The High-Pressure Behavior of NaClO₃

H. Sowa

*Institut für Mineralogie, Petrologie und Kristallographie der Philipps-Universität Marburg, Hans-Meerwein-Strasse,
D-35032 Marburg, Germany*

At high pressures $NaClO_3$ undergoes two phase transitions, one below 2 GPa ($NaClO_3$ II) and the other below 4 GPa ($NaClO_3$ III). Both transformations proceed very slowly, making it possible to study the high-pressure behavior of the low-pressure phase I up to 5.30(7) GPa on powders and up to 3.81(7) GPa on single crystals with X-ray diffraction. $NaClO_3$ I is highly compressible. The cubic lattice parameter a decreases from 6.5718(3) to 6.290(1) Å at 5.30 GPa. While the ClO_3 groups remain nearly unchanged, the volume of the NaO_6 octahedra is distinctly reduced. Both phase transitions could be identified optically. $NaClO_3$ III shows a structural relationship to $NaClO_3$ I, but the structures of both high-pressure phases are unknown. © 1995 Academic Press, Inc.

INTRODUCTION

The crystal structure of $NaClO_3$ has been determined on single crystals by several groups, most recently by Burke-Laing and Trueblood (1) and Abrahams and Bernstein (2). Under ambient conditions $NaClO_3$ crystallizes in the cubic space group $P2_13$. The Na atoms occupy slightly distorted octahedra while ClO_3 groups are of pyramidal shape.

Bridgman has already found that at room temperature there are two pressure-induced phase transitions at about 1.6 GPa and at about 3.6 GPa (3). He described both phase transitions as sluggish. The different phases are named $NaClO_3$ I, $NaClO_3$ II, and $NaClO_3$ III, respectively. Vijaya *et al.* (4) observed that the phase transition from $NaClO_3$ I to $NaClO_3$ II is accompanied by a change in the pressure dependence of chlorine nuclear quadrupole resonance frequency. The transition pressure of 1.1 GPa was more precisely determined than in Bridgman's studies (3). High-pressure Raman investigations were done by Ganguly *et al.* (5) and by Adams *et al.* (6). Both groups observed a phase transition at about 3.6 GPa but they could not detect a transition at 1.1 or 1.6 GPa. Fransson and Ross (7) investigated the thermal conductivity and the specific heat capacity of $NaClO_3$ in the temperature range 100–300 K up to 2 GPa. They also found no evidence for a phase transition from $NaClO_3$ I to $NaClO_3$ II.

The purpose of this work was to investigate the structural behavior of $NaClO_3$ at high pressure.

EXPERIMENTAL

Specimen

Sodium chlorate 99+% was obtained from Aldrich-Chemie, Germany. The sample contained clear tetrahedral-shaped crystals of different sizes from which plate-like fragments were broken for single-crystal investigations. For powder diffraction measurements very fine ground powder was produced.

Measurements on Powders

For the powder diffraction studies a lever-arm diamond-anvil cell very similar to the NBS cell (8) was used. Due to the low scattering power of $NaClO_3$, a very thick stainless steel gasket (400 μm) which was preindented to 350 μm was employed. The diameter of the hole was 300 μm. Isopropanol and a 4 : 1 mixture of methanol : ethanol were used as the pressure transmitting media (9). Pressure was determined by the ruby fluorescence technique (10). The estimated error in pressure was ±0.07 GPa. The X-ray experiments were carried out with monochromatized $MoK\alpha_1$ radiation ($\lambda = 0.7093$ Å) or $MoK\beta$ radiation ($\lambda = 0.6323$ Å) in a Debye–Scherrer film technique.

No phase transition could be detected in a first run and therefore unit cell parameters of the low-pressure phase $NaClO_3$ I could be obtained up to 5.30 GPa. The lattice parameter a decreased continuously. A Debye–Scherrer photograph which was taken after the sample had been compressed for one week showed no phase transition.

Therefore $NaClO_3$ was observed between the diamond anvils under nonhydrostatic conditions using an ungasketed sample. For this purpose the powder sample was mixed with nickel dimethyglioxime as a pressure indicator. The color of this compound changes with increasing pressure (11). After one day in the center of the diamond anvils a coarse-grained high-pressure phase could be observed. From the color of the pressure indicator it could be concluded that this was the high-pressure phase

TABLE 1
Interplanar Spacings in NaClO₃ III at 4.28 GPa Compared with Those in NaClO I at 4.31 GPa

