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High Pressure X-Ray Diffraction Study of a Grossular–Andradite Solid Solution and the Bulk Modulus Variation along this Solid Solution *

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In-situ angle-dispersive x-ray diffraction measurements on three samples of $Gr_{14}An_{84}$, $Gr_{34}An_{64}$ and $Gr_{63}An_{34}$ were performed by using a diamond anvil cell instrument with synchrotron radiation at the Beijing Synchrotron Radiation Facility at up to 13.7 GPa. A least-square fit of the pressure-volume to the Birch–Murnaghan equation of state, when fixed K_0'=4.0 yields bulk modulus values of K_0=166±2, 168±3, 173±2 GPa for $Gr_{14}An_{84}$, $Gr_{34}An_{64}$ and $Gr_{63}An_{34}$, respectively. The bulk modulus increases from 166±2 GPa for $Gr_{14}An_{84}$ and to 173±2 GPa for $Gr_{63}An_{34}$ with the increasing An content. Furthermore, by linear interpolation, the bulk modulus of the Gr-An binary system as a function of An content can be expressed as K_0(GPa) =176.9(9)-0.12(1)X_{An} (R^2=0.987).

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Garnet is a group name and there are many varieties of garnet. Six common species of garnet are recognized by their chemical composition. They are pyrope, almandine, spessartine, grossular, andradite and uvarovite. Garnets are nesosilicates having the general formula $A_3^{2+}B_2^{3+}(SiO_4)_3$. The A site is usually occupied by divalent cations (Ca^{2+}, Mg^{2+}, Fe^{2+} and Mn^{2+}) and the B site by trivalent cations ($A1^{3+}$, Fe^{3+} or Cr^{3+}).[1] The structure of the group consists of alternating SiO_4 tetrahedra and BO_6 octahedra that share corners, thus forming a continuous three-dimensional network, the configuration is cubic and belongs to the space group *Ia3d*.[2]

Many petrological models of the Earth indicate that garnet is an important mineralogical component of the Earth's upper mantle.[3] Therefore, an accurate knowledge of the physical properties of garnet is essential for interpretation of the seismic data and for better understanding of the chemical composition and physical states in the Earth's mantle.[4] Grossular and andradite are a calcium-aluminium garnet with the formula $Ca_3Al_2Si_3O_{12}$ and a calcium-iron garnet with the formula $Ca_3Fe_2Si_3O_{12}$, respectively. To date, the elastic properties of grossular and andradite have been extensively studied using both the multianvil apparatus and the diamond anvil cell.[5–12] However, most previous studies were constrained to the elastic properties of grossular and andradite end members. There are few works dealing with the elastic properties of grossular-andradite solid solution.[7] However, it is known that a variety of different cations can be incorporated in the garnet structure and that changes in composition affect the elastic properties.[10] It is necessary, therefore, to study composition-bulk modulus relationships. Furthermore, equation-of-state data plays a central role in efforts to describe the layered mineralogical structure and convective dynamics of the Earth's deep interior.[13]

Thus, in this study we investigate three garnet samples along the grossular (Gr)-andradite (An) binary system by *in situ* x-ray diffraction techniques and a liquid pressure medium under hydrostatic conditions at high pressures using a diamond anvil cell. The aim of this study is to determine the evolution of the bulk modulus as a function of composition along the join of grossular-andradite binary system in order to provide better constraints for thermodynamic models of mantle garnets.

Three grossular-andradite solid solution specimens in this study were extracted from the Shizhuyuan polymetallic mine in Hunan Province, China. The samples were ground under acetone in an agate mortar to an average grain size of 5 μm before further drying. The structure of these samples was of cubic systems characterized by conventional x-ray diffraction, and their chemical composition was determined by using an electron microprobe which was proved to have the following composition: ($Gr_{14}An_{84}Py_2$),

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($Gr_{34}An_{64}Py_1Spe_1$) and ($Gr_{63}An_{34}Py_1Spe_2$), respectively, where Py and Spe are pyrope and spessartine, respectively.

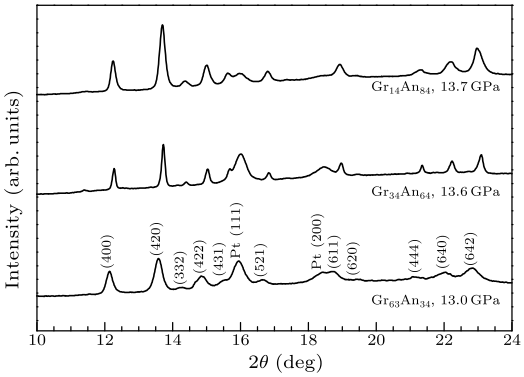


Fig. 1. Sections of the x-ray powder diffraction patterns of $Gr_{14}An_{84}$, $Gr_{34}An_{64}$ and $Gr_{63}An_{34}$ at pressures of 13.7, 13.6 and 13.0 GPa, respectively.

