Single-crystal hydrostatic compression of synthetic pyrope, almandine, spessartine, grossular and andradite garnets at high pressures

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ORIGINAL PAPER

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Single-crystal hydrostatic compression of synthetic pyrope, almandine, spessartine, grossular and andradite garnets at high pressures

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Abstract The compression of synthetic pyrope Mg_3Al_2 $(SiO_4)_3$, almandine $Fe_3Al_2(SiO_4)_3$, spessartine Mn_3Al_2 $(SiO_4)_3$ grossular $Ca_3Al_2(SiO_4)_3$ and andradite Ca_3Fe_2 $(SiO_4)_3$ was studied by loading the crystals together in a diamond anvil cell. The unit-cell parameters were determined as a function of pressure by X-ray diffraction up to 15 GPa using neon as a pressure transmitting medium. The unit-cell parameters of pyrope and almandine were measured up to 33 and 21 GPa, respectively, using helium as a pressure medium. The bulk moduli, K_{T0}, and their first pressure derivatives, K'_{T0}, were simultaneously determined for all five garnets by fitting the volume data to a third order Birch-Murnaghan equation of state. Both parameters can be further constrained through a comparison of volume compressions between pairs of garnets, giving for K_{T0} and K'_{T0} 171(2) GPa and 4.4(2) for pyrope, 185(3) GPa and 4.2(3) for almandine, 189(1) GPa and 4.2 for spessartine, 175(1) GPa and 4.4 for grossular and 157(1) GPa and 5.1 for andradite, where the K'_{T0} are fixed in the case of spessartine, grossular and andradite. Direct comparisons of the unit-cell volumes determined at high pressures between pairs of garnets reveal anomalous compression behavior for Mg^{2+} in the 8-fold coordinated triangular dodecahedron in pyrope. This agrees with previous studies concerning the compression behaviors of Mg^{2+} in 6-fold coordinated polyhedra at high pressures. The results show that simple bulk modulus–volume systematics are not obeyed by garnets.

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Introduction

Garnet is one of the major phases of Earth's upper mantle and transition zone. The high pressure garnets that are stable at mantle conditions are magnesium-rich solid solutions. It is known, however, that a variety of different cations can be incorporated in the garnet structure and that changes in composition affect the elastic properties. It is necessary, therefore, to study composition–bulk modulus relationships. Extensive studies have been carried out in this area, but reliable experimental results have, however, only been obtained at ambient conditions or at relatively low pressures (Babuska et al. 1978; O'Neill et al. 1989; Bass 1986; Webb 1989). An extrapolation of these data to higher pressures is required for modeling, for example, mantle densities. This is difficult because of disagreements over the first pressure derivatives of the bulk moduli (K'_{T0}) determined on various garnet compositions. Moreover, until recently most measurements at pressures exceeding 10 GPa were performed under nonhydrostatic conditions (Takahashi and Liu 1970; Weaver et al. 1976; Leger et al. 1990; Olijnyk et al. 1991). We have shown that such conditions may severely bias the measured parameters (Zhang et al. 1998; Zhang and Ahsbahs 1998).