	NaClO₃ I at 4.31 GPA		NaClO₃ III at 4.28 GPa	
hkl	d(Å)	Intensity[a]	d(Å)	Intensity[a]
			6.294	vw
110	4.477	m	4.482	s
			3.988	m
			3.851	vw
111	3.657	m	3.654	m
200	3.167	s	3.169	s
			3.068	m
210	2.835	vs	2.835	vs
			2.768	w
211	2.586	s	2.582	s
			2.473	vw
			2.354	vw
311	1.909	m	1.914	vw
321	1.693	s	1.693	s

[a] vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

NaClO₃ III which is stable above 3.6 GPa. The examination under a polarizing light microscope showed that the crystals were optically anisotropic. After about two weeks the second phase transition observed by Bridgman (3) and Vijaya et al. (4) could be detected. The refractive indices of NaClO₃ I and NaClO₃ II are very similar.

Subsequently, powder diffraction studies were performed again. A pressure of 5.55 GPa was applied and

after three weeks an X-ray photograph showed diffraction lines belonging to NaClO₃ III. Table 1 gives the interplanar spacings of NaClO₃ III at 4.28 GPa compared with those of NaClO₃ I at nearly the same pressure. Upon release of pressure metastable NaClO₃ III could be maintained at 1.68 GPa. Again the phase transition proceeded slowly within four days. The first photograph taken after two days indicated that NaClO₃ III still existed, while the second one taken after two further days showed only the diffraction pattern of NaClO₃ I. The X-ray powder photographs gave no evidence of NaClO₃ II.

Single Crystal Investigations

Due to the fact that NaClO₃ I can be preserved metastable up to high pressures, it should be possible to perform single-crystal investigations even in the range of metastable NaClO₃ I.

Data Collections

X-ray data collections were carried out on an automated STOE four-circle diffractometer using monochromatized MoKα radiation (λ = 0.7107 Å).

Diffraction data of a NaClO₃ single crystal with the approximate dimensions of 120 × 150 × 50 μm³ were first collected outside the diamond-anvil cell at ambient conditions. The Ω-scan technique and the fixed-Φ mode (12) were used, and only those reflections that could be measured inside the pressure cell were collected. In order to find systematic errors caused by the pressure cell, room-pressure data of the same crystal were also collected within the diamond-anvil cell.

TABLE 2
Details of Data Collections and Final R Values

Pressure (GPa)	0.0001	0.0001[a]	1.11	2.46	3.81
$2\theta_{max}$ (°)	50	50	51	51.5	52
Step width (°)	0.01	0.01	0.01	0.02	0.02
Scan width (°)	1.0	1.0	1.0	1.6	1.6
Counting time per step (sec)	2	6	4	4	4
No. of reflections	782	791	791	782	781
No. of used reflections	782	791	771	770	767
No. of independent reflections (all)	168	168	172	172	172
With $F > 3\sigma(F)$	151	109	131	126	132
R_{int} (%)	2.83	6.10	4.08	3.64	4.50
R (all refl.) (%)	5.89	7.31	6.94	5.83	5.81
R $(F > 3\sigma(F))$ (%)	5.20	4.12	4.70	3.59	3.81
R_w (%)	2.39	2.10	2.01	2.05	2.03

[a] Crystal inside the presure cell.

The high-pressure investigations were carried out in a Merrill–Bassett-type high-pressure cell (13). The crystal was fixed with vaseline onto one of the diamond anvils. An Inconel 718 type gasket with a thickness of 250 μm preindented to 95 μm was employed. The 300 μm hole was obtained by spark erosion (14). It was intended that a 4:1 mixture of methanol:ethanol would be used as the pressure transmitting liquid, but the solubility of the crystal was too high. Therefore another crystal with a size of 135 × 135 × 65 μm³ was used and isopropanol was chosen as the pressure medium (9). A ruby splinter was inserted for the pressure calibration (10). Centering of the sample was done in a first step by bringing the center of the gasket hole into the center of the diffractometer. Therefore, a 2θ scan of the primary beam was done at $\Omega = \pm 30°$. In a second step, the high-pressure cell was shifted parallel to its axis corresponding to the thickness of the gasket and the crystal.

Unit cell parameters were obtained at various pressures. At each pressure 18 to 20 reflections with $15° \le 2\theta \le 32°$ were centered at eight equivalent positions, following the method of King and Finger (15). For the crystal inside the pressure cell at ambient conditions only 12 reflections could be used, because the intensities were too low. Unit cell refinements performed without constraints lead to unit cell angles α, β, and γ of 90° and equal cell parameters $a = b = c$ within two estimated standard deviations. The cell parameters given in Table 3 were determined by the vectors–least-squares method with constraints (16).

