High-pressure crystal chemistry of neighborite, NaMgF₃: An angle-dispersive diffraction study using monochromatic synchrotron X-radiation

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Abstract

The crystal structure of neighborite (NaMgF₃) is determined at high pressure using monochromatic synchrotron X-ray powder diffraction data with Rietveld structural refinement methods. The previously assumed regularity of the MgF₆ octahedra at high pressure in the perovskite structure is demonstrated to be valid. The pressure-induced dimensional changes are expressed empirically as a combination of compression of the Mg-F bond length and tilting of the MgF₆ octahedral framework. We demonstrate that the dominant compression mechanism involves shortening of the octahedral Mg-F bond, which contributes about 80% to the overall compression, with the remaining 20% due to an increase in octahedral tilting. Linear compressibilities are consistent with single-crystal elasticity data, with the significant anisotropy observed being directly related to the tilting freedom of the octahedra along each axis of the unit cell.

Introduction

Members of the orthorhombic ABX₃ perovskite group (Pbnm, Z = 4), which includes NaMgF₃ and MgSiO₄, have structures that are distorted from the ideal cubic structure by two independent octahedral tilts, θ and ϕ (Fig. 1). The tilt θ is about one of the diad axes, [110]p, of the BX₆ octahedron; this is equivalent to a tilt about the orthorhombic b axis in the Pbnm phase. The tilt ϕ is about the [001]p axis of the BX₆ octahedron and corresponds to tilting about the c axis. The subscript p refers to the pseudocubic structure of the high-symmetry prototype. The θ tilting causes the bending of the (B-X-B) angle and thus a shortening of a and c, whereas the ϕ tilt causes a shortening of a and b. On the basis of the assumption that the BX₆ octahedra are regular, the unit-cell volume of a centrosymmetrically distorted ABX₃ perovskite with a space group of Pbnm can be readily written according to the formalism of O’Keeffe and Hyde (1977):

$$V = abc = 32[B-X]^{3}\cos^{2}\phi$$

(1)

where B-X is the bond length within the BX₆ octahedron and Φ is the tilting about the pseudo-threefold axis of the octahedra (Fig. 1). The quantitative relationship between the angles θ, ϕ, and Φ can be found in Zhao et al. (1993a, 1993b).

The pressure- and temperature-induced dimensional change of the perovskite structure can be decoupled into two constituent parts: (1) the compression or expansion of the octahedral bond length B-X and (2) the compression or expansion due to the BX₆ octahedral tilting, (Megaw, 1971; Hazen and Finger, 1982). Thus the volumetric expansion can be expressed as

$$\alpha_V = \alpha_{\theta_0} + \alpha_{\phi_0} = \frac{3\delta[B-X]}{[B-X]\partial T} + \frac{2\delta \cos \Phi}{\cos \Phi \partial T} \quad (2a)$$

and the volumetric compression as

$$\beta_V = \beta_{\theta_0} + \beta_{\phi_0} = -\frac{3\delta[B-X]}{[B-X]\partial P} - \frac{2\delta \cos \Phi}{\cos \Phi \partial P} \quad (2b)$$

We have demonstrated that this structural model is applicable to the thermal expansion of many perovskite materials (Zhao and Weidner, 1991; Zhao et al., 1993a, 1993b). Further, our observations at high pressure suggested that the proposed model may also be applicable to the compression of the perovskite structure (Zhao et al., 1993c). Single-crystal elasticity data also support this conclusion (Zhao and Weidner, 1993). There were, however, two remaining problems related to our previous high-pressure compressional data. First, significant deviatoric stress existed during the cold-compression part of the experiment. Second, information on the octahedral tilting and the octahedral bond length were derived indirectly from the lattice parameters (O’Keeffe and Hyde, 1977). This approach uses the assumption that the octahedra remain regular under high-pressure conditions.

The present study is designed to obtain high-quality monochromatic diffraction data from powdered neigh-
borite under hydrostatic pressure conditions. By performing structural refinements, we can directly test the validity of published structural models for the compression mechanism. We also sought to evaluate the potential of a large volume apparatus for collecting powder diffraction data suitable for Rietveld refinement. It was hoped that the heating capabilities built into the DIA-type apparatus would alleviate the problem of strain broadening due to deviatoric stress at high pressure; this issue has dogged efforts to obtain sharp patterns in unheated high-pressure apparatus in the past.