Anderson and Anderson (1970) proposed a simple bulk modulus–volume systematics, where K_0V_0 = constant. It has been shown in different studies (Hazen et al. 1994 and references therein), however, that this simple systematics is not obeyed in the silicate garnets. Several studies (e.g. Weaver et al. 1976; Olijnyk et al. 1991) have attempted to rationalize the bulk modulus–volume observations based on considerations of crystal field effects, bonding type of the X^{2+} dodecahedral cations and other structural properties. Recently, it was found in different mineral phases that the magnesium endmembers are more compressible at high pressures than their iron endmember equivalents (Hazen 1993; Zhang et al. 1997; Zhang and Reeder 1997; Zhang 1998), which is inconsistent with bulk modulus–volume systematics. Moreover, it has been shown that for a given crystal structure type containing just transition metal cations, like Mn^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+}, that the bulk modulus–volume systematics are obeyed (Zhang 1998). In order to better understand structural compression mechanisms, it is necessary to consider systematically factors like crystal structure type, cation valence states, electronic configurations of cations, and polyhedral coordination number. Following our studies on clinopyroxenes and olivines (Zhang et al. 1997; Zhang 1998), we have continued, here, the study of these properties by investigating the silicate garnets. The garnet structure contains different divalent cations in eight-fold coordination, which allows us to study the effect of electronic configuration on K_{T0} and K'_{T0}. The polyhedral coordination of the divalent cations is also different from that in pyroxene and olivine. Therefore, the garnets present an additional structure type in our study of compression mechanisms in silicates. We have chosen five synthetic endmember silicate garnets $Mg_3Al_2(SiO_4)_3$, $Fe_3Al_2(SiO_4)_3$, $Mn_3Al_2(SiO_4)_3$, $Ca_3Al_2\ (SiO_4)_3$, and $Ca_3Fe_2(SiO_4)_3$ and determined their equations of state.

Experimental details

Samples

Well-characterized single crystals of synthetic pyrope $Mg_3Al_2(SiO_4)_3$, almandine $Fe_3Al_2(SiO_4)_3$, spessartine $Mn_3Al_2(SiO_4)_3$, grossular $Ca_3Al_2(SiO_4)_3$, and andradite $Ca_3Fe_2(SiO_4)_3$ were chosen for study. The different garnet crystals were synthesized in a piston-cylinder device or in Tuttle-type autoclaves under hydrothermal conditions. Therefore all the garnets have very small, but measurable amounts of OH. Details about the synthesis and characterization of the crystals and their structural refinements by X-ray diffraction from 100 to 500 K are described in Ambruster et al. (1992), Ambruster and Geiger (1993) and Geiger and Ambruster (1997). For the current study, polished crystals with dimensions of about 80 × 80 × 40 μm to about 80 × 80 × 25 μm were used.

High pressure X-ray diffraction technique

Modified Merill-Bassett type diamond anvil cells were used in our experiments. The diameter of the diamond culet was 600 μm. Gaskets made of Thyrodur 2709, preindented to about 60–85 μm, were used. The diameters of the sample hole ranged from about 300 to 420 μm. For the experiments, single crystals of pyrope, almandine, spessartine, grossular and andradite were loaded together in one diamond cell which was filled with neon in a gas apparatus at 0.2 GPa. This procedure ensures identical pressure conditions for all crystals, so that the compression determined on individual crystal can be directly compared with each other (Hazen 1993; Zhang et al. 1997; Zhang 1998). Several ruby grains were also placed in the gasket hole to serve as pressure calibrants. The presence of radial pressure gradients was checked in each experimental run. There was no pressure gradient measurable below the solidifying pressure of neon at about 4.2 GPa. At pressures above 11 GPa, however, gradients were observable. The maximum gradient was determined to be about 1 GPa at pressures around 15 GPa over a gasket hole of about 400 μm in diameter. The magnitude of the pressure gradient at pressures was different in the different loadings. A heterogeneous pressure distribution results in a broadening of reflections, which prevented the further use of the multiple-crystal loading technique. Therefore, some of the unit-cell parameters determined on almandine and pyrope at the highest pressures were made by loading individual crystals in different pressure cells, using helium as the pressure transmitting medium. In this way, a hydrostatic pressure environment can be secured to very high pressure conditions (Zhang and Ahsbahs 1998).

A Stoe four circle diffractometer with graphite monochromated Mo$K\alpha$ radiation (0.71073 Å) was used for the diffraction experiments. The diffractometer was operated to 55 kV and 35 mA. The unit-cell parameter of garnet was determined from up to 21 reflections with 2θ ranging between 13° and 39°. Each reflection was centered in eight positions (King and Finger 1979) to reduce zero and crystal-centering errors. The unit-cell parameters were calculated using the procedure of Ralph and Finger (1982). There was no significant deviation between unit-cell parameters constrained or not constrained to cubic symmetry.

