

Thermo-compression of pyrope-grossular garnet solid solutions: Non-linear compositional dependence

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ABSTRACT

Unit-cell parameters of a series of synthetic garnets with the pyrope, grossular, and four intermediate compositions were measured up to about 900 K and to 10 GPa using synchrotron X-ray powder diffraction. Coefficients of thermal expansion of pyrope-grossular garnets are in the range $2.10\text{--}2.74 \times 10^{-5} \text{ K}^{-1}$ and uniformly increase with temperature. Values for the two end-members pyrope and grossular are identical within experimental error $2.74 \pm 0.05 \times 10^{-5} \text{ K}^{-1}$ and $2.73 \pm 0.01 \times 10^{-5} \text{ K}^{-1}$, respectively. Coefficients of thermal expansion for intermediate compositions are smaller than those of end-members and are not linearly dependent on composition. Bulk modulus of grossular is $K_0 = 164.3(1) \text{ GPa}$ (with K'_0 the pressure derivative of the bulk modulus fixed to 5.92) and bulk modulus of pyrope is $K_0 = 169.2(2) \text{ GPa}$ (with K'_0 fixed to 4.4) using a third-order Birch-Murnaghan equation of state, which are consistent with previously reported values. The bulk moduli of garnets of intermediate composition are between ~ 155 and $\sim 160 \text{ GPa}$, smaller than those of the end-members no matter which K'_0 is chosen. The compositional dependence of bulk modulus resembles the compositional dependence of thermal expansion. Intermediate garnets on this binary have large positive excess volume, which makes them more compressible. We find that excess volumes in the pyrope-grossular series remain relatively large even at high pressure ($\sim 6 \text{ GPa}$) and temperature ($\sim 800 \text{ K}$), supporting the observation of crystal exsolution on this garnet join. The curiously “W”-shaped compositional variation of thermal expansion and bulk modulus is anti-correlated with the compositional dependence of microstrain documented in our companion paper (Du et al. in preparation) on the excess volumes in this series of garnets. Minimum thermal expansions and bulk moduli go with maximum microstrains.

Keywords: Pyrope-grossular garnet solid solution, thermal expansion, compressibility, excess volume

INTRODUCTION

Garnets have the general chemical composition $A_3B_2(\text{SiO}_4)_3$, where A and B are 2+ and 3+ cations, respectively. In nature, garnets predominately exist as solid solutions between the following six end-member minerals: pyrope ($\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$), grossular ($\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$), almandine ($\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$), spessartite ($\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$), uvarovite ($\text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$), and andradite ($\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$). Garnet is a major phase in Earth mantle models such as pyrolite and piclogite (Irifune and Ringwood 1987, 1993) and garnet volume fraction may increase to more than 40% in the Earth's transition zone (410–660 km) (Duffy and Anderson 1989). They are stable over a wide pressure and temperature range and compatible with phases such as mica, pyroxene, and olivine, making them important candidates for geothermal barometers and thermometers. Knowledge of the effect of compositional change on the elastic properties of garnet is essential

for the correct interpretation of regional lateral variations in seismic velocity imaged by seismic tomography and geodynamic studies of the continental lithosphere in terms of thermal and chemical properties. Least-squares techniques might succeed in inverting the elastic properties of natural solid solution samples based on interpolation of end-member properties if those elastic properties were strictly linear in compositional dependence or if there is sufficient compositional coverage to resolve some more complex dependence.

Substitution for magnesium by calcium along the pyrope-grossular join involves a large change in cation size and might produce a large change in thermoelastic properties. The mixing volumes and enthalpies of solid solutions of several synthetic and natural garnets along this join have been determined experimentally at ambient temperature and pressure (Newton et al. 1977; Geiger et al. 1987; Wood 1988; Ganguly et al. 1993; Bosenick et al. 1995, 1996, 1997; Geiger and Feenstra 1997). These previous studies all show that garnet solid solutions on this binary have large, positive, excess mixing volumes. There have been many measurements of the compressibility and thermal expansion of

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the end-member garnets (Hazen and Finger 1978; Bass 1986; O'Neill et al. 1989; Olijnyk et al. 1991; Gillet et al. 1992; Zhang et al. 1998, 1999; Conrad et al. 1999; Zou et al. 2012), and a few measurements for their solid solutions (Babuska et al. 1978; Bosenick and Geiger 1997). So far there has been no reported measurement of compressibility along the pyrope-grossular join. There has been one measurement of thermal expansion made at low temperature (Bosenick and Geiger 1997), but the data they reported for end-member compositions did not agree well with previous study by Skinner (1956).

In this paper, we present the unit-cell volumes of pyrope, grossular, and garnets with four intermediate compositions to ~900 K and ~10 GPa. We calculate thermal expansion coefficients and bulk moduli from these data, and compare our results for the end-member compositions to those reported in previous studies. Both thermal expansion and bulk moduli show non-linear compositional dependence and closely correlate with the non-ideal mixing volume on this join. These new data extend our understanding of the thermoelasticity of garnet solid solutions to high pressure and high temperature as a function of Mg-Ca cation substitution.

Our broader objective in this study is to evaluate whether garnets in this solution series are likely to have a stable two-phase region at high pressures and temperatures that may be relevant to the Earth's upper mantle and transition zone. The large excess volume at higher *P-T* condition calculated from bulk modulus and thermal expansion together with the observed larger excess volume of garnet, which will be discussed in a companion paper, strongly encourage the expectation that a two-phase garnet region should be encountered in the laboratory at less than 100 kbar. Such garnet exsolution has now been observed experimentally, as it would not be if excess volumes were as small as previously reported.