**EXPERIMENTAL METHODS**

A powdered sample of the neighborite was synthesized following the method described by Chao et al. (1961). Stoichiometric proportions of NaF and MgF₂ were ground dry in an agate mortar. The mixture was sintered in a covered alumina crucible at 750 °C for 5 h. The resultant polycrystalline product had an X-ray diffraction pattern consistent with that published by Chao et al. (1961) and identical to the Rietveld refinement result of Zhao et al. (1993a).

High-pressure X-ray diffraction measurements were performed on the DIA-type cubic-anvil press (MAX-80) at the accumulator ring of the KEK, at the Tsukuba synchrotron radiation source (Shimomura et al., 1992). A portion of the sample was packed into a cylindrical amorphous-C furnace embedded in a boron-epoxy (BE) cube. A layer of NaCl powder, which serves as a pressure standard (Decker, 1971), was also packed into the sample chamber.

Before each data collection using monochromatic radiation, the instrument was operated in an energy-dispersive mode with white X-ray radiation to locate the sample position and to determine the cell pressure. The incident X-ray beam was collimated to 500 μm (width) × 200 μm (height). The energy-dispersive spectra were collected with a Ge solid-state detector at a fixed Bragg angle of 2θ = 7.5° and displayed on a multichannel analyzer. The volumetric variation of the NaCl standard was determined from peak shifts, and the cell pressure was calibrated using the Decker (1971) equation of state.

The experiment was then switched to the angle-dispersive mode (Shimomura et al., 1992) to collect monochromatic synchrotron X-ray data at a wavelength of 0.3100(7) Å. The wavelength was selected using a double-bounce (Bragg-Bragg) monochromator assembly consisting of two Si₁₁₁ crystals. The incident beam was decreased to 300 μm wide × 200 μm high, and a slit 300 × 100 μm was placed before the detector. With these beam optics, a peak full width at half maximum (FWHM) of ~0.05° is expected (Cox et al., 1988). The measured FWHM is actually ~0.06°, and with this resolution the peak-splitting of 200, 112, and 002 near 2θ = 6.5° (d ~ 2.7 Å) was clearly distinguished in the spectrum (Fig. 2).

Angle-dispersive data were collected from 4° > 2θ > 16° in steps of 0.01°, with a counting time of 60 s per step. The average ring current was 30 mA at 6.5 GeV. Data were normalized by monitoring the incident beam using an Ar ionizing chamber. No correction was made for absorption.

Previous experience (Weidner et al., 1994) with a DIA-type apparatus indicates that deviatoric stress at high pressure tends to broaden diffraction peaks because of microstrain induced by grain-to-grain contact. The FWHM of the diffraction peaks of the powder sample of neighborite increases dramatically with increasing pressure and becomes saturated at pressures of about 3–4 GPa, where the deviatoric stress reaches the yield strength of the sample (Zhao et al., 1993c). Upon heating, the yield strength of the sample, and thus the FWHM of the diffraction peaks, decreases continuously, reproducing the ambient value at about 500 °C (Zhao et al., 1993c). This indicates a vanishing of the deviatoric stress. In the present study, following the initial data collection at room pressure and temperature, the cell assembly was first taken to high pressure and then heated to 600 °C for ½ h to ensure that sample compression was hydrostatic. Data collected at several places within the sample assured us that this treatment is effective in reducing the deviatoric stress to zero while not promoting significant grain growth. The pressure was then calibrated. The ability to remove stresses within the sample by annealing is a distinct advantage in this type of work.

The diffraction patterns of neighborite were analyzed using the Rietveld refinement technique (Rietveld, 1969) built into the generalized structure analysis system...
TABLE 1. Structural parameters refined* using powder-diffraction data collected in MAX-80 apparatus at ambient and high-pressure conditions

<table>
<thead>
<tr>
<th>Atom**</th>
<th>$P$ (GPa)</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$U_{iso} \times 10^2$ (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>0.00</td>
<td>0.9851(9)</td>
<td>0.0455(8)</td>
<td>0.25</td>
<td>4.2(1)</td>
</tr>
<tr>
<td></td>
<td>4.9</td>
<td>0.9824(9)</td>
<td>0.0473(10)</td>
<td>0.25</td>
<td>4.6(2)</td>
</tr>
<tr>
<td>Mg</td>
<td>0.00</td>
<td>0.9680(7)</td>
<td>0.0422(7)</td>
<td>0.25</td>
<td>4.1(1)</td>
</tr>
<tr>
<td></td>
<td>4.9</td>
<td>0.7022(5)</td>
<td>0.2946(6)</td>
<td>0.25</td>
<td>3.9(2)</td>
</tr>
</tbody>
</table>