Results and discussion

The unit-cell parameters measured for almandine, spessartine, grossular and andradite to a maximum pressure of 21 GPa are listed in Table 1. The pyrope data were previously published (Zhang et al. 1998). All unit-cell parameters decrease continuously with increasing pressure with no evidence for phase transitions. Previous compression experiments on single crystals in a diamond anvil cell have been carried out on synthetic endmember pyrope and a natural grossular to 5 GPa and on andradite to 19 GPa (Levien et al. 1979; Hazen and Finger 1989), respectively. To the best of our knowledge, the unit-cell parameters of endmember almandine and spessartine have been measured for the first time using single crystal diffraction techniques at high pressures. The volume compression data for pyrope, almandine, spessartine and grossular are shown in Figs. 1, 2, 3 and 4 and compared with other published data. Our results show smaller scatter compared to most of the previous measurements.

Equation of state

The isothermal bulk modulus at zero pressure, K_{T0}, and its first pressure derivative, K'_{T0}, were calculated together through unweighted fits of the volume data using a third order Birch-Murnaghan equation of state:

$$P = 3/2K_{T0}[(V_0/V)^{7/3} - (V_0/V)^{5/3}] \times \{1 + 3/4(4 - K_{T0})[(V_0/V)^{2/3} - 1]\} \quad (1)$$

The calculated K_{T0} and K'_{T0} values are the same within errors with or without V_0 constrained to its experimental value. The K_{T0} and K'_{T0} values listed in Table 3 are those obtained without constraining V_0.

K_{T0} and K'_{T0} of almandine were determined previously by X-ray diffraction experiments at high pressures

Table 1 Unit-cell parameters of the four garnet at pressures

P (GPa)	$Fe_3Al_2(SiO_4)_3$	$Mn_3Al_2(SiO_4)_3$	$Ca_3Al_2(SiO_4)_3$	$Ca_3Fe_2(SiO_4)_3$
0.00	11.5195(8)	11.6068(8)	11.8410(8)	12.0537(9)
2.30(2)	11.4757(9)	11.5631(8)	11.7910(7)	12.0012(7)
2.49(5)	11.4713(7)	11.5577(8)	11.7859(8)	11.9947(8)
3.28(5)	11.4561(8)	11.5433(9)	11.7691(9)	11.9775(8)
4.85(5)	11.4276(7)	11.5139(8)	11.7386(9)	11.9432(7)
4.97(5)			11.7351(9)	11.9361(9)
5.99(5)	11.4003(10)			11.9129(10)
6.17(5)		11.4874(9)	11.7099(7)	
6.88(5)	11.3906(9)	11.4765(8)	11.6982(8)	11.9002(9)
8.03(5)	11.3683(10)	11.4556(10)	11.6752(9)	11.8764(10)
9.36(5)	11.3461(10)	11.4326(10)	11.6516(9)	11.8508(12)
10.75(5)	11.3227(8)	11.4087(9)	11.6260(8)	11.8232(10)
11.8(3)	11.3062(8)		11.6110(12)	11.8009(10)
12.0(3)		11.3905(9)		
13.0(3)	11.288(1)			11.7822(10)
13.3(3)		11.3722(10)		
14.0(5)				11.7611(10)
14.03(5)	11.2694(10)			
14.6(3)		11.3509(12)		
11.6(3)[a]	11.3072(8)			
12.67(5)[a]	11.289(3)			
14.9(5)[a]	11.2563(7)			
17.3(2)[a]	11.2216(8)			
19.4(3)[a]	11.1885(13)			
21.3(3)[a]	11.1630(13)			