EXPERIMENTAL PROCEDURES

Crystalline garnet samples with six different compositions [pyrope ($\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$), $\text{Py}_{80}\text{Gr}_{20}$ ($\text{Mg}_{2.4}\text{Ca}_{0.6}\text{Al}_2\text{Si}_3\text{O}_{12}$), $\text{Py}_{60}\text{Gr}_{40}$ ($\text{Mg}_{1.8}\text{Ca}_{1.2}\text{Al}_2\text{Si}_3\text{O}_{12}$), $\text{Py}_{40}\text{Gr}_{60}$ ($\text{Mg}_{1.2}\text{Ca}_{1.8}\text{Al}_2\text{Si}_3\text{O}_{12}$), $\text{Py}_{20}\text{Gr}_{80}$ ($\text{Mg}_{0.6}\text{Ca}_{2.4}\text{Al}_2\text{Si}_3\text{O}_{12}$), and grossular ($\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$)] were synthesized from an anhydrous glass starting material in a multi-anvil (MA) high-pressure cell. The garnet glasses were prepared by melting a finely ground mixture of CaCO_3 , MgO , Al_2O_3 , and SiO_2 powders. The magnesia, alumina, and silica were rigorously dehydrated shortly before weighing into the mix. The mixed powders were heated slowly to 1000 °C for several hours in a covered Pt crucible to decarbonate the CaCO_3 . After heating to 1500–1600 °C for several hours, the garnet glasses were cooled rapidly by quenching the Pt crucible in water. The glasses of the six solid solution compositions were checked by both microprobe and optical methods. The compositions of these six glasses agree very well with the targeted initial proportion of oxides (Table 1).

These glass precursors were then held at ~6 GPa and 1400 ± 2 °C in the MA for 0.5 h to produce the desired crystalline garnets. We found by in situ XRD observations at Station 16.4 of the Daresbury, U.K., Synchrotron Radiation Source that the key to synthesis of phase-pure garnets by this method is to ensure that garnet growth occurs without previous clinopyroxene nucleation, which we found to occur predominantly in the range 700–1100 °C at the same pressure. Description of the Daresbury 16.4 facility can be found in Clark (1996) and the calibration procedures used there were described by Walker et al. (2000, 2002) and Johnson et al. (2001). So it is crucial to ramp the temperature up above 1100 °C as rapidly as possible. Annealing at 1400 °C ensures reproducible unit-cell sizes and ambient excess volumes by resetting the Mg-Ca disordering [to slightly smaller excess volumes] inherited from the glass starting material. Garnet crystals synthesized in MA were checked by both microprobe and XRD methods. The compositions of these garnets are consistent with the starting glasses within the microprobe measurement error (Table 1) and homogeneous within the counting statistics. The clean XRD peaks

TABLE 1. Microprobe analyses of starting glasses and corresponding MA garnets synthesized from those glasses (averaged compositions for 10 analyses in wt%) and their calculated Ca/(Mg+Ca) atomic ratio

Molecular formula	MgO	CaO	SiO ₂	Al ₂ O ₃	Sum	Ca/(Ca+Mg)
Pyrope (glass)	31.21	0.04	44.53	25.19	100.97	0
Pyrope (crystal)	31.58	0.05	44.08	25.00	100.71	0
$\text{Py}_{80}\text{Gr}_{20}$ (glass)	23.22	8.40	44.00	24.63	100.26	0.206
$\text{Py}_{80}\text{Gr}_{20}$ (crystal)	23.04	8.54	45.26	24.08	100.91	0.210
$\text{Py}_{60}\text{Gr}_{40}$ (glass)	17.55	16.46	41.86	24.02	99.99	0.403
$\text{Py}_{60}\text{Gr}_{40}$ (crystal)	17.74	16.66	41.95	23.93	100.27	0.403
$\text{Py}_{40}\text{Gr}_{60}$ (glass)	11.69	24.21	40.78	23.61	100.29	0.598
$\text{Py}_{40}\text{Gr}_{60}$ (crystal)	11.69	24.80	40.21	23.30	100.00	0.603
$\text{Py}_{20}\text{Gr}_{80}$ (glass)	5.56	31.64	40.19	22.26	99.66	0.804
$\text{Py}_{20}\text{Gr}_{80}$ (crystal)	5.60	32.05	40.08	22.85	100.58	0.805
Grossular (glass)	0.01	37.76	39.13	22.31	99.22	1
Grossular (crystal)	0.01	37.83	39.17	22.28	99.29	1

of these pyrope-grossular garnets indicate that these MA synthetic garnet solid solutions are phase-pure garnet with *Ia3d* symmetry (Fig. 1).

X-ray powder diffraction patterns from our synthesized garnets at a range of temperatures (300 to 900 K) and then a range of pressures (0 to 10 GPa) were collected at the Advanced Light Source, Lawrence Berkeley National Laboratory (ALS) on beamline 12.2.2, in angular-dispersive mode using a MAR345 image plate detector (Kunz et al. 2005). Precisely measuring the sample to detector distance is essential for the determination of accurate lattice parameters. Beamline 12.2.2 has an automated sample positioning system that allows the sample to detector distance to be set for samples contained in complex sample environments to better than 10 µm (Clark et al. 2012). Two series of measurements were carried out: first powder diffraction patterns were measured as a function of temperature and then as a function of pressure.

High-temperature data were collected between 300 and 900 K in steps of about 70 K using a furnace that was specially designed to take advantage of the automated sample positioning system. This consisted of two diamond windows mounted on Invar seats held inside a stainless steel tube mounted inside a nichrome-wound resistance heater. The furnace was designed so that the heating element was as close to the sample as practically possible. Samples were mixed together with sodium chloride powder as a temperature calibration standard and loaded into 120 µm diameter holes drilled in to 60 µm thick stainless steel disks. This assembly was then held loosely between the diamond windows in the furnace. The design of this cell ensures that no pressure can be applied to the sample during heating. Enclosing the sample in a furnace minimizes temperature gradients and allows control of the temperature to better than ±1 °C. The temperature was monitored and controlled using a feedback loop by a chromel-alumel (type K) thermocouple placed in contact with the metal gasket and as close to the sample as possible. Because the thermocouple cannot be exactly at the point sampled by the X-ray beam, we were concerned that temperature gradients within the sample area induced by radiative losses through the diamond windows might lead to some difference between the thermocouple temperature and the sample temperature. We therefore

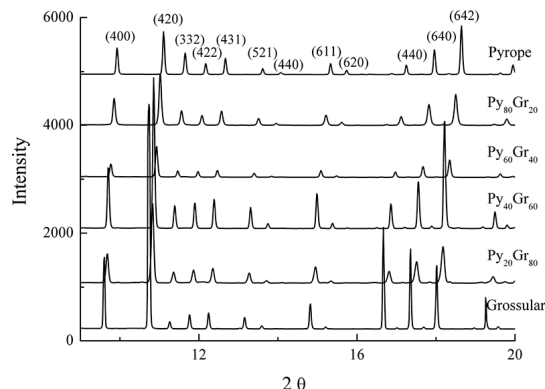


FIGURE 1. X-ray profiles of the synthetic pyrope-grossular garnets at ambient conditions. X-ray diffraction scans were collected at the ALS, Lawrence Berkeley National Laboratory on beamline 12.2.2, in angular-dispersive mode with $\lambda = 0.4959$ Å (25 keV).

used the sodium chloride as an internal temperature sensor.