Modified Merill–Bassett-type diamond anvil cells were used in our experiments. The diameter of the diamond culet was 500 μm. T301 stainless steel gaskets pre-indented and drilled to a diameter of 200 μm served as pressure chamber. The sample powder was loaded with the inner pressure standard Pt powder in the center of the gasket hole. Cell pressures were determined by fitting the P–V data of Pt using the equation of state of Holmes *et al.*[14] The pressure transmitting medium was a 16:3:1 mixture ethanol-methanol-water. P–V experiments were conducted at the High Pressure Experiment Station, Beijing Synchrotron Radiation Facility (BSRF). The incident x-ray beam was monochromatized to a wavelength of 0.6199 Å. The doubly focused x-ray ($\lambda = 0.6199$ Å) beam size was $12\times27\,\mu m^2$. The angle-dispersive x-ray diffraction patterns were obtained on an imaging plate x-ray data collection system. Typical exposure times for collecting diffraction patterns of the sample and the pressure marker were 600 s and later integrated as a function of 2θ using the Fit2D code software package[15] to obtain conventional one-dimensional diffraction profiles. The cell parameters were calculated using a UnitCell process.[16] For all patterns, sample diffraction lines 400, 420, 332, 422, 431, 521, 611, 620, 444, 640 and 642 were used to refine the parameters, and 220 and 800 were also used when available.

Table 1. Unit-cell lattice parameters collected at different pressures for the samples along the grossular-andradite join in this study. Gr and An stand for grossular and andradite, respectively. The numbers in brackets are 1σ error in the last digits.

P (GPa)	a (Å)	V (Å^3)	P (GPa)	a (Å)	V (Å^3)	P (GPa)	a (Å)	V (Å^3)
$Gr_{14}An_{84}$			$Gr_{34}An_{64}$			$Gr_{63}An_{34}$		
0.0001	11.899(1)	1684.8(3)	0.0001	11.913(1)	1690.9(4)	0.0001	11.933(1)	1699.2(5)
0.5	11.892(2)	1681.2(7)	0.8	11.900(1)	1685.2(5)	0.9	11.918(2)	1693.0(7)
3.1	11.829(2)	1655.2(8)	2.6	11.849(2)	1663.5(6)	2.4	11.877(2)	1675.4(8)
4.1	11.806(2)	1645.4(5)	4.5	11.808(1)	1646.4(7)	4.8	11.824(2)	1653.0(5)
5.5	11.776(2)	1633.0(6)	6.0	11.773(2)	1631.7(7)	5.5	11.809(4)	1646.9(6)
6.0	11.765(2)	1628.4(7)	8.5	11.727(1)	1612.6(7)	6.4	11.791(3)	1639.2(5)
7.2	11.735(2)	1616.2(7)	10.1	11.701(2)	1602.2(7)	7.9	11.760(2)	1626.3(7)
10.3	11.681(2)	1593.9(4)	13.6	11.656(2)	1583.5(8)	9.9	11.731(2)	1614.2(5)
13.7	11.629(2)	1572.4(2)				11.3	11.709(3)	1605.3(6)
						13.0	11.687(1)	1596.2(4)

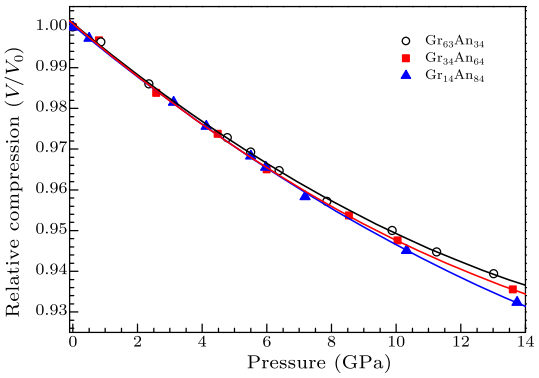


Fig. 2. Evolution with pressure of the unit-cell volumes (relative compression) of the grossular-andradite join

The unit-cell parameters measured for $Gr_{14}An_{84}$, $Gr_{34}An_{64}$ and $Gr_{63}An_{34}$ to a maximum pressure of 13.7 GPa are listed in Table 1, which show a smooth continuous decrease with increasing pressure with no evidence for phase transitions. The x-ray powder diffractions of the three samples obtained at highest experimental pressures of this study are shown in Fig. 1.