[a] Measured in helium pressure medium

on polycrystalline samples (Takahashi and Liu 1970; Sato et al. 1978). Babuska et al. (1978) estimated K_s = 177.9(8) GPa from ultrasonic measurements on a natural almandine-rich solid solution at ambient conditions. Bass (1989) proposed K_s = 177(3) GPa based on Brillouin measurements made on garnets of other compositions and a consideration of bulk modulus systematics. The K' value of 1.5 reported by Sato et al. (1978) for almandine is unreasonably low compared with, for example, that of pyrope, where K'_{T0} = 4.4 (Zhang et al. 1998). The K_{T0} value of 185(3) GPa obtained in this study for almandine is about 2% larger than the estimated values (Babuska et al. 1978; Bass 1989), if the conversion between K_s and K_{T0} is considered. By fixing K_{T0} to 177.9 GPa in the fitting procedure, a K'_{T0} of 4.9(1) is obtained, compared to K'_{T0} = 4.2(3) without any imposed constrains.

K_s of endmember spessartine was estimated by Babuska et al. (1978) and measured by Bass (1989) on a natural crystal of nearly endmember spessartine composition. The estimated K_s from ultrasonic experiments is about 2.5% lower than the value measured by Brill-

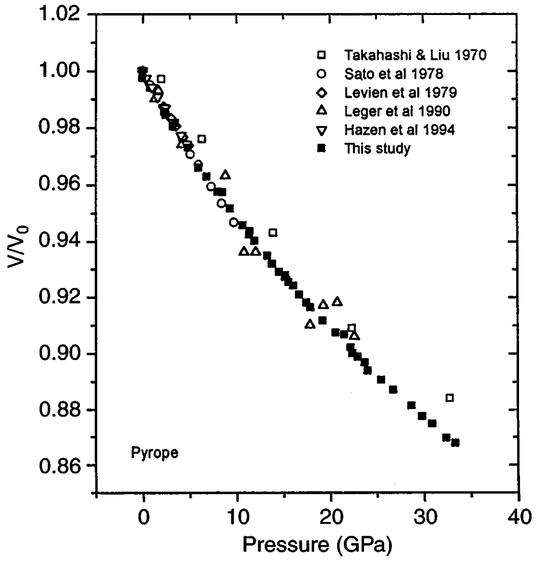

Fig. 1 Volume compression of pyrope at high pressures

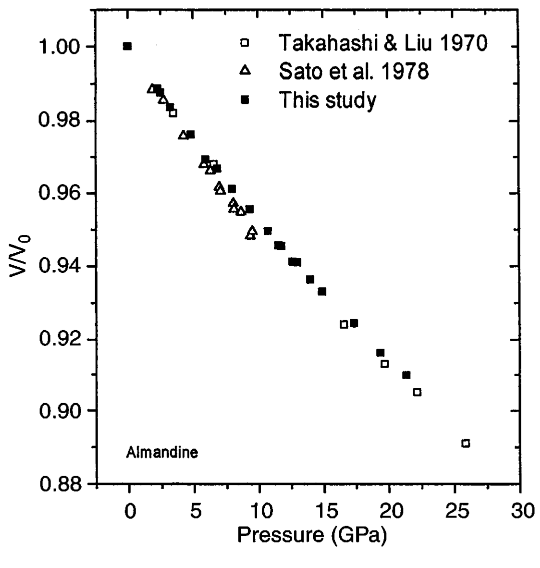

Fig. 2 Volume compression of almandine at high pressures

