rich garnets to 11 GPa by Brillouin scattering. Journal of Geophysical Research,
588   109, B10210.

589   Karato, S., Wang, Z., Liu, B., and Fujino, K. (1995) Plastic deformation of garnets: systematics
590   and implications for the rheology of the mantle transition zone. Earth and Planetary Science
591   Letters, 130, 13-30.
592   Klemme, S. (2004) The influence of Cr on the garnet-spinel transition in the Earth's mantle:
593   Experiments in the system $MgO-Cr_2O_3-SiO_2$ and thermodynamic modelling. Lithos, 77,
594   639-646.
595   Klemme, S., Van Miltenburg, J.C., Javorsky, P., and Wastin, F. (2005) Thermodynamic properties
596   of uvarovite garnet ($Ca_3Cr_2Si_3O_{12}$). American Mineralogist, 90, 663-666.
597   Kono, Y., Gréaux, S., Higo, Y., Ohfuji, H., and Irifune, T. (2010) Pressure and temperature
598   dependences of elastic properties of grossular garnet up to 17 GPa and 1 650 K. Journal of
599   Earth Science, 21:782-791.
600   Larson, A.C., and Von Dreele, R.B. (2000) GSAS general structure analysis system operation
601   manual. Los Alamos National Laboratory LAUR 86–748:1-179.
602   Le Bail, A., Duroy, H., and Fourquet, J.L. (1988) Ab initio structure determination of $LiSbWO_6$ by
603   X-ray powder diffraction. Materials Research Bulletin, 23:447-452.
604   Leger, J.M., Redon, A.M., and Chateau, C. (1990) Compressions of synthetic pyrope, spessartine
605   and uvarovite garnets up to 25 GPa. Physics and Chemistry of Minerals, 17, 161-167.
606   Leitner, B.J., Weidner, D.J., and Liebermann, R.C. (1980) Elasticity of single crystal pyrope and
607   implications for garnet solid solution series. Physics of the Earth and Planetary Interiors, 22,
608   111-121.
609   Li, B., and Liebermann, R.C. (2007) Indoor seismology by probing the Earth's interior by using
610   sound velocity measurements at high pressures and temperature. Proceedings of the National
611   Academy of Sciences, 104, 9145–9150.
612   Liu, W., Kung, J., Wang, L.P., and Li, B.S. (2008) Thermal equation of state of $CaGeO_3$ perovskite.
613   American Mineralogist, 93:745-750.
614   Liu, X., Shieh, S.R., Fleet, M.E., and Akhmetov, A. (2008) High-pressure study on lead
615   fluorapatite. American Mineralogist, 93:1581-1584.
616   Lu, C., Mao, Z., Lin, J.F., Zhuravlev, K.K., Tkachev, S.N., and Prakapenka, V.B. (2013) Elasticity
617   of single-crystal iron-bearing pyrope up to 20 GPa and 750 K. Earth and Planetary Science
618   Letters, 361, 134-142.
619   Milman, V., Akhmatskaya, E., Nobes, R., Winkler, B., Pickard, C., and White, J. (2001)
620   Systematic *ab initio* study of the compressibility of silicate garnets. Acta Crystallographica
621   Section B, 57, 163-177.
622   Nishihara, Y., Aoki, I., Takahashi, E., Matsukage, K.N., and Funakoshi, K.I. (2005) Thermal
623   equation of state of majorite with MORB composition. Physics of the Earth and Planetary
624   Interiors, 148, 73-84.
625   Nishihara, Y., Takahashi, E., Matsukage, K.N., Iguchi, T., Nakayama, K., and Funakoshi, K. (2004)
626   Thermal equation of state $(Mg_{0.91}Fe_{0.09})_2SiO_4$ ringwoodite. Physics of the Earth and Planetary
627   Interiors, 143-144, 33-46.
628   Nixon, P.H. (1995) A review of mantle xenoliths and their role in diamond exploration. Journal of
629   Geodynamics, 20, 305-329.
630   O'Neill, H.S.C., and Palme, H. (1998) Composition of the silicate Earth: Implications for accretion
631   and core formation. In Jackson, I., Ed., The Earth's Mantle: Composition, Structure and
632   Evolution, p. 3-126. Cambridge University Press, Cambridge.

