

## Compressibility of grunerite

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## ABSTRACT

The unit-cell parameters of natural grunerite were measured in a diamond anvil cell at nine different pressures up to 5.1 GPa. The bulk modulus  $K_0$  and its pressure derivative  $K_0'$  were calculated by fitting the pressure-volume data to a Birch-Murnaghan equation of state:  $K_0 = 50(1)$  GPa and  $K_0' = 13(1)$ . The linear compressibilities  $\beta_a$ ,  $\beta_b$ , and  $\beta_c$  are 4.97(6), 3.50(4), and  $3.62(5) \times 10^{-3}$  GPa $^{-1}$ , respectively, yielding the ratio  $\beta_a:\beta_b:\beta_c = 1.418(1):1.000(2):1.032(5)$ . Grunerite exhibits strong anisotropic compression in the low-pressure region ( $P < 1$  GPa). With increasing pressure, the compression becomes more isotropic. This behavior and the larger volume compressibility compared to that of Ca-rich clinopyroxenes in the pressure range studied are proposed to be due to the strong compression of the empty A cavities in the crystal structure at low pressures.

## INTRODUCTION

The crystal structure of the iron magnesium manganese amphibole grunerite (Finger, 1969) consists of corner-linked tetrahedral double chains connected by ribbons of edge-sharing octahedra. Four crystallographically non-equivalent polyhedral positions, designated as M1, M2, M3, and M4 may be distinguished. Mg and Fe occupy all four positions, Fe generally preferring M4 (Hafner and Ghose, 1971). A large empty cavity (A site) exists between the back-to-back tetrahedral double chain. With this structure in mind, it is interesting to compare compressibilities, e.g., with those of pyroxenes, in which there are only two types of polyhedra, M1 and M2, and no large A-type cavities. The purpose of this study was to compare the compression between amphibole and pyroxene and to evaluate correlations between the compression of the bulk volume and local field parameters at structure sites measured with  $^{57}\text{Fe}$  gamma resonance at high pressures (Zhang et al., 1989a), using the same amphibole of relatively simple chemical composition.

## EXPERIMENTAL DETAILS

## Sample

The grunerite sample is from a metamorphic rock of greenschist to low amphibolite facies in the Gongchangling iron mine, China. The mineral associated with garnet and magnetite occurs as veins in the iron ore or in amphibolites. The yellowish green crystals appear in the form of fibrous needles, which have dimensions of 1 mm or more in length and 0.1 mm or less in width. They often contain small fractures. The composition is  $(\text{Na}_{0.05}\text{K}_{0.01}\text{Fe}_{5.33}^{2+}\text{Mg}_{1.46}\text{Fe}_{0.14}^{3+}\text{Al}_{0.01})$  for the seven M positions,  $(\text{Si}_{7.92}$

$\text{Al}_{0.08})$  for the eight tetrahedral positions, and  $(\text{O}_{22}, \text{OH}_{1.92}, \text{F}_{0.05}, \text{Cl}_{0.01})$  for the anions (Chen et al., 1984). A single crystal with dimensions of approximately  $0.15 \times 0.1 \times 0.05$  mm $^3$  was selected optically and with the X-ray precession method to ensure diffraction quality.

## High pressure X-ray diffraction technique

The measurements were made by use of a modified miniature Merrill-Bassett diamond anvil cell with four screws, similar to that of Mao and Bell (1980). An Inconel 750X gasket preindented to 0.085 mm with a hole of 0.3 mm was used. A 4:1 methanol to ethanol mixture served as a hydrostatic pressure transmitting medium (Piermarini et al., 1973), and a ruby chip of about 0.025 mm was included in the cell as pressure calibrant. The hydrostatic pressure was measured before and after each X-ray diffraction experiment by use of the pressure-induced shift of the R1 fluorescence line of ruby. The error in pressure calibration was estimated to be 0.05 GPa. Data measurement was carried out on a Stoe four circle diffractometer

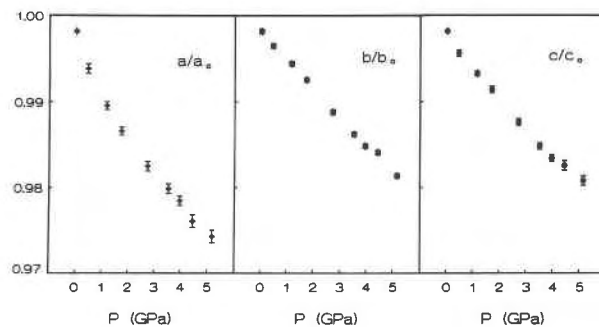


Fig. 1. Compression of the unit-cell axes;  $a/a_0$ ,  $b/b_0$ , and  $c/c_0$ . The symbols  $a_0$ ,  $b_0$ ,  $c_0$  represent the cell parameters measured at ambient conditions.