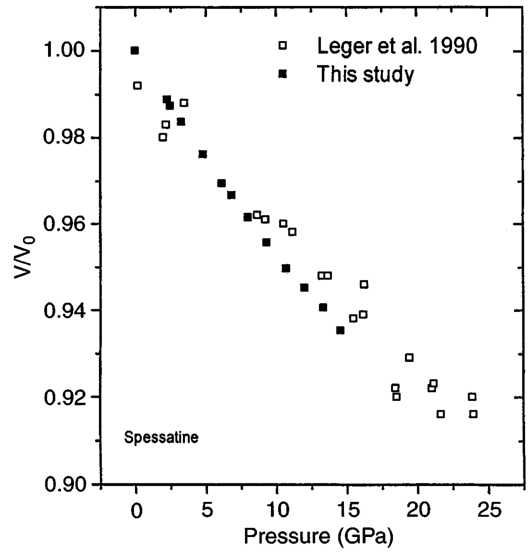

Fig. 3 Volume compression of spessartine at high pressures

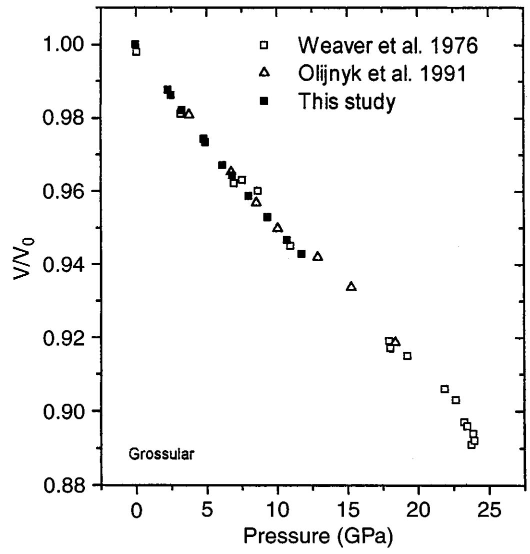

Fig. 4 Volume compression of grossular at high pressures

ouin spectroscopy, which was attributed to the crystal quality used in the ultrasonic study (Bass 1989). In our study, K_{T0} = 183(4) GPa and K'_{T0} = 5.1(6) were determined. The value of K'_{T0} = 7.0(10) (Leger et al. 1990) appears too large, because the compressibility of almandine and spessartine at high pressures is similar (Fig. 5). This implies a similar K'_{T0} value for both almandine and spessartine.

The Bulk modulus of grossular is well constrained by ultrasonic and Brillouin studies, whereas its pressure derivative is less well known (Olijnyk et al. 1991). The K_{T0} of andradite has only been measured using Brillouin techniques, giving $K_s = 157(2)$ GPa. Our result of $K_{T0} = 162(5)$ GPa is, therefore, consistent with this value. The value of $K'_{T0} = 4.4(7)$ for andradite is derived here for andradite for the first time. The estimated value

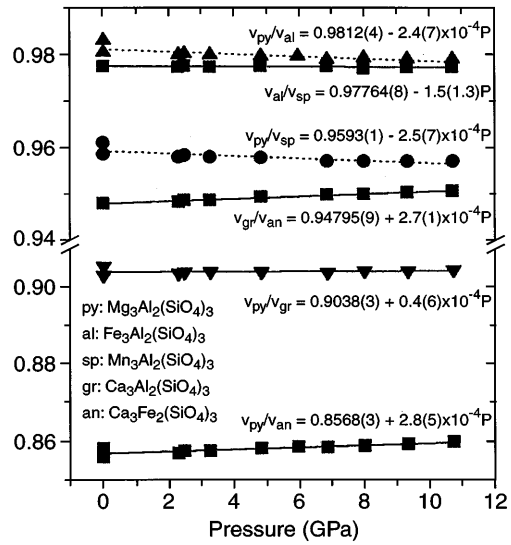

Fig. 5 Comparison of unit-cell volumes between pairs of garnet [*py* $Mg_3Al_2(SiO_4)_3$, *al* $Fe_3Al_2(SiO_4)_3$, *sp* $Mn_3Al_2(SiO_4)_3$, *gr* $Ca_3Al_2(SiO_4)_3$, *an* $Ca_3Fe_2(SiO_4)_3$]

of K_s = 137.9(1.7) GPa (Babuska et al. 1978) is clearly too low.