15

633 Pavese, A., Diella, V., Pischedda, V., Merli, M., Bocchio, R., and Mezouar, M. (2001)
634   Pressure-volume-temperature equation of state of andradite and grossular, by high-pressure
635   and -temperature powder diffraction. Physics and Chemistry of Minerals, 28, 242-248.

636 Proenza, J., Sole, J., and Melgarejo, J.C. (1999) Uvarovite in podiform chro-mitite: The
637   Moa-Baracoa ophiolitic massif, Cuba. The Canadian Mineralogist, 37, 679-690.

638 Rath S., Knorr K. and Morgenroth W. (2003) High-pressure investigation on single crystal
639   uvarovite, $Ca_3Cr_2Si_3O_{12}$. Hasylab Annual Report.

640 Ringwood, A.E. (1977) Synthesis of pyrope-knorringite solid solutions series. Earth and Planetary
641   Science Letters, 36, 443-438.

642 Shannon, R.D. (1976) Revised effective ionic-radii and systematic studies of interatomic distances
643   in halides and chalcogenides. Acta Crystallographica Section A, 32,751-767

644 Sinogeikin, S.V., and Bass, J.D. (2000) Single-crystal elasticity of pyrope and MgO to 20 GPa by
645   Brillouin scattering in the diamond cell. Physics of the Earth and Planetary Interiors, 120,
646   43-62.

647 Stachel, T. and Harris, J.W. (1997) Syngenetic inclusions in diamond from the Birim field
648   (Ghana)-A deep peridotitic profile with a history of depletion and re-enrichment.
649   Contributions to Mineralogy and Petrology, 127, 336-352.

650 Stachel, T., Viljoen, K.S., Brey, G.P., and Harris, J.W. (1998) Metasomatic processes in lherzolitic
651   and harzburgitic domains of diamondiferous lithospheric mantle-REE in garnets from
652   xenoliths and inclusions in diamonds. Earth and Planetary Science Letters, 159, 1-12.

653 Stixrude, L., and Lithgow-Bertelloni, C. (2005) Thermodynamics of mantle minerals—I. Physical
654   properties. Geophysical Journal International, 162, 610-632.

655 Turkin, A.I., Doroshev, A.M., and Malinovskii, I.Y. (1983) A study of the phase composition of
656   garnet-bearing assemblages in the system $MgO-Al_2O_3-Cr_2O_3-SiO_2$ at high temperatures and
657   pressures. In Silicate Systems at High Pressures. Institute of Geology and Geophysics,
658   Novosibirsk, 5-24 (in Russian).

659 Vinet, P., Ferrante, J., Rose, J.H., and Smith, J.R. (1987) Compressibility of solids. Journal of
660   Geophysical Research, 92, 9319-9325.

661 Vinet, P., Ferrante, J., Smith, J.R., and Rose, J.H. (1986) A universal equation of state for solids.
662   Journal of Physics C: Solid State Physics, 19, L467.

663 Wang, Y., Weinder, D.J., and Guyot, F. (1996) Thermal equation of state of $CaSiO_3$ perovskite.
664   Journal of Geophysical Research, 101, 661-672.

665 Wang, Y., Weidner, D.J., Zhang, J., Gwanmesia, G.D., and Liebermann, R.C. (1998) Thermal
666   equation of state of garnets along the pyrope-majorite join. Physics of the Earth and Planetary
667   Interiors, 105, 59-71.

668 Wang, Z.C., and Ji, S.C. (2001) Elasticity of six polycrystalline silicate garnets at pressure up to
669   3.0 GPa. American Mineralogist, 86, 1209-1218.

670 Weidner, D.J., and Wang, Y. (2000) Phase transformations: implications for mantle structure.
671   Geophysical Monograph Series, 117, 215-235.

672 Wildner, M., and Andrut, M. (2001) The crystal chemistry of birefringent natural uvarovites: Part
673   II. Single-crystal X-ray structures. American Mineralogist, 86, 1231-1251.

674 Toby, B.H. (2001) EXPGUI, a graphical user interface for GSAS. Journal of Applied
675   Crystallography, 34, 210-213.