The diffraction patterns were collected from 5 to 30° 2 θ . The diffraction images were obtained with $\lambda = 0.4959$ Å (calculated from energy 25 keV) and the distance between sample and the detector ~440 mm was determined for each run through collection of a standard LaB₆ diffraction pattern. To collect clear XRD patterns, exposure time was as long as five minutes and temperature readings before and after XRD data collection were recorded. The difference between them is not larger than 2 °C. Powder diffraction patterns were collected for the garnet sample containing the sodium chloride internal standard at each temperature. The unit-cell volume of the sodium chloride was used to calculate the temperature from the thermal part of the BE-2 equation of state of sodium chloride (Birch 1986). We found that as the temperature of the sample increased, the difference between the temperature given by the thermocouple and that from the sodium chloride also increased. The difference is given by the following equation:

$$T_2 = -3.6E - 5 * T_1^2 + 0.982 * T_1 - 0.565 \quad (1)$$

where T_1 (°C) is the K thermocouple temperature and T_2 (°C) is calculated temperature from the EOS of internal standard NaCl. At about 900 K, the temperature reading from thermocouple (T_1) was about 25 °C higher than that calculated from the sodium chloride (T_2), and this discrepancy is an order of magnitude larger than any probable measurement error. Therefore, we used the temperatures given by the sodium chloride (T_2) throughout this work. Thermal expansion of the garnets samples was then calculated based on the unit-cell parameters measured at temperatures between 300 and 900 K.

A four-screw symmetric DAC was used for the compressibility measurements. High pressures were generated by applying force with these four drive screws onto the small area of the tips of two opposed diamond anvils. The polycrystalline garnet samples were loaded into stainless steel gaskets produced as described above together with one or two ruby chips and a 4:1 mixture of methanol:ethanol that acted as a pressure-transmitting medium. This stainless steel gasket serves two purposes: it keeps the diamonds from crushing the crystals and it allows us to surround the crystal with this fluid pressure medium that provides hydrostatic conditions for the crystals. Pressure determination was performed by measuring the ruby fluorescence shift (Mao et al. 1986) excited by an Ar laser. Pressure values measured before and after each XRD data collection were almost equivalent to each other, the difference being no more than 0.2 GPa, and the average value was taken as the pressure of the sample during the unit-cell measurements with an error bar of 0.2 GPa. At the end of each depressurization process, the unit-cell parameter under ambient conditions was measured to give a zero pressure value.

FIT2D software package was used to integrate the two-dimension diffraction rings into one-dimensional diffraction patterns (Hammersley et al. 1996). Since the garnet sample and internal standard peaks were not overlapped, single peak fitting was the most appropriate method for determining the peak positions. The program XFIT (Cheary and Coelho 1996) was used to do this. Once the peak positions were determined for each diffraction pattern, the program REFCEL (Cockcroft and Barnes 1997) was used to refine the unit-cell parameters through least-squares analysis of the fitting positions of the peaks.

RESULTS AND DATA ANALYSIS

Thermal expansion of pyrope, grossular, and the solid solutions

The volume changes with temperature for the six garnet compositions are presented in Table 2 and Figure 2. The volume of garnet on the join pyrope-grossular increases with temperature systematically. We found that a second-order polynomial equation fitted our measured volume data for each of these six garnet compositions (Fig. 2). Thermal expansion coefficients, α , for all six garnet compositions were then calculated from the following expression:

$$\alpha(T) = \frac{1}{V_T} \left(\frac{\partial V}{\partial T} \right)_p \quad (2)$$

where V_T is taken as the measured unit-cell volume at temperature, T . For example, thermal expansion at 300 K is the temperature derivative of the unit-cell volume calculated from