The different K_{T0} values between the different endmember garnets are confirmed in this study. In contrast to some previous studies, which proposed K'_{T0} values (Table 2) lower than 4 or higher than 5 for some garnets, we obtain K'_{T0} values between 4 and 5. Although we can bracket K'_{T0} values for the five endmembers to a relatively narrow range, the upper pressure limit for the compression experiment on spessartine, grossular and andradite is too low to allow a quantitative comparison of their K'_{T0} values. The errors in K'_{T0} values do not permit a close examination of the various K'_{T0} values of the five garnets. However, using the multi-crystal loading technique it is possible to compare unit-cell volume compressions between pairs of garnets determined at high pressures (Fig. 5).

The slopes in Fig. 5 can be described by the relationship:

$$\frac{d(V_a/V_b)}{dP} = \frac{V_a}{V_b}(\beta_b - \beta_a) \tag{2}$$

where V_a and V_b are the unit-cell volumes of crystal a and b, and β_a and β_b are their compressibilities. The compressibility difference, $\beta_b - \beta_a$, between two crystals can be determined by the value of $d(V_a/V_b)/dP$. Since $K = 1/\beta$, it follows from Fig. 5 that $K_T(\mathrm{al}) \approx K_T(\mathrm{sp}) > K_T(\mathrm{py}) \approx K_T(\mathrm{gr}) > K_T(\mathrm{an})$, within errors, at high pressure. If we assume that K_T can be described by the linear relationship

$$K_T = K_{T0} + K'_{T0}P \ , \tag{3}$$

then the difference $(K'_{T0})_a - (K'_{T0})_b$ between crystal a and b depends only on $(K_{T0})_a - (K_{T0})_b$. The relative magnitudes of these K_{T0} values are well constrained for silicate garnets by Brillouin spectroscopy, ultrasonic experi-

Table 2 A summary of previous experimentally determined bulk moduli and their pressure derivatives (*SC* single crystal, *PC* polycrystalline)

K (GPa)	K'	P (GPa)	Sample	Method	References
$Mg_3Al_2(SiO_4)_3$					
171(2)	4.4(2)	33	SC	X-ray diffraction	Zhang et al. (1998) and references therein
$Fe_3Al_2(SiO_4)_3$					
177.9(8)	–	0	SC	Calculated	Babuska et al. (1978)
177(3)	–	0	SC	Calculated	Bass (1989)
168(5)	5.45[a]	35	PC	X-ray diffraction	Takahashi and Liu (1970)
175(7)	1.5(1.6)	10	PC	X-ray diffraction	Sato et al. (1978)
$Mn_3Al_2(SiO_4)_3$					
178.8(8)	–	0	SC	Brillouin scattering	Bass (1989)
174.2(9)	–	0	SC	Ultrasonic	Babuska et al. (1978)
174.2	7.0(10)	25	PC	X-ray diffraction	Leger et al. (1990)
$Ca_3Al_2(SiO_4)_3$					
169.1(8)	–	–	SC	Ultrasonic	Babuska et al. (1978)
168.4	–	0	SC	Brillouin scattering	O'Neill et al. (1989)
174(4)	4.25[a]	25	PC	X-ray diffraction	Weaver et al. (1976)
168(25)	6.2(4.0)	18.4	PC	X-ray diffraction	Olijnyk et al. (1991)
$Ca_3Fe_2(SiO_4)_3$					
157(2)	–	0	SC	Brillouin scattering	Bass (1986)
137.9(17)	–	–	SC	Ultrasonic	Babuska et al. (1978)

[a] Fixed

ments (Babuska et al. 1978; O'Neill et al. 1989; Bass 1986) or from experiments of X-ray diffraction performed at very high pressures (e.g. Zhang et al. 1998).

For almandine and spessartine, $\mathrm{d}(V_{\mathrm{al}}/V_{\mathrm{sp}})/\mathrm{d}P \approx 0$ (Fig. 5) is determined over the pressure range measured. This means

$$K_T(\mathrm{al}) \approx K_T(\mathrm{sp})$$

and thus $K_{T0}(\mathrm{al}) + K'_{T0}(\mathrm{al})P \approx K_{T0}(\mathrm{sp}) + K'_{T0}(\mathrm{sp})P$.

