Linear compressibilities of NaNO₂ and NaNO₃

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The linear compressibilities of sodium nitrite and sodium nitrate have been determined from x-ray diffraction of synthetic single crystals mounted in a miniature diamond-anvil high-pressure cell at pressures to 27 kbars. Compressibilities of both compounds are anisotropic; compression perpendicular to rigid N-O bonds is approximately 3.5 times greater than compression within the plane of N-O bonding. In NaNO₂ axial compression ratios are a:b:c=1.0:0.46:0.28. For a second-order Birch-Murnaghan equation of state, $K_0=219\pm2$ kbars and $K'=4.3\pm0.8$. The a:c axial compression ratio of NaNO₃ is 0.35:1.0. Linear compressibilities are in agreement with data of Bridgman, who determined bulk modulus, $K_0=258\pm6$ kbars, and $K'=6.6\pm1.5$. The product of bulk modulus and molar volume (K_0V_0) is a constant for alkali halides with the NaCl structure, and the same value is observed for NaNO₂, which is only slightly distorted from an NaCl arrangement of Na⁺ and NO⁻₂. Sodium nitrate, which does not possess the NaCl topology of Na⁺ and NO⁻₃, deviates from this constant. Broadening of x-ray diffraction maxima of NaNO₂ above 10 kbars may be due to twinning in a high-pressure phase of NaNO₂. Such twinning could indicate reduced symmetry; however, the high-pressure diffraction data indicate a deviation from orthogonality of less than 1°.

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The variation of crystal structures with pressure may provide fundamental information about bonding in solids. Anisotropies in compressibilities, for example, may be closely related to bonding anisotropies, as observed in layer structures. In addition, high-pressure solid-solid phase transitions reveal the relative stabilities of different bonding configurations. The nitrite and nitrate of sodium are compounds in which highly anisotropic compression might be expected because of differences between Na-O and N-O bonding. In addition, several nonquenchable phase transitions at moderate pressures have been reported. The objectives of this study, therefore, are to determine the unit-cell dimensions of NaNO2 and NaNO3 at several pressures, to relate anisotropic cell compression to anisotropies in bonding, and to look for changes in the dimensional symmetry of either phase that might indicate a reversible phase transition at high pressure. Single-crystal x-ray-diffraction experiments using the diamond-anvil high-pressure cell result in increased precision in unit-cell determinations compared with powder methods; thus, this technique is well suited to the problem.

Crystals of synthetic NaNO₂ were kindly provided by Dr. S.K. Sharma. Crystals of NaNO₃ were grown from solution using reagent-grade NaNO₃ powder. Both kinds of crystals were euhedral and colorless. Unit-cell dimensions under room conditions (see Table I) are in agreement with previously published values.² Crystals of sodium nitrite and nitrate were cut to flat plates, approximately $120 \times 120 \times 50$ μ m, and were mounted in gasketed miniature diamond-anvil high-pressure cells³ as modified by Hazen and Finger.⁴ A 4:1 methanol-to-ethanol pressure transmitting fluid was used for NaNO₂. The crystals of NaNO₃ dissolved in this fluid at high pressure, and an index-of-refraction oil (n = 1.540, hydrostatic to 25 kbars) was used for that mate-

TABLE I. Unit-cell dimensions of NaNO2 and NaNO3 at several pressures.