* The three entries for each set of parameters refer to the data collected in MAX-80 under ambient conditions at room pressure (top rows), at 4.9 GPa (middle rows), and from the decompressed sample at room pressure (bottom rows). Final agreement factors and cell parameters for the three refinements are $R_{int} = 11.83$, $R_p = 8.27\%$, $R_{wp} = 4.76\%$, $\chi^2 = 2.61$, $a = 5.3603(7)$, $b = 5.4864(7)$, $c = 7.666(1)$ Å at initial room pressure; $R_{int} = 12.89\%$, $R_p = 9.26\%$, $R_{wp} = 3.94\%$, $\chi^2 = 2.03$, $a = 5.2386(5)$, $b = 5.3796(6)$, $c = 7.5052(9)$ Å at 4.9 GPa; and $R_{int} = 11.83\%$, $R_p = 8.29\%$, $R_{wp} = 4.83\%$, $\chi^2 = 2.64$, $a = 5.3609(8)$, $b = 5.4826(8)$, $c = 7.667(1)$ Å at room pressure following decompression.

** Space group Pbnm.

Fig. 2. The angle-dispersive synchrotron X-ray diffraction patterns of neighborite observed (a) at ambient conditions, (b) at $P = 4.9$ GPa, and (c) at ambient conditions after depressurization. Structural distortions and phase transitions can be monitored from the relative intensities of reflections and peak splitting resulting from the removal of symmetry elements from the $Pm3m$ perovskite substructure shown in Fig. 1. For example, a triplet of reflections associated with the orthorhombic distortion from the cubic substructure ($a = 3.8$ Å) to the $\sqrt{2}a \times \sqrt{2}a \times 2a$ superstructure is indicated by an arrow in a; in this case the distortion results in the cubic (110) reflection splitting into the orthorhombic (020), (112), and (200). Some of the low angle extra reflections, not associated with the cubic subcell, are also indicated with asterisks in a. Experimental data are shown as crosses, and the calculated profile is drawn as a continuous line. Tick marks below the patterns and above the difference curves are at position of all possible reflections in the range of data.

The peak shapes were modeled using the pseudo-Voigt function incorporated into GSAS (Larson and Von Dreele, 1988). Three parameters, a Gaussian of constant width, an asymmetry term, and the strain component of the Lorentzian, were sufficient for this purpose. This last correction was found to be constant, within experimental error, for the three data sets—testament to the efficacy of the strategy to minimize deviatoric stress outlined above. The addition of other parameters either did not significantly improve the discrepancy between observed and calculated data or led to such physically unreasonable results as negative particle sizes. The fit to the observed data is presented graphically in Figure 2 and in Table 1.

Interestingly, although there is no indication of preferred orientation in the uncompressed sample, both the 4.9-GPa and room-pressure data collected after decompression show this effect. The consequences of this observation are discussed below.

**ANALYSIS OF THE COMPRESSION MECHANISM**

The overall volumetric compression of the orthorhombic $Pbnm$ phase of neighborite at 4.9 GPa was determined to be 6.3%. The $a$, $b$, and $c$ dimensions of the unit cell are compressed by 2.3, 2.0, and 2.1%, respectively.

(GSAS), distributed by Larson and Von Dreele (1988). A structure model previously refined using room-pressure data was used as a starting point. The results for the three data sets, collected before compression, at 4.9 GPa, and following decompression, quickly converged to the models summarized in Table 1. At low angles, the patterns contain some contaminant reflections from the cell assembly materials, magnesium oxide and boron nitride. The strongest of these has about 15% of the intensity of the largest perovskite reflection; the rest have < 10%. Fortunately, only a few reflections from NaMgF$_3$, below $9^\circ 2\theta$ were affected. Those regions were excluded from the refinement (Fig. 2).