The P–V data reported in Table 1 are plotted in Fig. 2 for the three samples studied. The volume compressibility clearly increases with increasing andradite component. The pressure-volume data at room temperature are fitted into the Birch–Murnaghan equation of state (BM-EOS):[17]

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

where V_0, K_0 and K_0' are the zero-pressure volume, isothermal bulk modulus and its pressure derivative, respectively. The experimental P–V data are fitted into the BM-EOS. The calculated K_0 value is sensitive to K_0' when we fit the data to BM-EOS.[18,19] There-

fore, we constrain K_0' to the same value ($K_0' = 4.0$) for comparison with K_0 for the three samples. By fixing K_0' to 4.0, using the software EOSFIT-5.2 we obtain $K_0 = 166(2)$ GPa, $K_0 = 168(3)$ GPa, $K_0 = 173(2)$ GPa for $Gr_{14}An_{84}$, $Gr_{34}An_{64}$ and $Gr_{63}An_{34}$, respectively. The bulk modulus K_0 increases from 166(2) GPa for $Gr_{14}An_{84}$ to 173(2) GPa for $Gr_{63}An_{34}$.

Elastic parameters of grossular end member, andradite end member and grossular-andradite solid solutions are summarized in Table 2. The bulk modulus of the grossular-andradite binary system with various compositions is also summarized in Figs. 3 and 4. Since the differences between the adiabatic and isothermal bulk moduli are small under the ambient condition, we made no corrections in this figure. With the exceptions of the synthetic andradite and grossular, the natural grossular-andradite solid solutions contain pyrope and spessartine. Therefore the chemical compositions of the natural garnet specimens were recalculated in terms of the grossular-andradite binary system. These recalculated values are listed in Table 2 in parentheses.

Table 2. Bulk moduli and first pressure derivative for the garnets along the grossular-andradite join. The chemical composition values in the parentheses indicate the mol% values recalculated for the andradite-grossular binary system. An: andradite, Gr: grossular, Py: pyrope, Spe: spessartine. The numbers in brackets are 1σ error in the last digits.

Sample	K_0(GPa)	K_0'	Method	Reference
Gr_{100}	171.4(1.7)		Ultrasonic	[9]
	169.1(8)		Ultrasonic	[5]
	168.4		Brillouin scattering	[6]
	174(4)	4.25(fixed)	x-ray diffraction	[7]
	167.8(25.0)	6.2(4.0)	x-ray diffraction	[8]
	170(4)	5.2(6)	x-ray diffraction	[10]
	176(4)	4(fixed)	x-ray diffraction	[7]
	177(1)	4(fixed)	x-ray diffraction	[10]
	168.2(1.7)	4(fixed)	x-ray diffraction	[11]
An_{100}	157(2)		Brillouin scattering	[12]
	162(5)	4.4(7)	x-ray diffraction	[10]
	165(1)	4(fixed)	x-ray diffraction	[10]
	158.0(1.5)	4(fixed)	x-ray diffraction	[11]
$Gr_{14}An_{84}Py_2$ ($Gr_{14.3}An_{85.7}$)	166(2)	4(fixed)	x-ray diffraction	This study
$Gr_{34}An_{64}Py_1Spe_1$ ($Gr_{34.7}An_{65.3}$)	168(3)	4(fixed)	x-ray diffraction	This study
$Gr_{63}An_{34}Py_1Spe_2$ ($Gr_{64.9}An_{35.1}$)	173(2)	4(fixed)	x-ray diffraction	This study

So far, the elasticity of grossular and andradite end members have been studied intensively by many methods,[5–12] and various reports on K_0 of grossular converge to $K_0 = 167.8$–174 GPa, which show about 7% higher K_0 of andradite ($K_0 = 157$–162 GPa). In addition, the pyrope and spessartine content in the two natural grossular-andradite solid solutions is very low, and the bulk modulii of pyrope[4,20] and spessartine[5,21] are relatively similar to grossular, so we ignore the effects of pyrope and spessartine on the bulk moduli of natural grossular-andradite solid solutions. When we made the least-square fit of the compositional dependences for $Gr_{14.3}An_{85.7}$, $Gr_{34.7}An_{65.3}$ and $Gr_{64.9}An_{35.1}$ of bulk moduli by using a linear equation, we can obtain the following relation as the compositional dependence of the bulk modulus: $K_0(\text{GPa}) = 177.8(7) - 0.14(2)X_{\text{An}}$ (R^2=0.983), where An is andradite mol% in the grossular-andradite binary system. We have found a linear relationship between K_0 and molar fraction (%) of K_0 along the Gr-An join, which shows that K_0 decreases with the increasing An content. This behavior is very similar to that observed for the Py-Al join.[4,22] The K_0 value of Py-Al join decreases with the increasing pyrope content. The bulk modulii of grossular and andradite determined in previous studies are also presented in Fig. 3 for purpose of comparison. However, the parameters K_0 and K_0' are usually strongly correlated in an EOS fit,[18,19] so we cannot just compare the bulk modulus and neglect its pressure derivative. Therefore, we refit the data of Weaver *et al.*[7] and Zhang *et al.*[10] for purpose of comparison by fixing K_0' at 4.0. Furthermore, by using linear interpolation for the bulk modulii of $Gr_{14.3}An_{85.7}$, $Gr_{34.7}An_{65.3}$ and $Gr_{64.9}An_{35.1}$, as well as grossular and andradite end members of Weaver *et al.*[7] and Zhang *et al.*[10] by fixing $K_0' = 4.0$, the bulk modulii of the grossular-andradite binary system as a function of andradite content can be expressed by $K_0(\text{GPa}) = 176.9(9)$–$0.12(1)X_{\text{An}}$ (R^2=0.987) (Fig. 4). The results also show that there are significant linear correlation between the present study and the previous results of Weaver *et al.*[7] and Zhang *et al.*[10] by fixing K_0' at 4.0.