P (kbar)	Crystal No.	Experiment No.	<i>a</i> (Å)	<i>b</i> (Å)	c (Å)	α (*)	<i>β</i> (*)	γ (*)	<i>V</i> (Å ³)
				N	aNO ₂ a				·. · · · ·
0.001	2 .	. 1	3.5665(5)	5.5756(7)	5.3880(8)	90.01(1)	89.95(1)	89.98(1)	107.14(3)
3.3(5)	2	2	3.5361(17)	5.5521(7)	5.3745(17)	90.00(2)	90.00(2)	90.03(2)	105.52(6)
6.8(5)	2	7	3.502(15)	5.531(11)	5.372(11)	89.92(2)	90.1(2)	90.2(2)	104.1(5)
12.6(5)	2	3	3.465(6)	5.501(2)	5.353(6)	90.01(3)	90.00(6)	90.05(6)	102.1(3)
16.3(5)	2	6	3.396(30)	5.481(6)	5.329(14)	90.1(1)	90.8(4)	90.3(3)	99.2(9)
6.4(5)	1	1	3.42(2)	5.48(1)	5.33(2)	89.9(2)	89.2(5)	90.2(3)	99.9(1.0)
2.5(5)	2	5	3.395(20)	5.441(4)	5.336(10)	90.0(1)	90.0(3)	90.0(2)	98.5(6)
22.7(5)	1	2	3.398(20)	5.448(3)	5.330(10)	90.0(1)	90.1(1)	90.0(1)	98.6(6)
27.3(5)	2	4	3.36(3)	5.424(11)	5.31(2)	90.0(2)	90.5(6)	90.2(3)	96.8(1.3)
				· N	aNO ₃ b			-	
0.001	1	1	5.0688(3)	5.0694(3)	16.8151(7)	90.007(5)	89.995(4)	119.996(3)	374.21(3)
10(1)	2	4	5.033(11)	5.038(9)	16.499(6)	89.8(2)	89.9(2)	120.1(1)	362(1)
17.3(5)	2	2	5.012(1)	5.012(1)	16.252(3)	90.00(2)	89.97(2)	120.2(1)	353.5(1)
25.9(5)	2	3	4.988(5)	4.987(4)	15.969(19)	89.95(8)	90.03(9)	120.00(5)	344.0(6)

a) The Im2m setting (z = 2) is used throughout.

b) The hexagonal unit cell (z = 6) is used throughout.

rial. Ruby chips (< 10- μ m diameter) were included in the mount as an internal pressure standard; pressures were calibrated using the shift of the R_1 fluorescence line. Pressures measured before and after each unit-cell determination agreed within reported estimated standard deviations.

Unit-cell dimensions were measured on an automated four-circle diffractometer using the procedure described by Hamilton⁶ as modified by King and Finger.⁷ With this technique errors in diffractometer alignment and crystal centering are removed by measuring reflections in eight different positions. Unit-cell dimensions were calculated from 10 to 20 reflections centered in this manner.

Structure refinements of NaNO2 and NaNO3 at high pressure were unsuccessful because of the poor scattering efficiency of these light atom materials, combined with the restrictions on crystal size in the gasketed diamond cell, and attenuation of the diffracted radiation by diamond and beryllium components of the pressure cell. The maximum pressure available, using crystals of sufficient size for measurement of positions for unit-cell determination, was about 30 kbars. Above that pressure the crystals (50 μ m thick) were crushed between the diamonds. Maximum crystal size is restricted by gasket deformation at high pressure. Although there were too few observed reflections for performing a meaningful structure refinement, complete data sets to 50° 2θ (Mo $K\alpha$ radiation) were collected at several pressures so a search could be made for strong violations of extinction conditions. No such deviations from room-pressure space groups were observed. Use of a monochromated x-ray beam might enhance peak-to-background ratios sufficiently for collection of an adequate data set.

Unit-cell dimensions of the two sodium compounds at several pressures are recorded in Table I. Cell dimensions were refined from reflection positional data with no constraints (i.e., as triclinic) to detect changes in dimensional symmetry. No deviations from orthorhombic dimensions for NaNO₂ or hexagonal dimensions for NaNO₃ were observed within experimental error.

Both compounds display highly anisotropic compression. Sodium nitrite is 3.6 times more compressible along the a axis, which is perpendicular to the plane of NO_2 groups, than along the c axis, which has a major component of N-O bonding and displays an intermediate compressibility. Small but significant curvature is observed in the compression of all three axial directions. Regression analysis of unit-cell data yields the following quadratic equations in P (kbar):

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\Delta a/a = 0.00263(10)P - 0.000021(7)P^2,

\Delta b/b = 0.00122(6)P - 0.000009(3)P^2,

\Delta c/c = 0.00073(7)P - 0.000011(4)P^2.
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The bulk modulus K_0 and its pressure derivative K' were calculated from regression analysis of P-V data in Table I using a second-order Birch-Murnaghan equation of state.⁸ Resultant values are $K_0 = 219 \pm 2$ kbar and $K' = 4.3 \pm 0.8$. Although a second-order transition in NaNO₂ has been reported at ~ 10 kbar,⁹ no change in slope of cell dimensions versus pressure was observed, and all data from 0 to 27 kbars were used to calculate the equation-of-state parameters.