If we assume $K_{T0}(\mathrm{al}) \approx K_{T0}(\mathrm{sp})$ (Babuska et al. 1978; and Bass 1989), then $K'_{T0}(\mathrm{al}) \approx K'_{T0}(\mathrm{sp})$. In the same way it is possible to deduce the relative K'_{T0} values among the five garnet compositions. Within experimental errors it follows that $K'_{T0}(\mathrm{an}) > K'_{T0}(\mathrm{py}) \geq K'_{T0}(\mathrm{gr}) > K'_{T0}(\mathrm{al}) \approx K'_{T0}(\mathrm{sp})$ in the pressure range of the experiments. Thus the relationships (2) and (3) put a strong constraint on the K'_{T0} values. The value $K'_{T0}(\mathrm{py}) = 4.4$ obtained by very high pressure single crystal measurements (Zhang et al. 1998) is in excellent agreement with other measurements to 20 GPa (Chai and Brown 1997). If we start with this value, then the values of $K'_{T0}(\mathrm{sp}) = 5.1(6)$ and $K'_{T0}(\mathrm{gr}) = 5.2(6)$, as determined above (Table 3), are overestimated and $K'_{T0}(\mathrm{an}) = 4.4(7)$ is underestimated by directly fitting an equation of state (EOS) to the volume data. For example, according to the volume ratio of the garnet pairs, $K'_{T0}(\mathrm{al}) \approx K'_{T0}(\mathrm{sp})$. However, values obtained by fitting the volume data to an EOS give $K'_{T0}(\mathrm{al}) = 4.2(3)$ and $K'_{T0}(\mathrm{sp}) = 5.1(6)$. We redetermined, therefore, the EOS for spessartine and grossular by fixing $K'_{T0}(\mathrm{gr}) = K'_{T0}(\mathrm{py}) = 4.4$ and $K'_{T0}(\mathrm{sp}) = K'_{T0}(\mathrm{al}) = 4.2$ in our fitting procedure. Since $K'_{T0}(\mathrm{an}) > K'_{T0}(\mathrm{gr})$, the upper limit of K'_{T0} for andradite has been fixed at 5.1, one standard deviation larger than $K'_{T0}(\mathrm{an}) = 4.4(7)$ determined without constraints. The bulk moduli of spessartine, grossular and andradite recalculated in this way are also listed in Table 3.

Table 3 Bulk moduli and their pressure derivatives of garnet

Mineral	K_T	K'_{T0}
$Fe_3Al_2(SiO_4)_3$	185(3)	4.2(3)
$Mn_3Al_2(SiO_4)_3$	183(4)	5.1(6)
$Ca_3Al_2(SiO_4)_3$	170(4)	5.2(6)
$Ca_3Fe_2(SiO_4)_3$	162(5)	4.4(7)
$Fe_3Al_2(SiO_4)_3^{a}$	185(3)	4.2(3)
$Mn_3Al_2(SiO_4)_3^{a}$	189(1)	4.2[b]
$Ca_3Al_2(SiO_4)_3^{a}$	175(1)	4.4[b]
$Ca_3Fe_2(SiO_4)_3^{a}$	157(1)	5.1[b]

[a] Constrained values by Fig. 5
[b] Fixed

The K_{T0} values determined in this study without any constraints are in good agreement with the Brillouin or ultrasonic measurements. Some of the previously published K'_{T0} are, however, as shown above, not consistent with our experimental data (Fig. 5). The bulk moduli of spessartine and grossular are about 3–5 percent higher than the values determined by Brillouin and ultrasonic measurements (Tables 2, 3) by constraining some of the K'_{T0} values.