To keep the background generated by the beryllium parts of the high-pressure cell low, an edge-formed collimator in front of the counter as described by Ahsbahs (17) was used. At room pressure, intensities of all accessible reflections up to $2\theta = 50°$ were collected. In order to always get the same number of reflections, the 2θ range was extended gradually to 52° at 3.81 GPa. Details of data collections are summarized in Table 2.

Bridgman (3) and Vijaya et al. (4) reported that the phase transition from $NaClO_3$ I to $NaClO_3$ II is accompanied by a very small volume change. Therefore it was suggested that $NaClO_3$ II possibly also has cubic symmetry. A subgroup of $P2_13$ is $P2_13$ with the triple lattice parameter a. To prove whether or not such a phase transition took place, at 1.53 and 2.33 GPa precession photographs ($\mu = 12°$) using monochromatized Mo$K\alpha$ radiation were taken perpendicular to [102]. Even after an exposure time of five days no reflections of a superstructure could be observed.

TABLE 3

Unit Cell Parameters and Atomic Parameters of $NaClO_3$ at Various Pressures (GPa)

Pressure	0.0001	0.0001[a]	1.11	2.46	3.81
a(Å)	6.5718(3)	6.5693(5)	6.4858(7)	6.4128(6)	6.3403(6)
V(Å³)	283.78(7)	283.36(6)	272.62(8)	263.59(8)	254.75(7)
Na x	.069(1)	.069(1)	.069(1)	.070(1)	.071(1)
U(Å²)	.025(1)	.026(1)	.022(1)	.019(1)	.019(1)
Cl x	.4179(7)	.4180(8)	.4165(7)	.4147(6)	.4137(6)
U(Å²)	.0197(7)	.0198(8)	.0158(8)	.0146(7)	.0144(7)
O x	.3033(5)	.3043(5)	.3012(5)	.2990(5)	.2962(5)
y	.5931(6)	.5917(7)	.5927(7)	.5933(6)	.5949(6)
z	.5048(6)	.5054(7)	.5051(6)	.5041(6)	.5045(6)
U(Å²)	.029(1)	.030(1)	.025(1)	.022(1)	.021(1)
g	.24(7)10⁻⁴	.22(7)10⁻⁴	.30(6)10⁻⁴	.24(6)10⁻⁴	.33(7)10⁻⁴

[a] Crystal inside the pressure cell.

Note. In addition, the following unit cell parameters were determined (numbers in parentheses represent e.s.d.'s):

P(GPa)	1.53	3.19
a(Å)	6.4559(7)	6.3678(6)
V(Å³)	268.94(8)	258.07(7)

TABLE 4

Bond Distances (Å) and Angles (°) of NaClO₃ at Various Pressures (GPa)

Pressure	0.0001	0.0001[a]	1.11	2.46	3.81
NaO₆ octahedron					
Na–O	2.412(5)	2.417(6)	2.383(6)	2.352(5)	2.317(6)
	2.498(5)	2.494(6)	2.456(6)	2.418(6)	2.381(6)
O–O	3.880(5)	3.888(6)	3.832(6)	3.785(5)	3.731(5)
	3.322(5)	3.321(6)	3.259(6)	3.212(5)	3.161(5)
	3.453(5)	3.463(6)	3.401(6)	3.339(5)	3.289(5)
	3.233(5)	3.244(6)	3.196(6)	3.161(5)	3.109(5)
O–Na–O	104.4(2)	104.4(2)	104.7(2)	104.9(2)	105.0(2)
	84.2(2)	84.3(2)	84.2(2)	84.4(2)	84.3(2)
	89.3(2)	89.4(2)	89.3(2)	88.8(2)	88.9(2)
	83.4(2)	83.1(2)	83.1(2)	83.3(2)	83.2(2)
ClO₃ group					
Cl–O	1.491(5)	1.480(5)	1.482(5)	1.481(5)	1.486(5)
	3.077(5)	3.079(5)	3.019(5)	2.973(5)	2.920(5)
O–O	2.392(5)	2.373(6)	2.377(6)	2.373(5)	2.381(5)
O–Cl–O	106.7(3)	106.6(3)	106.6(3)	106.5(3)	106.5(3)
Na–Cl	3.350(5)	3.350(5)	3.305(5)	3.267(5)	3.232(5)
	3.518(5)	3.515(5)	3.480(5)	3.451(5)	3.416(5)

[a] Crystal inside the pressure cell.

Note. Parenthesized figures represent e.s.d.'s.

Data Reduction

All reflections which overlap with reflections of the diamonds or the ruby crystal were omitted. Also, reflections coinciding with steel powder rings generated by the gasket were removed. The intensities measured from the sample inside the pressure cell were corrected with respect to the absorption of the incident and diffracted X-ray beams in the diamond anvils and the beryllium parts of the cell. Finally, corrections for the Lorentz and polarization effects were applied.