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**TABLE 1.** Unit-cell parameters of grunerite between ambient pressure and 5 GPa

<i>P</i> (GPa)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\beta$ (°)	<i>V</i> (Å <sup>3</sup> )	<i>a</i> sin $\beta$ (Å)
0.0	9.5390(5)	18.321(1)	5.3345(4)	101.82(1)	912.5(1)	9.337
0.4	9.495(5)	18.288(2)	5.320(2)	101.95(5)	903.9(5)	9.289
1.1	9.451(4)	18.248(1)	5.307(1)	102.26(4)	894.5(4)	9.234
1.7	9.422(4)	18.211(1)	5.296(2)	102.42(4)	887.5(4)	9.202
2.7	9.380(5)	18.139(2)	5.275(2)	102.63(5)	875.8(6)	9.153
3.5	9.353(5)	18.089(2)	5.259(2)	102.73(6)	868.1(7)	9.124
3.9	9.339(5)	18.061(2)	5.251(2)	102.78(5)	863.8(6)	9.109
4.4	9.315(7)	18.047(3)	5.246(3)	102.87(8)	859.7(9)	9.081
5.1	9.297(7)	17.994(2)	5.236(3)	103.02(6)	853.4(7)	9.058

Note: Standard deviations in the last decimal place are given in parentheses.

using MoK $\alpha$  radiation monochromated by a graphite crystal ( $\lambda = 0.7107 \text{ \AA}$ ).

The unit-cell parameters were measured at nine different pressures between ambient pressure and 5.1 GPa. For this, reflections were selected as follows: The  $2\theta$  ranges of the powder lines from Be disks supporting the diamond anvils were determined first. Subsequently, those reflections that are not in the  $2\theta$  ranges of the powder lines from Be were centered. The unit-cell parameters were determined from 15 to 19 reflections,  $2\theta$  ranging from 15 to 42°. Each reflection was centered in eight positions (King and Finger, 1979) to reduce zero and crystal-centering errors. The influence of counting times on the results of refinement was estimated through experiments. The unit-cell parameters obtained by centering a reflection in 20 s per step exhibited half the standard deviation of those measured in 1 s per step. The results presented here were measured using a counting time of 20 s per step. The cell parameters at ambient pressure were determined by use of an automated Siemens-D500 powder diffractometer.

The unit-cell parameters were calculated by means of the procedure of Ralph and Finger (1982). There was no significant deviation between the results without monoclinic constraints and with the constraints. The results presented here were refined with the constraints.

## RESULTS

The unit-cell parameters of grunerite are listed in Table 1. They are generally 1 order of magnitude more precise

than those of a powdered sample of the same specimen measured in a lever-arm NBS diamond anvil cell up to 10 GPa (Zhang et al., 1989a). As shown in Table 1, the  $\beta$  angle increases with increasing pressure. To facilitate the comparison with the results of Ca-rich clinopyroxenes (Zhang et al., 1989b), the cell parameters were recalculated for space group  $I2/m$  (Sueno et al., 1973); they are presented in Table 2. Here  $\beta$  decreases with increasing pressure, showing the same trend as that of Ca-rich clinopyroxenes. No discontinuity in the unit-cell parameters over the entire range of pressure studied was observable within the experimental error.

The data reveal an anisotropic compression of the unit cell. The linear compressibilities  $\beta_a$ ,  $\beta_b$ , and  $\beta_c$  are shown in Table 3, and axial compressions are plotted in Figure 1. It is clear from Table 3 that the *a* axis is the most compressible direction, whereas *b* and *c* have nearly the same compressibilities.