676 Trots, D.M., Kurnosov, A., Ballaran, T.B., Tkachev, S., Zhuravlev, K., Prakapenka, V., Berkowski,

16

677   M., Frost, D.J. (2013) The Sm:YAG primary fluorescence pressure scale. Journal of
678   Geophysical Research, 118, 5805-5813.

679   Xiao, W.S., Tan, D.Y., Zhou, W., Liu, J., and Xu, J. (2013) Cubic perovskite polymorph of
680   strontium metasilicate at high pressures. American Mineralogist, 98, 2096-2104.

681   Xie, H.S., Zhang, Y., Xu, H.G., Hou, W., Guo, J., and Zhao, H. (1993) A new method of
682   measurement for elastic wave velocities in minerals and rocks at high temperature and high
683   pressure and its significance. Science China Chemistry, 36, 1276-1280.

684   Xie, H.S., Zhou, W.G., Liu, Y.G., Guo, J., Hou, W., and Zhao, Z.D. (2002) Comparative
685   experimental study on several methods for measuring elastic wave velocities in rocks at high
686   pressure. Science China Earth Sciences, 45, 990-998.

687   Yagi, T., Akaogi, M., Shimomura, O., Tamai, H., and Akimoto, S.I. (1987) High pressure and high
688   temperature equations of state of majorite. Geophysical Monograph Series, 39, 141-147.

689   Zhang, J. (1999) Room-temperature compressibilities of MnO and CdO: further examination of
690   the role of cation type in bulk modulus systematic. Physics and Chemistry of Minerals, 26,
691   644-648.

692   Zhang, L., Ahsbahs, H., Kutoglu, A., and Geiger, C.A. (1999) Single-crystal hydrostatic
693   compression of synthetic pyrope, almandine, spessartine, grossular and andradite garnets at
694   high pressure. Physics and Chemistry of Minerals, 27, 52-58.

695   Zhuravlev, K.K., Goncharov, A.F., Tkachev, S.N., Dera, P., Prakapenka, V.B. (2013) Vibrational,
696   elastic, and structural properties of cubic silicon carbide under pressure up to 75 GPa:
697   Implication for a primary pressure scale. Jouranl of Applied Physics, 113, 113503.

698   Zou, Y., Gréaux, S., Irifune, T., Whitaker, M.L., Shinmei, T., and Higo, Y. (2012) Thermal
699   equation of state of $Mg_3Al_2Si_3O_{12}$ pyrope garnet up to 19 GPa and 1700 K. Physics and
700   Chemistry of Minerals, 39, 589-598.

701   Zou, Y., Irifune, T. (2012) Phase relations in $Mg_3Cr_2Si_3O_{12}$ and formation of majoritic knorringite
702   garnet at high pressure and high temperature. Journal of Mineralogical and Petrological
703   Sciences, 107, 197-205.

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724   **Fig. 1** Experimental P-T conditions for angle-dispersive synchrotron X-ray diffraction of
725   uvarovite garnet. The *solid circle symbolds* represent the pressures after heating, while *open*
726   *circle symbols* show those before heating.

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728   **Fig. 2** Le Bail profile fitting of the diffraction profiles at 15.33 GPa and 900 K of uvarovite.
729   Observed spectra (*black line*), fitted spectra (*red solid line*), difference plot (*blue solid line*)
730   and Bragg peak positions (*tick marks*) are shown. Inset shows the two-dimensional image of
731   X-ray pattern before the integration of uvarovite at 15.33 GPa and 900 K. (Color online)

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733   **Fig. 3** Volume compression of uvarovite at high pressure and room temperature in this study
734   compared with the previous study by Diella et al. (2004). The third-order Birch–Murnaghan
735   equation of state fitted with K_0 and K'_0 are 162 GPa and 4.5 for uvarovite in this study. The
736   error bars of the data points are smaller than the symbols.

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738   **Fig. 4** Volume Eulerian strain-normalized pressure (F_E-f_E) plot of uvarovite. The solid lines
739   represent the linear fit through the data.