The overall volumetric compression of the orthorhombic $Pbnm$ phase of neighborite at 4.9 GPa was determined to be 6.3%. The $a$, $b$, and $c$ dimensions of the unit cell are compressed by 2.3, 2.0, and 2.1%, respectively.
TABLE 2. Selected interatomic distances (Å) and angles (°)

<table>
<thead>
<tr>
<th>Atoms</th>
<th>0 GPa (before)</th>
<th>4.9 GPa</th>
<th>0 GPa (after)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-F1</td>
<td>3.187(6)</td>
<td>3.166(9)</td>
<td>3.182(6)</td>
</tr>
<tr>
<td>Na-F1</td>
<td>3.214(6)</td>
<td>3.223(9)</td>
<td>3.218(6)</td>
</tr>
<tr>
<td>Na-F1</td>
<td>3.098(8)</td>
<td>3.083(9)</td>
<td>3.119(6)</td>
</tr>
<tr>
<td>Na-F1</td>
<td>3.221(8)</td>
<td>2.244(7)</td>
<td>2.229(6)</td>
</tr>
<tr>
<td>Mg-F2 x 2</td>
<td>2.563(5)</td>
<td>2.496(8)</td>
<td>2.576(4)</td>
</tr>
<tr>
<td>Na-F2 x 2</td>
<td>2.302(5)</td>
<td>2.234(6)</td>
<td>2.315(6)</td>
</tr>
<tr>
<td>Na-F2 x 2</td>
<td>2.710(5)</td>
<td>2.705(4)</td>
<td>2.705(4)</td>
</tr>
<tr>
<td>Na-F2 x 2</td>
<td>3.393(5)</td>
<td>3.354(5)</td>
<td>3.358(4)</td>
</tr>
<tr>
<td>Mg-F1 x 2</td>
<td>1.979(1)</td>
<td>1.950(1)</td>
<td>1.985(1)</td>
</tr>
<tr>
<td>Mg-F2 x 2</td>
<td>1.988(3)</td>
<td>1.947(3)</td>
<td>1.973(2)</td>
</tr>
<tr>
<td>Mg-F2 x 2</td>
<td>1.981(3)</td>
<td>1.948(4)</td>
<td>1.984(3)</td>
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<td>F1-Mg-F1</td>
<td>180</td>
<td>180</td>
<td>180</td>
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<tr>
<td>F1-Mg-F2 x 2</td>
<td>88.3(2)</td>
<td>88.7(2)</td>
<td>88.9(2)</td>
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<tr>
<td>F1-Mg-F2 x 2</td>
<td>90.6(2)</td>
<td>91.4(2)</td>
<td>91.8(2)</td>
</tr>
<tr>
<td>F1-Mg-F2 x 2</td>
<td>91.7(2)</td>
<td>91.3(2)</td>
<td>91.1(2)</td>
</tr>
<tr>
<td>F1-Mg-F2 x 2</td>
<td>89.4(2)</td>
<td>88.8(2)</td>
<td>88.2(2)</td>
</tr>
<tr>
<td>F2-Mg-F2 x 2</td>
<td>89.37(6)</td>
<td>89.35(7)</td>
<td>89.4(1)</td>
</tr>
<tr>
<td>F2-Mg-F2 x 2</td>
<td>180</td>
<td>180</td>
<td>180</td>
</tr>
<tr>
<td>F2-Mg-F2 x 2</td>
<td>90.63(6)</td>
<td>90.65(7)</td>
<td>90.59(5)</td>
</tr>
<tr>
<td>F2-Mg-F2 x 2</td>
<td>180</td>
<td>179.97(2)</td>
<td>180</td>
</tr>
<tr>
<td>Mg-F1-Mg</td>
<td>151.1(3)</td>
<td>148.3(3)</td>
<td>150.0(2)</td>
</tr>
<tr>
<td>Mg-F2-Mg</td>
<td>150.1(2)</td>
<td>149.02</td>
<td>151.4(2)</td>
</tr>
</tbody>
</table>

These results are in good agreement with the elastic bulk modulus of $K = 75.6$ GPa and the linear compressibilities of $\beta_p = 4.88 \times 10^{-1}$, $\beta_s = 3.90 \times 10^{-1}$, and $\beta_L = 4.29 \times 10^{-1}$, as derived from single-crystal elastic data (Zhao and Weidner, 1993). This is also consistent with our previous high-pressure experiments in which significant anisotropy in the linear compressibilities, $\beta_p > \beta_s > \beta_L$, was observed (Zhao et al., 1993c).