The unit-cell volume at 5.1 GPa is 6.5% smaller than at ambient pressure. In Figure 2 the least-squares fit of the pressure-volume data to a Birch-Murnaghan equation of state is presented. It yields an isothermal bulk modulus  $K_0$  of 50(1) GPa, and its pressure derivative  $K_0'$  yields one of 13(1). Assumption of  $K_0' = 4$  yields  $K_0 = 63(1)$  GPa. This, however, does not seem appropriate for grunerite, since the pressure-volume data could not be fitted properly.

The axial ratios *a/b* and *a/c* decrease with increasing pressure, whereas the ratio *b/c* is nearly invariable. The relationships are shown in Figure 3.

**TABLE 2.** Unit-cell parameters of grunerite at pressures assuming space group  $I2/m^*$ 

<i>P</i> (GPa)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\beta$ (°)	<i>V</i> (Å <sup>3</sup> )	<i>a</i> sin $\beta$ (Å)
0.0	9.929	18.321	5.3345	109.90	912.5	9.337
0.4	9.876	18.288	5.320	109.85	903.9	9.289
1.1	9.807	18.248	5.307	109.66	894.5	9.234
1.7	9.765	18.211	5.296	109.56	887.5	9.202
2.7	9.704	18.139	5.275	109.40	875.8	9.153
3.5	9.667	18.089	5.259	109.32	868.1	9.124
3.9	9.649	18.061	5.251	109.28	863.8	9.109
4.4	9.619	18.047	5.246	109.25	859.7	9.081
5.1	9.587	17.994	5.236	109.13	853.4	9.058

\* Calculated according to the  $I2/m$  cell with transformation matrix 101/0-10/00-1 based on the data of the  $C2/m$  cell listed in Table 1. This was carried out for comparison with pyroxene.

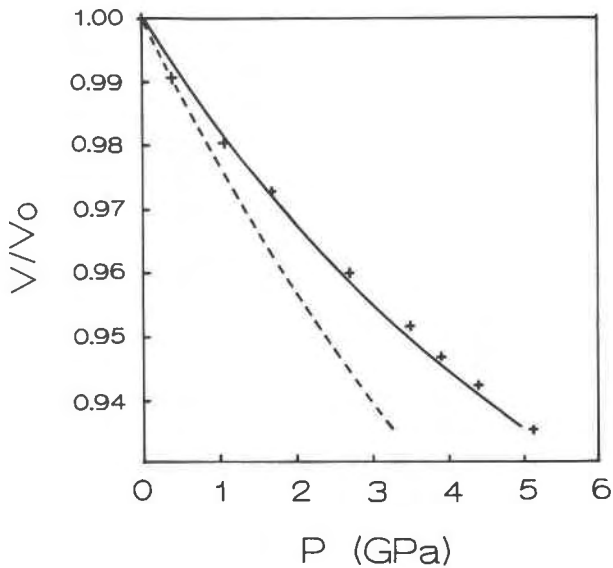


Fig. 2. Compression of unit-cell volume.  $V_0$  is the value measured at ambient conditions. The solid line was calculated with  $K_0 = 50(1)$  GPa and  $K_0' = 13(1)$ ; the dashed line was calculated with  $K_0 = 63(1)$  GPa and  $K_0' = 4$ .

### DISCUSSION

It is interesting to note that the axial ratios  $a/b$  and  $a/c$  decrease significantly with increasing pressure between ambient pressure and approximately 1 GPa, whereas at pressure between 1 and 5 GPa they are nearly constant (Fig. 3). This indicates that  $a$  is compressed more strongly relative to  $b$  and  $c$  in the low-pressure region, while at higher pressures it is compressed approximately the same as  $b$  and  $c$ . Thus, the apparently larger linear compressibility  $\beta_a$  relative to  $\beta_b$  and  $\beta_c$  between ambient pressure and 5 GPa is the result of greater compression of the  $a$  axis at low pressures. At pressures  $P > 1$  GPa the linear compressibilities approach each other. In other words, the anisotropic compression in the low-pressure range becomes more or less isotropic with increasing pressure.