TABLE 2. The unit-cell volume and thermal expansion of pyrope-grossular^a

Composition	T (K)	a (Å)	V_{cell} (Å ³)	$\alpha \times 10^5$ (K ⁻¹)
Pyrope	294.4	11.4543(11)	1502.8(4)	2.741(52)
	365.2	11.4633(8)	1506.3(3)	2.824(34)
	416.7	11.4685(9)	1508.4(3)	2.886(21)
	462.5	11.4729(9)	1510.1(3)	2.941(8)
	509.8	11.4781(10)	1512.2(4)	2.997(16)
	557.4	11.4836(7)	1514.4(3)	3.053(28)
	605.3	11.4891(10)	1516.6(4)	3.109(46)
	672.2	11.4990(11)	1520.5(4)	3.186(46)
	750.7	11.5071(11)	1523.7(4)	3.278(60)
	295.3	11.4552(9)	1503.2(4)	2.637(11)
	332.5	11.4602(9)	1505.1(4)	2.702(7)
	390.4	11.4649(10)	1507.0(4)	2.806(1)
	434.9	11.4713(11)	1509.5(4)	2.883(6)
	481.0	11.4745(9)	1510.8(4)	2.966(12)
	525.0	11.4808(10)	1513.3(4)	3.042(18)
	575.6	11.4869(7)	1515.7(3)	3.130(24)
	638.2	11.4937(7)	1518.4(3)	3.240(32)
	698.5	11.5025(8)	1521.9(3)	3.343(39)
Py ₈₀ Gr ₂₀	738.3	11.5066(7)	1523.5(3)	3.412(45)
	300.0	11.5466(4)	1539.4(2)	2.382(11)
	379.1	11.5543(4)	1542.5(2)	2.487(6)
	451.0	11.5601(4)	1544.8(2)	2.582(2)
	513.8	11.5675(4)	1547.8(2)	2.664(1)
	581.0	11.5741(4)	1550.5(2)	2.752(5)
Py ₆₀ Gr ₄₀	645.1	11.5817(4)	1553.5(2)	2.835(9)
	701.2	11.5877(4)	1555.9(2)	2.908(12)
	771.2	11.5951(4)	1558.9(2)	2.998(16)
	837.1	11.6032(6)	1562.2(2)	3.082(20)
	296.1	11.6433(6)	1578.4(2)	2.425(4)
	358.7	11.6497(5)	1581.0(2)	2.521(4)
	409.3	11.6538(5)	1582.7(2)	2.599(4)
	458.7	11.6587(6)	1584.7(2)	2.674(3)
	505.1	11.6636(4)	1586.7(2)	2.744(2)
	559.9	11.6703(6)	1589.5(2)	2.826(1)
	611.7	11.6754(4)	1591.5(2)	2.904(1)
	656.5	11.6822(5)	1594.3(2)	2.97(1)
Py ₄₀ Gr ₆₀	710.7	11.6869(6)	1596.2(2)	3.052(1)
	750.5	11.6928(6)	1598.6(2)	3.110(1)
	801.4	11.6977(6)	1600.7(2)	3.186(1)
	842.7	11.7034(5)	1603.0(2)	3.246(1)
	309.8	11.7252(6)	1612.0(2)	2.258(1)
	391.8	11.7330(6)	1615.2(2)	2.364(5)
	458.7	11.7388(5)	1617.6(2)	2.451(1)
	526.3	11.7467(5)	1620.9(2)	2.537(1)
	589.6	11.7522(5)	1623.1(2)	2.619(1)
	652.7	11.7583(6)	1625.7(2)	2.700(1)
Py ₂₀ Gr ₈₀	716.4	11.7653(6)	1628.6(2)	2.780(1)
	771.2	11.7710(5)	1630.9(2)	2.850(2)
	831.5	11.7791(6)	1634.3(2)	2.924(3)
	310.8	11.7889(6)	1638.4(2)	2.129(33)
	360.6	11.7934(6)	1640.3(3)	2.232(24)
	428.7	11.7991(5)	1642.7(2)	2.372(12)
	507.0	11.8061(8)	1645.6(3)	2.532(1)
	573.4	11.8138(4)	1648.8(2)	2.667(12)
	643.2	11.8210(7)	1651.8(3)	2.808(24)
	704.0	11.8282(6)	1654.8(2)	2.931(35)
Grossular	764.6	11.8351(7)	1657.7(3)	3.052(45)
	802.3	11.8412(5)	1660.3(2)	3.126(51)
	846.5	11.8440(12)	1661.5(5)	3.216(58)
	296.1	11.8505(4)	1664.2(2)	2.729(4)
	393.7	11.8548(3)	1666.0(1)	2.731(4)
	447.1	11.8602(3)	1668.3(1)	2.733(4)
	501.2	11.8678(4)	1671.5(2)	2.733(4)
	547.4	11.8719(4)	1673.3(2)	2.735(4)
	581.0	11.8762(3)	1675.1(1)	2.735(4)
	584.9	11.8762(5)	1675.1(2)	2.736(5)
	633.6	11.8833(4)	1678.1(2)	2.736(5)
	678.4	11.8881(4)	1680.1(1)	2.737(5)
	727.7	11.8924(3)	1681.9(1)	2.739(5)
	767.5	11.8962(6)	1683.5(3)	2.740(5)
	816.5	11.9008(4)	1685.5(2)	2.742(5)
	859.6	11.9064(4)	1687.9(2)	2.743(5)

^a Temperature is calculated from NaCl internal standard with an error bar of 0.2 °C. Values in parentheses represent estimated standard deviation through least-square fitting for unit-cell parameter. Thermal expansion of these garnet solid solutions was calculated with Equation 1.

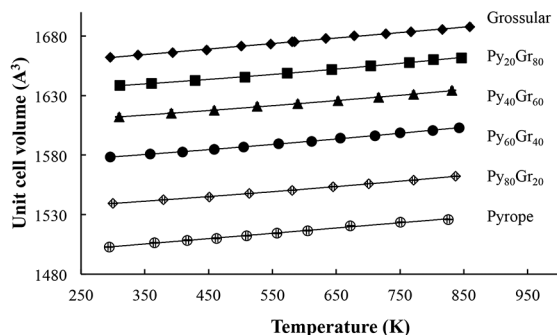


FIGURE 2. Unit-cell volumes of pyrope-grossular garnet at ambient pressure with temperature from 300 to about 900 K. Error bars are not apparent because they are smaller than the marker symbols.

the fitted polynomial equation divided by the measured unit-cell volume at 300 K.

The thermal expansion coefficients of the pyrope-grossular garnet solid solution increase with temperature but the compositional dependence at ambient conditions is not monotonic (Table 2 and Fig. 3). The unit-cell volume and calculated thermal expansion from Equation 2 of our MA synthesized end-members show consistency with previous studies, yielding $\alpha = 2.74(5) \times 10^{-5} \text{ K}^{-1}$ for pyrope with a unit-cell volume $1502.8(4) \text{ Å}^3$; $\alpha = 2.73(1) \times 10^{-5} \text{ K}^{-1}$ for grossular with a unit-cell volume $1664.2(2) \text{ Å}^3$, which agrees with previous studies (Bosenick and Geiger 1997; Gréaux et al. 2011; Zou et al. 2012) (Table 3). Garnets with intermediate composition show smaller thermal expansion than the two end-members at ambient condition; and the thermal expansions of garnets with compositions near the end-members ($\text{Py}_{80}\text{Gr}_{20}$, $\text{Py}_{20}\text{Gr}_{80}$) show relatively smaller thermal expansions than garnets with composition more central to the solution series ($\text{Py}_{60}\text{Gr}_{40}$, $\text{Py}_{40}\text{Gr}_{60}$). Normalized volume ($V_T/V_{273.15}$) gives rough estimates of the temperature dependence of thermal expansion for different compositions. We see that the normalized volumes of end-members pyrope and grossular increase faster with temperature than the garnet solid solutions with intermediate