There are two possible sources for K_0 along the Gr-An join, showing that K_0 decreases with the increasing An content. First, the ionic radii of Al and Fe increase [Al^{3+}(0.535 Å)<Fe^{3+} (0.645 Å)]. Second, the Ca^{2+}-O bond distance in andradite (2.433 Å) is greater than that in grossular (2.405 Å), furthermore, the Fe^{3+}-O bond distance in andradite (2.024 Å) is much greater than the Al^{3+}-O bond distance in

grossular (1.924 Å).[23] The inoic radii and the bond distances may have a significant influence on bulk modulus.[24,25] The smaller the inoic radius and the bond distance, the stronger the attraction for bonding electrons, the greater the electron density between cation and anion. Then crystals have greater compressed resisted capacity.[24,25] Therefore, we infer that the ionic radii and bond distances are the main reasons for the bulk moduli reduce in turn with the increase of andradite.

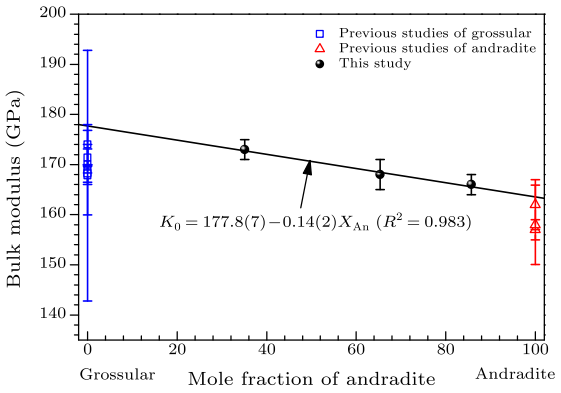


Fig. 3. Variation of the bulk modulus K_0 as a function of composition along the grossular-andradite join. The solid line is a weighted linear fit through the data of this study represented as filled circles. The two filled circles in the end members of Gr and An is the value obtained from the linear relationship of this study.

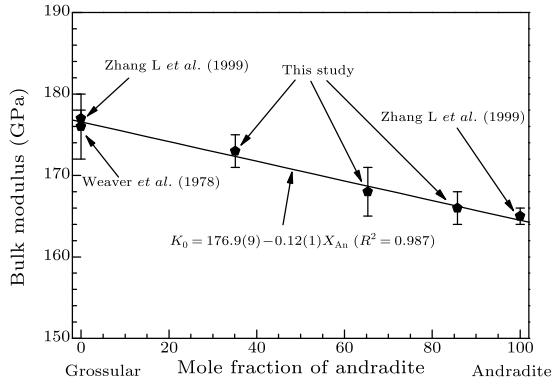


Fig. 4. Variation of the bulk modulus across the grossular-andradite solid-solution series of this study and Weaver *et al.*[7] and Zhang L *et al.*[10] by fixing K_0' to 4.0. The solid line is a weighted linear fit through the data of this study and Weaver *et al.*[7] and Zhang L *et al.*[10] by fixing K_0' to 4.0.

In summary, the P–V measurements on three samples of $Gr_{14}An_{84}$, $Gr_{34}An_{64}$ and $Gr_{63}An_{34}$ at pressures up to 13.7 GPa have been carried out using the DAC technique. Elastic properties have been derived by using the P–V data set by the Birch–Muranghan equation of state. When fixed $K_0' = 4.0$, we obtain the bulk modulus values of $K_0 = 166 \pm 2$ GPa, $K_0 = 168 \pm 3$ GPa, $K_0 = 173 \pm 2$ GPa for $Gr_{14}An_{84}$, $Gr_{34}An_{64}$ and $Gr_{63}An_{34}$, respectively. It is realized that the K_0 value of Gr-An solid solution increases with the increasing An content. In addition, the bulk modulus of the Gr-An binary system can be expressed as a function of An content by $K_0(\text{GPa}) = 176.9(9) - 0.12(1)X_{An}$ ($R^2 = 0.987$).

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