Structure Refinements

For the structure refinements the program AKUT8602 (18) was used. Reflections with $I < 3\sigma(I)$ were considered unobserved. The weighting scheme was $w = 1/(F) + 0.0001F^2)$. Atomic form factors for neutral atoms were taken from the International Tables for X-Ray Crystallography (19).

The oxygen atoms occupy positions 12(b) x, y, z. The Na and Cl atoms lie on positions 4(a) x, x, x, with $x \approx 0.069$ and $x \approx 0.418$, respectively. The arrangement of the

oxygen atoms corresponds to a deformed configuration of the cubic invariant lattice complex S (20). At ambient conditions the positional parameters refined from the data collected without a high-pressure cell are in good agreement with the literature data (1, 2); the thermal displacement factors were slightly higher. Due to the lower precision of the anisotropic thermal parameters refined from the data collected at high pressure, only the isotropic parameters are reported here. The parameters refined from the data measured at ambient conditions in the high-pressure cell deviate only slightly from those measured without a pressure cell.

Final R values are given in Table 2. The results of the refinements are summarized in Table 3.

Precession Photographs and Optical Investigations

In spite of the fact that isopropanol solidifies at about 4 GPa (9), a pressure of 4.6 GPa was applied. Precession photographs were taken perpendicular to [102], [103], and [001] showing additional weak spots in $hk\frac{1}{3}$, $hk\frac{1}{2}$, and $hk\frac{2}{3}$.

Observation of the crystal under a polarizing light mi-

croscope showed that the whole crystal was not transformed into the high-pressure phase, yet more than 90% of it was. The rest behaved optically isotropic. On release of pressure the amount of the high-pressure phase III did not change up to 1.92 GPa. At 1.65 GPa, 50% of $NaClO_3$ III were transformed. The intensity of the additional spots on the precession photographs decreased distinctly. On further decompression three sets of parallel lines could be observed that made the position of the original threefold axis visible. At 1.09 GPa about 25% $NaClO_3$ III still existed. Further decompression was employed until the high-pressure phase disappeared. After that the pressure was slightly increased to 0.75 GPa. The crystal now behaved optically isotropic and no superstructure reflections could be detected.

RESULTS AND DISCUSSION

The low-pressure phase of $NaClO_3$ is highly compressible. The altering lattice parameter a can be expressed by

$$a = 6.564(2) - 0.076(2)P + 0.0047(4)P^2,$$

with a in Å and P in GPa.

The bulk modulus of $NaClO_3$ I is $K = 22.8(7)$ GPa (Birch–Murnaghan equation of state with $K' = 9.3(7)$).

As can be seen by the selected atomic distances and bond angles given in Table 4, the volume of a NaO_6 octahedron is reduced by about 13%. The polyhedral bulk modulus for a NaO_6 octahedron is $K_p = 28$ GPa. It is mainly the polyhedral compression of the NaO_6 octahedra that is responsible for the bulk compression. Bond angles remain nearly unchanged. Also, no changes could be found concerning the ClO_3 group.

From the precession photographs and the results of the powder diffraction measurements it is obvious that the crystal structures of $NaClO_3$ I and $NaClO_3$ III are closely related. The additional reflections indicate an enlargement of the unit cell in only one direction with $c' = 6c$. Due to the splitting of modes in the Raman spectra, Ganguly et al. (5) suggested that $NaClO_3$ III may have tetragonal symmetry. This can be excluded because there is no tetragonal subgroup of $P2_13$. From the inspection of the diffraction pattern on the precession photographs it could be concluded that the highest possible symmetry is $P2_1$. Possibly only the metric of the unit cell is tetragonal, while the crystal structure has lower symmetry.

The phase transition from $NaClO_3$ I to $NaClO_3$ III may possibly be accelerated by shear stress due to nonhydro-

static pressure effects: Using isopropanol as the pressure transmitting medium which solidifies at about 4 GPa, the first additional powder lines could be observed after one week at a pressure of 5.5 GPa. The use of a highly ductile gasket made from rhenium metal caused the phase transition to occur after only three days.

Although the phase transition from $NaClO_3$ I to $NaClO_3$ II could clearly be seen optically on powders under nonhydrostatic conditions, X-ray powder and single-crystal experiments gave no evidence of this phase.

Further investigations are necessary to determine the crystal structures of the high-pressure phases and the conditions of the phase transformation from $NaClO_3$ I to $NaClO_3$ II.

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