The change in slope of  $a/b$  and  $a/c$  near 1 GPa may be correlated with those of the isomer shifts  $\delta$  and quadrupole splittings  $\Delta E_Q$  plotted vs. unit-cell volume (Figs. 5, 6 in Zhang and Hafner, 1992a). Between ambient pressure and 1 GPa,  $\delta$  and  $\Delta E_Q$ , which are directly related to the relevant polyhedral volumes, remain approximately constant. This means that the M polyhedra are not responsible for the observed bulk compression of the unit-

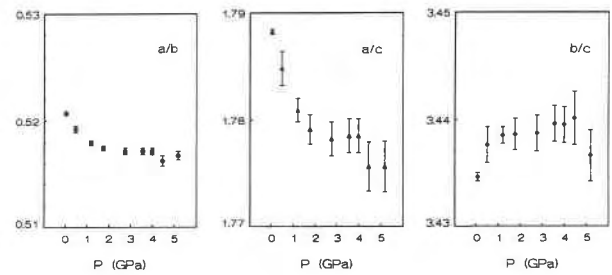


Fig. 3. Axial ratios  $a/b$ ,  $a/c$ , and  $b/c$  vs. pressure.

cell volume in that pressure range. The study of the structure of diopside at high pressures (Levien and Prewitt, 1981) and that of amphibole at high temperature (Sueno et al., 1972, 1973) showed that compression and expansion of single and double chain silicates are mainly due to compression and expansion of the A and M polyhedra. Based on this and related hyperfine data, it is reasonable to conclude that at pressures  $< 1$  GPa the large volume compressibility of the unit cell must be accounted for by a collapse of the A cavities.

Preferential compression of the A cavities exists only at pressures  $< 1$  GPa. At pressures  $> 1$  GPa, the compression of M polyhedra may be the dominant factor governing the bulk unit-cell compression, similar to the compression mechanism in Ca-rich clinopyroxenes where the unit cell is compressed by the same amount as the volumes of the M1 and M2 polyhedra (Levien and Prewitt, 1981).

The close relation between the large linear compressibility  $\beta_a$  and the collapse of A cavities in the low-pressure range explains why the largest linear compressibility in grunerite is parallel to the  $a$  axis while it is parallel to the  $b$  axis in Ca-rich pyroxenes. Sueno et al. (1973) showed that  $a$  is the direction of largest thermal expansion in tremolite because of the considerable expansion of the A cavity in the direction perpendicular to the  $b,c$  plane. This observation is also consistent with our analysis. From the discussion above, it is to be expected that with greater shrinking of the A cavities, the compression mechanism in grunerite will be more similar to that in pyroxenes.

The significantly larger volume compressibility of grunerite,  $\beta = 12.69(8) \times 10^{-3}$  GPa $^{-1}$ , compared with that of Ca(Fe,Mg)Si $_2$ O $_6$  clinopyroxenes (hedenbergite:  $\beta = 7.62 \times 10^{-3}$  GPa $^{-1}$ ) in the pressure range studied (Zhang and Hafner, 1992b) may be attributed partly to the compression of the A cavity, although the change in geometrical configuration of the M4 polyhedron may be important as well. For further substantiation, precise structure determinations of grunerite at high pressures will be necessary.

Comparison of the unit-cell parameters of grunerite between ambient temperature and 4.5 K (Ghose et al., 1987) with those at high pressures and ambient temperature (Table 1) shows that the effect of decreasing temperature from ambient temperature to 4.5 K is about equal to the effect of increasing pressure from ambient pressure to 0.4 GPa at 293 K. Whether or not this is an inverse pressure,

TABLE 3. The linear compressibilities of grunerite (in units of  $\times 10^{-3}$ /GPa)

$\beta_a$	$\beta_b$	$\beta_c$	$\beta_v$	$\beta_a:\beta_b:\beta_c$
4.97(6)	3.50(4)	3.62(5)	12.69(8)	1.418(1):1.00(2):1.032(5)

Note:  $\beta_a$ ,  $\beta_b$ ,  $\beta_c$  are the linear compressibilities. The errors in the last decimal place are given in parentheses. They were calculated through an error propagation procedure using standard deviations of Table 1.

temperature behavior of the unit cell, as shown for hedenbergite (Zhang and Hafner, 1992b), needs to be investigated in more detail. Technically a pressure of about 0.5 GPa can be generated through differential thermal contraction of the sample holder and sample at low temperatures.

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