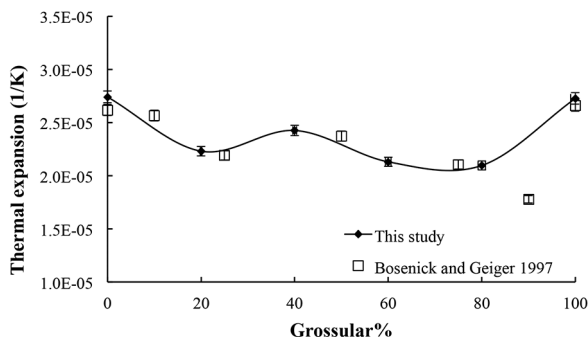


FIGURE 3. Thermal expansion coefficients of pyrope-grossular garnet solid solution at ambient conditions. The thermal expansion of our MA synthesized garnet solid solution calculated from high-temperature (300–900 K) data shows excellent agreement at 300 K with the 300 K results of the previous study of Bosenick and Geiger (1997) calculated from low temperature 20–300 K data, with the exception of Gr_{90} . Error bars are calculated from e.s.d. of garnet unit-cell parameters.

TABLE 3. The unit-cell volume and thermal expansion of end-members pyrope and grossular at ambient conditions

	Pyrope		Grossular	
	$\alpha (10^{-5} \text{ K}^{-1})$	$V_0 (\text{Å}^3)$	$\alpha (10^{-5} \text{ K}^{-1})$	$V_0 (\text{Å}^3)$
Bosenick and Geiger (1997)	2.61(3)	1503.2(1)	2.66(2)	1664.4(2)
Gréaux et al. (2011)			2.62 \pm 0.23	1664(2)
Zou et al. (2012)	2.89 \pm 0.33	1500(2)		
This study	2.74(5)	1502.8(4)	2.73(1)	1664.2(2)

composition; and among all the garnets with intermediate composition, the normalized volume of $\text{Py}_{40}\text{Gr}_{60}$ shows the smallest temperature dependence (Fig. 4).

The agreement on unit-cell volume and thermal expansions for end-members from different groups suggests that we did not experience any systematic cell measurement problems, therefore, the thermal expansion coefficients of garnet solid solutions with intermediate composition we present in this paper are also reliable and carry very important information for discussing thermal properties of garnet structure. Moreover, with the exception of Gr_{90} , our nonmonotonic compositional dependence of the high-temperature thermal expansions quite closely tracks the low-temperature thermal expansions of Bosenick and Geiger (1997) when compared at the temperature of overlap, 300 K. This suggests that the complex thermal expansion dependence on composition shown by both studies may be more than noise.

Different groups have used different numerical equations to describe molar volume changes with respect to temperature, and there is some uncertainty in the calculated thermal expansion coefficient of garnet caused by using these different numerical methods (Skinner 1956; Bosenick and Geiger 1997). Therefore, for our comparison we took the unit-cell parameters of pyrope and grossular measured at lower temperature to about 25 K from Bosenick and Geiger (1997), and fitted all the unit-cell volume data set with a second-order polynomial equation as we did for our own MA synthesized garnets. We find the non-linear volume thermal expansion from our MA synthesized garnets is remarkably consistent in detail with those from Bosenick and Geiger (1997): garnets with intermediate compositions having smaller thermal expansion than the two end-members. Furthermore, garnet solid solution with larger excess volume (composition close to $\text{Py}_{50}\text{Gr}_{50}$) shows relatively larger thermal expansion than the other intermediate compositions, which shows a similar compositional dependence with isothermal bulk moduli of garnet solid solution on this join as discussed later in this paper.

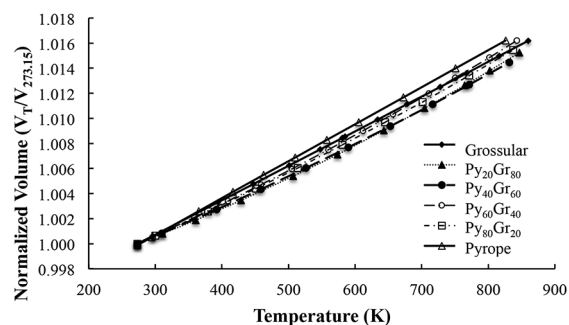


FIGURE 4. Change of normalized unit-cell volume as a function of temperature for pyrope, grossular, and four intermediate compositions.

Compressibility of pyrope-grossular solid solutions

Use of a hydrostatic pressure-transmitting medium is important in high-pressure experiments. Non-hydrostatic stress propagated by frozen or crystallized pressure-transmitting medium at extreme pressures will affect the measurement of the elastic properties of the samples, including the bulk modulus. Therefore, to keep a hydrostatic condition for garnet sample during high-pressure measurements, we do not increase pressure higher than 10 GPa, the freezing pressure of the 4:1 mixture of the methanol:ethanol medium (Eggert et al. 1992).

The volume changes with pressure of the six garnet compositions are presented in Table 4 and Figure 5, which shows that with increasing pressure, the volumes of garnets on the join pyrope-grossular decrease systematically. Bulk moduli of garnets on this join were calculated by fitting a third-order Birch-Murnaghan EOS (Birch 1986) to these data.

Birch-Murnaghan equation of state

In the case of isothermal hydrostatic compression, the pressure can be written with BE₂ form (Birch 1986):

$$P_i = 3K_0 f(1 + 2f)^{\frac{5}{2}}(1 + Af + Bf^2). \quad (3)$$

Here, f is the Eulerian strain, with sign reversed so f is positive for compression

$$f = \frac{1}{2} \left[\left(\frac{V}{V_0} \right)^{\frac{2}{3}} - 1 \right]$$

and

$$A = \frac{3}{2} [K'_0 - 4];$$

the isothermal EOS for cubic symmetry samples such as pyrope-grossular garnets can be obtained as BE₁ by setting $B = 0$ in form BE₂. V_0 is the volume at $P = 0$; K_0 is isothermal bulk modulus at zero pressure and K'_0 is its first derivative of K vs. pressure at $P = 0$. In this study, the upper limit of the pressure during compression is ~10 GPa, which may still not be high enough to allow a precise calculation of K'_0 because compressions of only about 5% was achieved in 10 GPa (Angel 2000).