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741   **Fig. 5** Unit-cell volume of uvarovite as a function of pressure and temperature. The solid lines
742   represent isothermal compression curve from fitting HTBM EoS at 300, 500, 700, 900 K
743   with the following parameters: K_0=162±3 GPa, K'_0=4.3±0.4, $(\partial K/\partial T)_P$=-0.021±0.004 GPaK^{-1}
744   and α_0=(2.72±0.14)×10^{-5} K^{-1}. The error bars of the data points are smaller than the symbols.

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746   **Fig. 6** Thermal pressure of uvarovite garnet against temperature. Solid circles are uvarovite data in
747   this study. Solid line is the fitting results using thermal pressure approach.

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

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753   **Fig. 8** The unit formula volume (V_0)—bulk modulus (K_0) relationship of the ugrandite garnets (see

754   Table 2). The K_0-V_0 data of the ugrandite garnets follow a excellent linear function as shown
755   in the plot. The vertical error bars show the estimated standard deviations of the
756   zero-pressure bulk modulus (see Table 2). The uncertainties of the unit formula volume are
757   smaller than the size of the symbols.

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759   **Fig. 9** Isothermal bulk modulus K_{T0} as a function of temperature. *Solid red*, *green* and *black* lines
760   represent the present results for fixed values of =4.0 and 4.5, as well as for no constraint on
761   the elastic parameters. *Solid blue*, *wine*, *magenta*, *olive lines* and *dashed blue lines* symbolize
762   the previous studies by Gréaux et al. (2011) for Grossular, Pavese et al. (2001) for andradite,
763   Zou et al. (2012) for Pyrope, Fan et al. (2009) for almandine and Gréaux and Yamada (2014)

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764   for spessartine, respectively. (Color online)

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Table 1 Unit cell parameters of uvarovite at various P-T conditions

P[a] (GPa)	T (K)	V (Å^3)	P (GPa)	T (K)	V (Å^3)
Compression before heating			9.63(43)	500	1652.58(63)
0.0	300	1736.94(54)	11.78(44)	500	1636.65(45)
3.82(55)	300	1698.55(46)	13.85(67)	500	1619.62(58)
7.49(44)	300	1665.80(76)	15.91(37)	500	1605.23(75)
10.26(48)	300	1642.42(72)	3.55(54)	700	1716.25(66)
Compression after heating			5.78(72)	700	1697.77(38)
1.17(13)	300	1724.71(58)	7.64(49)	700	1679.27(46)
2.70(42)	300	1709.10(22)	9.82(58)	700	1659.47(52)
5.00(34)	300	1686.74(45)	12.43(66)	700	1638.15(61)
6.18(25)	300	1676.44(34)	13.89(69)	700	1624.75(46)
8.74(53)	300	1654.34(54)	15.63(72)	700	1614.55(39)
11.49(63)	300	1631.99(77)	4.54(62)	900	1715.27(84)
13.06(48)	300	1619.53(64)	5.73(47)	900	1705.54(47)
14.75(46)	300	1607.71(58)	7.85(46)	900	1682.69(53)
16.20(31)	300	1598.37(45)	9.41(58)	900	1670.45(54)
2.58(43)	500	1718.38(62)	11.62(47)	900	1652.56(57)
4.24(54)	500	1701.54(36)	13.84(55)	900	1632.62(43)
5.73(58)	500	1690.48(53)	15.33(77)	900	1621.43(48)
7.55(45)	500	1671.43(54)			

Numbers in parenthesis represent standard deviations

[a] Pressure is based on EoS of Au by Fei et al. (2007)