Selected interatomic distances and angles for the NaF$_2$ dodecahedron and the MgF$_2$ octahedron are listed in Table 2. The octahedral tilts of $\theta$, $\phi$, and $\psi$ and the mean octahedral Mg-F bond length (see Appendix 1 in Zhao et al., 1993a) are given in Table 3. One can readily identify that the relative changes in the octahedral tilts are in the order: $\theta > \phi > \psi$, which contributes only about 20% to the overall volumetric compression. This estimation agrees remarkably well with the values derived from single-crystal elastic compliances (Zhao and Weidner, 1993). This also demonstrates that our previous estimation of structural distortions based on lattice parameters observed at high pressures is justified. Zhao et al. (1993a) defined an octahedral strain, $e^{oc}$, to describe the distortion of the octahedra, i.e.,

$$e^{oc} = \frac{[B-X]/[B-X]_m}{\pi/2 - (X_B-B-X_B)}$$

where $[B-X]_m$ is the mean octahedral bond length, $\delta[B-X]$ is the deviation of individual bond lengths from the mean, and $\langle X_B-B-X_B \rangle$ is the angle in radians between two octahedral bonds. The magnitude of $e^{oc}$ is calculated as

$$|e^{oc}| = \sqrt{\sum (e^{oc})^2}.$$  (5)

From the structure refinement data (Table 2), we have derived the following octahedral strain values: Before compression, $|e^{oc}| = 0.0335$, at 4.9 GPa, $|e^{oc}| = 0.0355$, and following decompression, $|e^{oc}| = 0.0385$. These values are virtually the same and small, implying that assumptions of regularity of the octahedra at high pressure made by Zhao et al. (1993c) were reasonable.

**Ferroelastic Transition**

The structural distortion observed in the neighborite can be characterized by the spontaneous strain, which is equivalent to the macroscopic thermodynamic order parameter often applied to characterize the ferroelasticity of the crystal (Aizu, 1970). It has been demonstrated that the magnitude of spontaneous strain for the ferroic species, $m3mFmmm$, which includes neighborite, can be related to the lattice parameters (Zhao et al., 1993).

$$e_s (m3mFmmm) = \sqrt{\frac{2}{3}} \left[\frac{(a + b)}{a_0}\left(\sqrt{2} - \frac{c}{\sqrt{2}}\right)^2 + 2\left(\frac{a - b}{2}\right)^2\right].$$  (6)

Here $a$, $b$, and $c$ are the lattice parameters referred to the orthorhombic $Z = 4$ cell, and $a_0$ is the lattice parameter of the cubic prototype. The spontaneous strain is derived as $e_s = 0.0167$ at ambient conditions, $e_s = 0.0188$ at $P = 4.9$ GPa, and $e_s = 0.0159$ after decompression. The spontaneous strain, and hence the structural distortion of the perovskite, is increased by 11% by increasing the hydrostatic pressure to 4.9 GPa. This observation is quite dif-

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**TABLE 3. Octahedral tilt angles (°) and bond lengths (Å) derived from the structural refinements**

<table>
<thead>
<tr>
<th>Unit</th>
<th>0 GPa (before)</th>
<th>4.9 GPa</th>
<th>0 GPa (after)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta$</td>
<td>14.5(2)</td>
<td>15.9(2)</td>
<td>15.0(1)</td>
</tr>
<tr>
<td>$\psi$</td>
<td>10.9(1)</td>
<td>10.7(1)</td>
<td>9.9(1)</td>
</tr>
<tr>
<td>$\phi$</td>
<td>18.2(1)</td>
<td>19.1(2)</td>
<td>17.8(2)</td>
</tr>
<tr>
<td>$\langle X_B-B-X_B \rangle$</td>
<td>1.983</td>
<td>1.948</td>
<td>1.981</td>
</tr>
</tbody>
</table>
perovskite (Chao et al., 1961; O'Keeffe et al., 1979). The borite is isostructural and isoelectronic to the MgSiO$_3$ perovskite, very much on their crystal structure (Salje, 1989). Neighboring crystals became aligned by twinning during compression. The {110} twinning in particular results in an interchange of the a and b axes between adjacent twin domains (Sapriel, 1975; Toledano and Toledano, 1980). This type of twinning was observed in virtually all the Pbnm perovskites (Wang et al., 1992) and can be produced either by phase transitions or by deformation. The geometry of the cell assembly used has a cylindrical symmetry, and previous studies have shown that the stress field of the sample is such that the principal stress, $\sigma_1$, parallel to the cylinder axis, is different from those perpendicular to the axis (Weidner et al., 1992). Thus, a deviatoric stress ($\sigma_1 - \sigma_2$) is present in the sample, subparallel to the diffraction vector. Under this deviatoric stress, the initially randomly oriented crystals became aligned by twinning during compression. The {110} twinning results in the switching of the a and b axes among the twin domains, giving rise to the observed preferred orientation in the diffraction pattern.