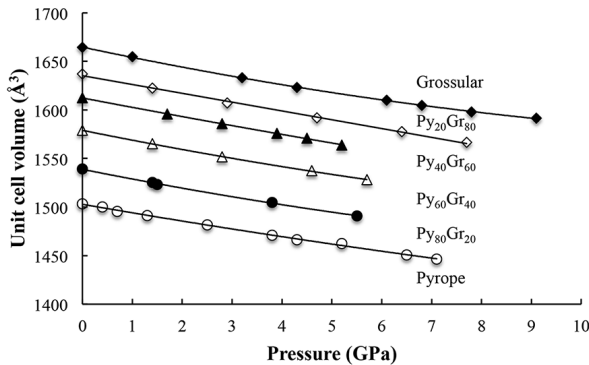


FIGURE 5. Unit-cell volume of pyrope-grossular garnets decrease systematically with pressure up to ~10 GPa. Error bars are not apparent because they are smaller than the marker symbols.

Numerous studies of elastic properties using X-ray diffraction techniques (Hazen and Finger 1989; Olijnyk et al. 1991; Zhang et al. 1998, 1999; Pavese et al. 2001; Grèaux et al. 2011; Zou et al. 2012) and ultrasonic interferometry (Gwanmesia et al. 2006) or resonant ultrasound spectroscopy as well as light scattering methods such as Brillouin spectroscopy (Conrad et al. 1999; Sinogeikin and Bass 2000; Jiang et al. 2004) have been performed at ambient and high pressure on garnet end-members. There is good agreement for elastic properties (K_0) of these end-members among various studies at ambient conditions, although the pressure derivative of the bulk modulus (K'_0) for end-members of garnet ranges from 4.0 to 6.1, and are less consistent (Table 5).

The P - V curve of grossular of up to about 37 GPa allowed a good estimate of the first pressure derivative of the bulk modulus ($K'_0 = 5.92$) (Pavese et al. 2001). Since our low-pressure P - V data (~7 GPa) are consistent with theirs, we calculated K_0 by fitting the measured P - V data to EOS with $K'_0 = 5.92$, which gave $K_0 = 164.3(1)$ GPa for the bulk modulus of grossular. The extrapolation of P - V value based on Birch-Murnaghan EOS and $K_0 = 164.3(1)$ GPa, $K'_0 = 5.92$ is in better agreement with those measured P - V from Pavese et al. (2001) experiment compared with extrapolation with $K'_0 = 4.4$ (Fig. 6). In addition, the calculated K value of

TABLE 4. The change of unit-cell volume of pyrope-grossular with pressure^a

Composition	P (GPa)	a (Å)	V_{cell} (Å ³)	V (cm ³ /mol)
Grossular	0	11.8505 (4)	1664.2(2)	125.23(2)
	1.0	11.8275(5)	1654.5(2)	124.50(2)
	3.2	11.7760(5)	1633.0(2)	122.88(2)
	4.3	11.7523(6)	1623.2(3)	122.15(1)
	6.1	11.7205(5)	1610.1(2)	121.16(1)
	6.8	11.7072(9)	1604.6(4)	120.74(3)
	7.8	11.6911(7)	1598.0(3)	120.25(2)
	9.1	11.6747(5)	1591.2(2)	119.74(2)
	0	11.7857(6)	1637.0(3)	123.19(2)
Gr ₈₀ Py ₂₀	1.4	11.7499(7)	1622.2(3)	122.07(2)
	2.9	11.7129(6)	1606.9(3)	120.92(2)
	4.7	11.6756(7)	1591.6(3)	119.77(2)
	6.4	11.6414(6)	1577.6(3)	118.72(2)
	7.7	11.6135(7)	1566.3(3)	117.87(2)
	1.7	11.6858(5)	1595.8(2)	120.08(2)
	2.8	11.6608(4)	1585.6(2)	119.31(2)
Gr ₆₀ Py ₄₀	3.9	11.6364(5)	1575.6(2)	118.57(1)
	4.5	11.6247(6)	1570.9(2)	118.21(2)
	5.2	11.6072(7)	1563.8(3)	117.68(2)
	0	11.7262(5)	1612.4(2)	121.33(2)
	0	11.6446(6)	1579.0(2)	118.82(2)
	1.4	11.6101(6)	1565.0(2)	117.76(2)
	2.8	11.5770(6)	1551.6(2)	116.76(2)
Gr ₄₀ Py ₆₀	4.6	11.5410(6)	1537.2(2)	115.68(1)
	5.7	11.5181(7)	1528.0(3)	114.99(1)
	0	11.5458(4)	1539.1(2)	115.82(2)
	1.4	11.5110(5)	1525.3(2)	114.78(1)
	1.5	11.5058(9)	1523.2(4)	114.62(3)
	3.8	11.4589(4)	1504.6(1)	113.22(1)
	5.5	11.4239(5)	1490.9(2)	112.19(1)
Pyrope	0.4	11.4470(6)	1500.0(3)	112.87(2)
	0.7	11.4357(7)	1495.5(3)	112.54(2)
	1.3	11.4245(6)	1491.1(2)	112.21(1)
	2.5	11.3996(8)	1481.4(3)	111.48(2)
	3.8	11.3727(7)	1470.9(3)	110.69(1)
	4.3	11.3608(4)	1466.3(1)	110.34(1)
	5.2	11.3506(4)	1462.4(2)	110.04(2)
	6.5	11.3199(7)	1450.5(3)	109.15(2)
	7.1	11.3091(5)	1446.4(2)	108.84(1)
	0	11.4553(6)	1503.2(2)	113.12(1)

^a Pressure is calculated from internal ruby standard with an error bar of 0.1 GPa. Values in parentheses represent estimated standard deviation through least-square fitting for unit-cell parameter.