Table 2 Bulk modulus and its pressure derivative of ugrandite garnets

Sample	K_0(GPa)	K'_0	V_0 (Å^3)	Methods	Reference
Synthetic Uva	164(1)	4.0[a]	1736.5(3)	XRD	This study (Au-F)[b]
Synthetic Uva	162(2)	4.5(3)	1736.9(5)	XRD	This study (Au-F)
Synthetic Uva	162(2)	—	—	Brillouin	Bass (1986)
Synthetic Uva	162[a]	4.7(7)	—	XRD	Leger et al. (1990)
Natural Uva	164.8(2)	4.7(9)	—	Ultrasonic	Wang and Ji (2001)
Natural Uva	160(1)	5.8(1)	1697.5[a]	XRD	Diella et al. (2004)
Natural Grs	170(4)	5.2(6)	1660.2(3)	XRD	Zhang et al. (1999)
Natural Grs	167.4(2.4)	6.2(5)	1666.4(4)	XRD	Pavese et al. (2001)
Synthetic Grs	171.5(8)	4.42(7)	—	Ultrasonic	Kono et al. (2010)
Synthetic Grs	166(3)	4.0[a]	1664(2)	XRD	Gréaux et al. (2011)
Synthetic Grs	172(2)	3.0(7)	1664[a]	XRD	Gréaux et al. (2011)
Natural And	157(2)	4.0[a]	—	Brillouin	Bass (1986)
Synthetic And	162(5)	4.4(7)	—	XRD	Zhang et al. (1999)
Natural And	159.8(2.5)	1.89(1.72)	1754.12(53)	XRD	Pavese et al. (2001)
Natural And	158.5(2.4)	4.0[a]	1753.91(51)	XRD	Pavese et al. (2001)

XRD, X-ray diffraction; Uva, Uvarovite; Grs, Grossular; And, Andradite

Numbers in parenthesis represent standard deviations

[a] Fixed during fitting

[b] Pressure was calculated from the equation of state of gold by Fei et al. (2007) (Au-F)

Table 3 Thermoelastic parameters of uvarovite compared with other silicate garnets

Sample	$V_0(\text{Å}^3)$	K_0(GPa)	K'_0	$(\partial K/\partial T)_P$ (GPaK^{-1})	α_0 (10^{-5}K^{-1})	Reference
Natural Grs	1666.08[a]	168.2(1.7)	4.0[a]	-0.016(3)	2.78(2)	Pavese et al. (2001)
Synthetic Grs	1663.0(10)	159.7(4.0)	5.10(48)	-0.021(2)	2.77(24)	Gréaux et al. (2011)
Synthetic Grs	1664[a]	166[a]	4.03(13)	-0.019(1)	2.62(23)	Gréaux et al. (2011)
Natural And	1754.05[a]	158.0(1.5)	4.0[a]	-0.020(3)	3.16(2)	Pavese et al. (2001)
Synthetic Py	1500.7(19)	164(9)	4.9(12)	-0.024(13)	2.97(45)	Zou et al. (2012)
Synthetic Py	1503.1(5)	170(2)	5.0[a]	-0.020(3)	2.30(20)	Wang et al. (1998)
Natural Py	1522.5(8)	167.0(1.8)	4.0(1)	-0.023(2)	—	Lu et al. (2013)
Natural Alm	1539.6(9)	177(2)	4.0[a]	-0.032(16)	3.10(70)	Fan et al. (2009)
Spe$_{38}$Alm$_{62}$	1544.6(6)	180(4)	4.0(4)	-0.028(5)	3.16(14)	Fan et al. (2014)
Spe$_{64}$Alm$_{36}$	1557.7(9)	176(4)	4.0(5)	-0.029(5)	3.04(16)	Fan et al. (2014)
Synthetic Spe	1564.96[a]	171(4)	5.3(8)	-0.049(7)	2.46(54)	Gréaux and Yamada (2014)
Synthetic Uva	1736.6(6)	164(1)	4.0[a]	-0.018(4)	2.69(12)	This study (Au-F)[b]
Synthetic Uva	1737.0(6)	161(1)	4.5[a]	-0.022(4)	2.76(13)	This study (Au-F)
Synthetic Uva	1736.8(8)	162(3)	4.3(4)	-0.021(4)	2.72(14)	This study (Au-F)
Synthetic Uva	1736.7(6)	164(1)	4.0[a]	-0.019(4)	2.60(13)	This study (Au-D)
Synthetic Uva	1736.8(8)	163(3)	4.1(3)	-0.020(3)	2.61(14)	This study (Au-D)

Uva, Uvarovite; Grs, Grossular; And, Andradite; Py, Pyrope; Alm, Almandine; Spe, Spessartine

Numbers in parenthesis represent standard deviations

[a] Fixed during fitting

[b] Pressure was calculated from the equation of state of gold by Fei et al. (2007) (Au-F) and Dorogokupets and Dewaele (2007) (Au-D)