The preferred orientation, once established, cannot be eliminated upon removal of the deviatoric stress by annealing nor can it be removed by releasing the load on the sample, as long as the deviatoric stress level remains low or does not reverse its sign. It can be inverted only through the changing of ferroelastic orientation states (i.e., twinning) by applying a deviatoric stress field in a direction opposite to that which originally created the preferred orientation.

**Possible Implications for the $\alpha_\gamma$ and $\beta_\gamma$ of Silicate Perovskite**

Physical properties of the perovskite materials depend very much on their crystal structure (Salje, 1989). Neighborite is isostructural and isoelectronic to the MgSiO$_3$ perovskite (Chao et al., 1961; O'Keeffe et al., 1979). The comparable ionic radii and the 1:2 electronic charge ratio for ions make neighborite an ideal analogue for silicate perovskite. The weaker bonding strength of the fluoride perovskite allows us to simulate the ultrahigh-pressure and -temperature behaviors of the silicate perovskite at relatively lower pressures and temperatures (O'Keeffe et al., 1979). The structural model of thermal expansion and compression demonstrated in the case of neighborite can also be applied to the MgSiO$_3$ perovskite.

Many experimental data on the compression and thermal expansion of MgSiO$_3$ perovskite have been collected in the past decade (Yagi et al., 1982; Knittle et al., 1986; Knittle and Jeanloz, 1987; Kudoh et al., 1987; Ross and Hazen, 1989, 1990; Wang et al., 1990; Parise et al., 1990; Mao et al., 1991). We can thus derive structural information on octahedral tilting and octahedral bond length from the unit-cell dimensions of MgSiO$_3$ perovskite (Zhao et al., 1993a), assuming regular SiO$_6$ octahedra throughout the perovskite structure. It is found that the response of the crystal structures of MgSiO$_3$ perovskites to pressure is quite different from their response to temperature. Plotted in Figures 3 and 4 are the structural data of tilting angle and bond length as functions of pressure and temperature. It is shown clearly in the diagrams that the compression of the MgSiO$_3$ perovskite structure is mostly...
By applying the structural model (Equations 2 and 3) to the single-crystal elastic compliance data of the MgSiO₃ perovskite (Yeganeh-Haeri et al., 1989), one can also assess the individual contribution of the octahedral bond and octahedral tilting to the overall volumetric compression of the perovskite. This assessment is in good agreement with the high-pressure compressional data; the dominant compressional mechanism for silicate perovskite is the compression of the octahedral Si-O bond length (Zhao et al., 1993c).

**CONCLUSIONS AND IMPLICATIONS**

Defining a complete description of the physical properties of materials as a function of temperature and pressure is indeed an onerous task. If the physical properties depend only on volume, where volume expresses the net effect of the P-T state of the material, then the equation of state is considerably simplified, and there is not such a great need to gather an extensive data base for all materials at varying pressure and temperature. Indeed, the Grünneisen equation of state is based on the assumption that the phonon eigen frequencies depend only on volume. With the data presented in this paper, along with our previous studies of the crystal structure of neighborite, we conclude that this simple picture is invalid for this perovskite. Pressure and temperature have very distinctive effects on the crystal structure. Thus, if one increases pressure and temperature in such a way as to maintain a constant volume, one finds that the octahedra get smaller and the tilt angle is reduced. Since crystal structure is more fundamental than volume in defining physical properties, one would not necessarily expect constant physical properties at a constant volume. Perhaps the most profound manifestation of the phenomenon is the observation that \((\partial a/\partial P)_{V} = 0\) for compression up to 12% of volume. Thus, the Anderson-Grünneisen parameter, \(\delta\), which is generally expected to be about 4, is instead 0. This study of neighborite suggests that we must be careful in estimating the physical properties of MgSiO₃ perovskite at any given conditions.

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