TABLE 5. Bulk moduli and their first pressure derivative of pyrope and grossular

Isothermal bulk modulus	Method	Pyrope		Grossular	
		K	K'	K	K'
Hazen and Finger (1989)	DAC and XRD	179 ± 3	4 ^a	159 ± 2	4 ^a
Olijnyk et al. (1991)	DAC and XRD			168 ± 2.5	6.1 ± 0.15
Conrad et al. (1999)	BS	171.32	3.22	165.68	5.46
Akhmatskaya et al. (1999)	Theoretically	170	4.2	166	4.3
Zhang et al. (1998)	DAC and XRD	171	4.4 ^a	175 ± 1	4.4 ^a
Sinogeikin and Bass (2000)	BS	171.2 ± 3	4.1 ± 0.3		
Pavese et al. (2001)	DAC and XRD			169.3 ± 1.2	5.92 ± 0.14
Jiang et al. (2004)	BS	174.9 ± 1.6	4.7 ± 0.3	169 ± 0.9	3.8 ± 0.2
Gwanmesia et al. (2006)	UI	175(2)	3.9(0.3)		
Gréaux et al. (2011)	MA and XRD			166	4.04–4.35
Zou et al. (2012)	MA and XRD	167 ± 6	4.6 ± 0.3		

^a Fixed K' number; DAC and XRD = synchrotron radiation powder diffraction on diamond-anvil cell; BS = Brillouin scattering; UI = ultrasonic interferometry; MA and XRD = synchrotron radiation powder diffraction on multi-anvil device.

grossular synthesized in MA is also in good agreement with the theoretically calculated value $K_0 = 166$ GPa (Akhmatskaya et al. 1999), Brillouin scattering result $K_0 = 165.68$ GPa, $K'_0 = 5.46$ (Conrad et al. 1999), and most recently result $K_0 = 166$ GPa from Gréaux et al. (2011).

In garnet structure, the dodecahedral cations Ca^{2+} and Mg^{2+} have a mean ionic radii of 1.26 and 1.03 Å (Shannon 1976), respectively, and are thus near the upper and lower limits for the X-cation size. The substitution between Ca^{2+} and Mg^{2+} in the dodecahedral X site may be an influential factor in K'_0 (the first derivative of bulk modulus) (Conrad et al. 1999), therefore, we expect the K'_0 might be different for pyrope and grossular garnets. Our P - V data of pyrope garnet is consistent with those reported by Zhang et al. (1998) using He as pressure-transmitting medium and successfully keeping their pyrope samples in hydrostatic condition until pressure about 30 GPa (Fig. 6). The fit of our pyrope P - V data to EOS with fixed $K'_0 = 4.4$ (Zhang et al. 1998) yield $K_0 = 169.2(2)$ GPa, in agreement with those previously reported. The extrapolations of P - V value of pyrope based on the Birch EOS with $K'_0 = 4.4$, $K_0 = 169.2$ GPa and $K'_0 = 5.92$, $K_0 = 164.1$ GPa, respectively, are also showed in Figure 6, and the extrapolation with $K'_0 = 4.4$ and $K_0 = 169.2$ GPa agrees better with Zhang et al. (1999) high-pressure P - V measurements.

There is no previous high-pressure data to constrain the K'_0 values for garnets with intermediate compositions on the join pyrope-grossular. Since our end-member data also confirm that the substitution of the dodecahedral cation Ca^{2+} for Mg^{2+} in the garnet structure decreases K_0 and increases K'_0 , we calculated the bulk moduli of garnet solid solution by using Birch-Murnaghan EOS with two different fixed K'_0 values. Our fitting results show that with a fixed K'_0 value, there is no large difference in bulk moduli for garnet with intermediate composition; they are all about 155 GPa by fixing $K'_0 = 5.92$ or about 160 GPa by fixing $K'_0 = 4.4$. There is a weak nonmonotonic compositional dependence that is reminiscent of the nonmonotonic thermal expansion dependence on composition seen in Figure 3 (Table 6, Fig. 7). However, the intermediate composition compressibilities are all relatively smaller than those of the end-members, no matter what K'_0 value was chosen to fit in the Birch-Murnaghan EOS.

DISCUSSION AND IMPLICATIONS

Our new synchrotron X-ray diffraction data on pyrope-grossular solid solution show that substitution of Mg^{2+} for Ca^{2+} along the pyrope-grossular join produces changes in thermo-

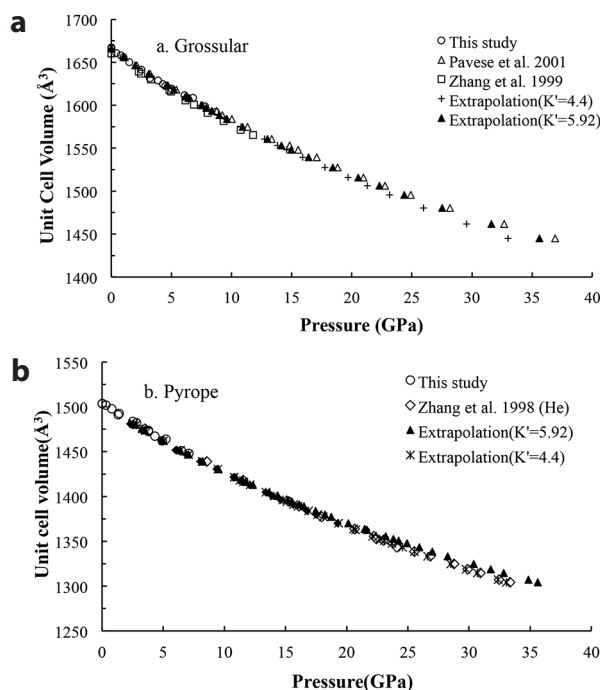


FIGURE 6. Volume of grossular and pyrope under high pressure calculated by fixing $K' = 5.92$ and $K' = 4.4$. For grossular, extrapolations of unit-cell volume to higher pressure with $K' = 5.92$ agree well with experiment result from Pavese et al. (2001); for pyrope, calculated unit-cell volumes agree well with Zhang et al. (1998) with $K' = 4.4$.

elastic properties. Garnets with intermediate composition show smaller thermal expansion and smaller bulk modulus than the two end-members.