Compression behavior and compression mechanism

The "anomalous" compression behavior observed in the structures of binary Mg-Fe phases, as observed by Hazen (1993) in the spinels, has now also been observed in the clinopyroxenes, olivines and garnets (Zhang et al. 1997; Zhang et al. 1998; this study). This anomaly arises from the discrepancy between the experimentally determined K values and those predicted by the bulk modulus–volume relationship, i.e. KV = constant (Anderson and

Anderson 1970). For example, in the case of pyrope and almandine $(KV)_{\mathrm{py}} \neq (KV)_{\mathrm{al}}$. Similar observations were made on structures with 6-fold coordinated Mg^{2+} and Fe^{2+} cations (Zhang et al. 1997; Zhang et al. 1998). Now it has been shown that structures with 8-fold coordinated Mg^{2+} and Fe^{2+} cations exhibit a similar anomalous compression behavior. For clinopyroxene Ca(Fe, Mg)Si_2O_6 and garnet (Fe, Mg)$_3$$Al_2(SiO_4)_3$ solid solutions it has been demonstrated that FeO_6 or FeO_8 polyhedra are less compressible than their Mg counterparts (Zhang et al. 1997; Zhang et al. unpublished). These results imply that the bonding character plays an important role in such anomalous compression, whereas structure type and polyhedral coordination may be less important. This consideration is supported by the compression behavior shown by different olivines (Zhang 1998), where transition metal olivines with cations of similar electronic configuration do follow the bulk modulus – volume relationship. The same observations have also been made on carbonates (Zhang et al. 1997).

It is noted that $K_{T0} = 157(1)$ GPa for $Ca_3Fe_2(SiO_4)_3$ (this study) and $K_{T0} = 157(3)$ GPa for $Fe_3Fe_2(SiO_4)_3$ (Koch et al. 1997) are the same despite the different electronic configurations of their dodecahedral cations. This is neither consistent with bulk modulus–volume systematics nor with the analysis made above. This might be a result of different K'_{T0} values, which were determined in different experiments. If we fix a value of $K'_{T0} = 6.7(8)$ determined on $Fe_3Fe_2(SiO_4)_3$ in fitting the EOS for $Ca_3Fe_2(SiO_4)_3$ from data in this study, the obtained K_{T0} will be several percent lower than the value listed in Table 3. This is a result of the trade-off between K_{T0} and K'_{T0}. On the other hand, the K_{T0} values of 157(3) GPa for $Fe_3Fe_2(SiO_4)_3$ and 151.6(8) GPa for $Mn_3Mn_2(SiO_4)_3$ (Koch et al. 1997; Arlt et al. in press) do follow the bulk modulus–volume systematics, because of the similar electronic configurations of the cations.

Hazen et al. (1994) concluded that the octahedra and tetrahedra framework in garnet controls the amount of compression, with the valence state of the octahedrally coordinated cation playing a primary role. Dodecahedra compression scales with the compression of the framework. In line with this proposal Zhang et al. (1998) showed that compression in garnet could be governed by the kinking degree of the Si-O-M angle, where M denotes the octahedral cation. Recent high pressure experimental data on almandine (Zhang, unpublished) shows that the Si-O-Al angle in almandine is less kinked than that in pyrope over the same pressure range. The similar bulk moduli of pyrope and grossular or of almandine and spessartine could thus be a result of a similar degree of kinking on their Si-O-Al angle. On the other hand, the bulk moduli of pyrope and grossular are smaller than those of almandine and spessartine despite the fact that all of them possess the same framework of AlO_6 and SiO_4 polyhedra. The difference in their compressibilities can be probably attributed to the different electronic configurations of the dodecahedral cations. Whereas the dodecahedral cations in pyrope and grossular are of the np^6 type, they are of the $3d^n$ type in almandine and spessartine. We believe that the electronic configurations of the dodecahedral cations can explain the similar bulk moduli of pyrope and grossular and of almandine and spessartine.

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