Linear compressibilities, bulk modulus, and K' for sodium nitrate were determined by Bridgman from dimensional changes of single crystals to 12 kbars¹⁰ and compressed powders to 100 kbar,¹¹ and by Barnett et al. on powders to 85 kbars.¹² The data presented in Table I agree within reported errors with Bridgman's values:

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\Delta a/a = 0.000718(6)P - 0.0000037(4)P^2 (this study),

\Delta a/a = 0.00071P - 0.000006P^2 (Bridgman);

\Delta c/c = 0.0025(1)P - 0.000024P^2 (this study-Ref. 13),

\Delta c/c = 0.0024P - 0.000024P^2 (Bridgman).
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Pressure-volume data in this study are similarly consistent with Bridgman's data of 50 years ago, which yield a bulk modulus of 258 kbar and K' = 6.6. In NaNO₃, as in NaNO₂, the direction of maximum compression is perpendicular to the plane of N-O bonding. Note also that the magnitudes of compression along these directions are the same within experimental errors.

Sodium nitrite (orthorhombic, Im2m) and sodium nitrate (rhombohedral, R3c) have been described as distorted NaCl-type arrangements of Na and NO₂ or NO₃ groups.14 Alkali halides with the NaCl structure demonstrate an inverse relationship between molar volume and bulk modulus: $K_0V_0 = 11.3 + 0.5$ (Mbar Å³) as calculated from data in Anderson and Nafe.15 Sodium nitrite $(K_0V_0 = 11.7)$ is consistent with this relationship, whereas NaNO₃ ($K_0V_0 = 16.1$) deviates significantly from the trend. Sodium nitrite, although distorted by the spatial requirements of the NO₂ anionic molecule, is topologically quite similar to NaCl, with each Na+surrounded by an octahedron of NO, and vice versa. Sodium nitrate, on the other hand, is not topologically similar to NaCl in terms of cation-anion coordination groups. These differences in degree of distortion from ideal NaCl structure may explain the observed differences in K_0V_0 compression behavior.

High-pressure phase transitions in NaNO₂ have been observed by several authors and are summarized by Pistorius. At 23 °C and \approx 8 kbars sodium nitrite is reported to undergo a second-order transition to a phase of lower symmetry, on the basis of measurements of low-frequency dielectric constants. Pistorius stated that there are "no marked crystallographic changes at the transition, and the space group of [this phase] can be expected to be a subgroup of Im2m." Adams and Sharma further documented the NaNO₂ transition, on the basis of discontinuities in high-pressure infrared spectra, and reported a transition pressure of 10 kbars at 39 °C. Data of the present study are consistent with these previous interpretations, although no direct evidence for a transition can be offered.

At room pressure both crystals of NaNO₂ had sharp diffraction maxima, but at pressures above 10 kbars maxima became significantly broader. This broadening is reflected in Table I by the larger errors in unit-cell dimensions determined after the pressure was raised above the supposed transition. For example, crystal No. 2 yielded excellent cell constants at room pressure and 3.3 kbars, with volume errors of 1 part in 2000. After the pressure was raised to 12.6 kbars,

volume errors were 1 part in 300 or greater using the same set of reflections for unit-cell measurements. This observed peak broadening at high pressure may be due to twinning of a pseudo-orthorhombic, but monoclinic in detail, high-pressure phase. Such twinning is ubiquitous in high-pressure second-order transitions. 18 The fact that the peaks appear broad, but not split, at 27 kbars indicates that deviations from orthogonality are less than 1° in this high-pressure form.

Sodium nitrate is known to transform at 23 °C and 50 kbars from $R\bar{3}c$ to $R\bar{3}c$ symmetry. 12 No other transitions at lower pressure have been documented, nor were any observed in this study.

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$$\times \{1 - (3/4)(4 - K_0')[(V_0/V)^{2/3} - 1]\}.$$

Note that the error in bulk modulus derived from this equation ($\pm 1\%$) is significantly smaller than the errors in $\Delta a/a$ and $\Delta c/c$ using second-order polynomials.

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