The relatively smaller bulk modulus of garnet solid solution is consistent with the positive excess volume reported by previous studies (e.g., Ganguly et al. 1993) and confirmed and increased in our companion study (Du et al. in preparation). Positive excess volume of garnets with intermediate composition makes them more compressible under high pressure, which is consistent with the relatively smaller calculated K_0 . If the positive excess volumes are comprised of defects or local strains in the lattice accommodating Ca-Mg size mismatches by incorporating void space around Mg cations, then the greater compressibility reflects

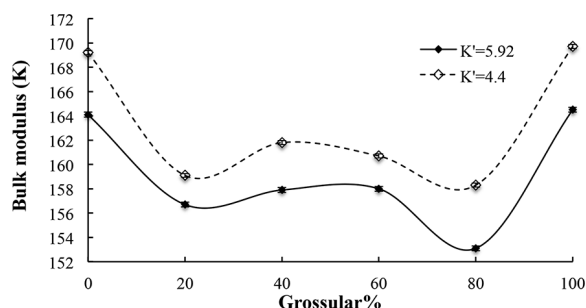


FIGURE 7. Bulk moduli of garnet solid solution calculated by fixing $K' = 5.92$ and 4.4 . Pyrope has larger bulk modulus than grossular, and garnets with intermediate composition on pyrope-grossular join have much smaller bulk moduli than the end-members.

TABLE 6. Bulk moduli of pyrope-grossular solid solution

Composition	Pyrope	Gr ₂₀ Py ₈₀	Gr ₄₀ Py ₆₀	Gr ₆₀ Py ₄₀	Gr ₈₀ Py ₂₀	Grossular
$K' = 4.4$	169.2(2)	159.1(2)	161.8(1)	160.7(1)	158.3(1)	169.7(4)
$K' = 5.92$	164.1(2)	156.7(1)	157.9(1)	158.0(1)	153.1(1)	164.3(1)

the greater compliance of the intermediate composition structures with extra mismatch room. Although more information about the distribution of Mg and Ca cations depends on further research, we do notice the similarity of the compositional dependence of thermal expansion and bulk modulus (Figs. 3 and 7). Garnets with composition close to the end-members show smaller thermal expansion and smaller bulk modulus compared with those on the middle of pyrope-grossular join. We observed that microstrain values calculated from XRD peak width (Du et al. in preparation) show correlation with the thermal expansion and bulk modulus. And XRD profiles analysis of these garnets (e.g., Py₈₀Gr₂₀) shows that these garnets carry more microstrain than those with composition close to the middle of this join (Py₄₀Gr₆₀). The different microstrain values along pyrope-grossular join could be a reflection of different degree of short range ordering of Ca and Mg achieved through high-pressure synthesis. Further results on microstrain and Mg-Ca ordering are reported in our companion paper (Du et al., in review).

The calculation of the thermal expansion coefficient in this paper was based on the assumption that a quadratic equation is good enough to describe the unit-cell volume of garnet as it changes with temperature. But it is doubtful whether this dependence can be extrapolated to temperatures in excess of 1300 K where additional interesting garnet petrogenesis occurs. We are limited at present to temperatures of 800 K for the excess mixing volume on this join, which is shown in Figure 8. Pyrope-grossular solid solutions show large positive excess volume at all conditions so far measured; this excess volume on the pyrope-grossular join decreases with temperature, but still does not vanish even at 800 K.

Excess volumes of pyrope-grossular garnets at 6 GPa were calculated by applying the bulk moduli to the Birch-Murnaghan EOS (with K'_0 fixed to 5.92), and are also presented in Figure 8. Excess volumes on the pyrope-grossular join decrease systematically with pressure, and positive unit-cell excess volume values as large as $10 \text{ \AA}^3/\text{cell}$ for garnet with a composition of Py₄₀Gr₆₀ persist at pressures as high as 6 GPa. Combined with the high-

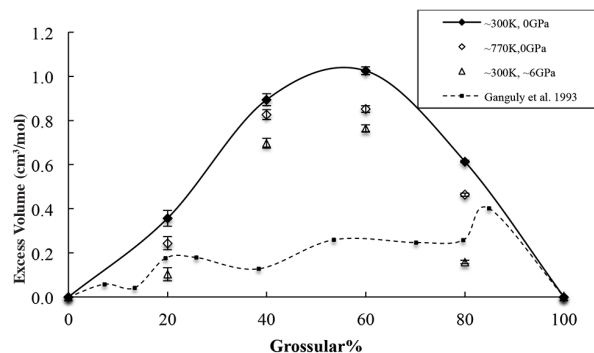


FIGURE 8. Positive excess volumes of garnets synthesized by using multi-anvil (MA) techniques at LDEO at high temperature and high pressure, which are larger than previous studies on garnets synthesized by using piston cylinder (PC) (e.g., Ganguly et al. 1993). The excess volumes on this join decrease with temperature and pressure, but still remain at a significant level at 770 K or 6 GPa.

temperature results calculated from thermal expansion coefficients, significant positive excess volumes persists as temperature and pressure increase, suggesting that phase exsolution at high pressure and high temperature should be observable. We confirm experimentally that such exsolution is observed. For example, two garnets with different composition along pyrope-grossular join were chosen as starting material, and heated at 8 GPa and 1200 °C for ~20 days. Quenched samples from these annealing experiments were checked by XRD scan, and both composition convergence and divergence were observed. Details about the phase separation experiments on pyrope-grossular join will be discussed in our companion paper.

ACKNOWLEDGMENTS

This work was supported by the U.S. National Science Foundation. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231 at Lawrence Berkeley National Laboratory. We thank Jean Hanley, Jinyuan Yan, Geoff Whelan, and Raj Dasgupta for their technical assistance. We thank Jibamitra Ganguly and an anonymous reviewer for helpful comments on the manuscript.

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MANUSCRIPT RECEIVED SEPTEMBER 20, 2013

MANUSCRIPT ACCEPTED JULY 19, 2014

MANUSCRIPT HANDLED BY CHARLES LESHNER