

Single-Crystal High-Pressure Studies of Na₃ScF₆

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The crystal structure of Na₃ScF₆ was investigated by high-pressure single-crystal X-ray diffraction techniques in the range from ambient conditions to 68.2 kbar. Pressure was measured by the ruby fluorescence method. The single-crystal structure determination at 27.9 kbar resulted in the cell parameters $a = 5.484(1)$ Å, $b = 5.732(1)$ Å, $c = 7.948(2)$ Å, and $\beta = 90.96(3)^\circ$ and the same space group symmetry, $P2_1/n$ ($Z = 2$), as at ambient conditions. The 19 structural parameters needed to describe a model with isotropic displacement parameters were refined by least-squares techniques. For the 143 most significant observed unique reflection amplitudes, the R value became 0.047. When the pressure was increased from ambient to 27.9 kbar, the change in the geometry and the relative change in the volume of the coordination polyhedron around the six-coordinated Sc³⁺ ion were negligible. Significant changes of the coordination volumes around the Na⁺ ions were observed. The volume decreases for the six-coordinated and the eight-coordinated Na⁺ ions were similar, viz., 7 and 8%. The layered stacking of the larger, low-charged F⁻ and Na⁺ ions along [103] offers an explanation for the pattern which determines the changes of the unit cell parameters with pressure. The relative change in unit cell volume versus pressure in the range from ambient to 68.2 kbar was fit to the Birch type equation of state. The isothermal bulk modulus at ambient pressure and its pressure derivative were determined to be $B_0 = 46.0(7)$ GPa and $B'_0 = 3.3(2)$, respectively. © 1998 Academic Press

Key Words: high pressure; single crystal; sodium scandium fluoride.

INTRODUCTION

The structure of Na₃ScF₆ is isotopic with that of cryolite, Na₃AlF₆, with two symmetry-independent Na⁺ positions. If only one of these Na⁺ positions is considered, a perovskite-type pattern of alternating ScF₆³⁻ (or AlF₆³⁻) and NaF₆⁵⁻ octahedra sharing corners results (see Fig. 1). The high-symmetry version of this structure type is that adopted by the elpasolites, e.g., K₂NaAlF₆. The present investigation of Na₃ScF₆ was performed to compare its structural features

at different pressures with those observed for Na₃MnF₆. The octahedral coordination around the d^4 ion in the manganese(III) compound is considerably Jahn–Teller distorted. Any effects induced by varying the pressure can be expected to be more normal for Na₃ScF₆ than for Na₃MnF₆, which exhibits *inter alia* a phase transition at elevated pressures (1). The latter is likely to be due to a spatial change of the uneven electron distribution around the Mn³⁺ ions. A short presentation of these results was given at the XVIIth IUCr international crystallography conference in Seattle, August 1996 (2).

The structure of Na₃ScF₆ at ambient conditions was reported by Dahlke and Babel in 1994 (3) and more recently by Bohnsack and Meyer in 1996 (4). A complete structural analysis of Na₃ScF₆ at ambient conditions has been performed, also by the present authors, to fully secure *inter alia* the quality and the representability of the synthesized crystals. Our results are fully consistent with those obtained by Dahlke and Babel and will therefore not be further considered.

EXPERIMENTAL

Synthesis

Stoichiometric mixtures of water-free NaF and ScF₃ were ground and mixed in a glovebox and put into a gold ampule. The ampule was sealed (welded) under an Ar atmosphere and inserted into a stainless steel bomb. This bomb was filled with water, heated to 500°C at an external pressure of 2.5 kbar, and kept under these conditions for 24 h. The synthetic product, containing white transparent crystals, was investigated by Guinier X-ray powder techniques. The powder diffraction pattern was consistent with that calculated from the results of the single-crystal investigation by Dahlke and Babel (3). Single-crystal photographic techniques (oscillation, de Jong, and precession methods) were utilized to find single crystals suitable for the subsequent high-pressure studies.

High-Pressure X-Ray Investigations.

The high-pressure investigations were performed using a Merrill–Bassett type diamond anvil cell (DAC) with

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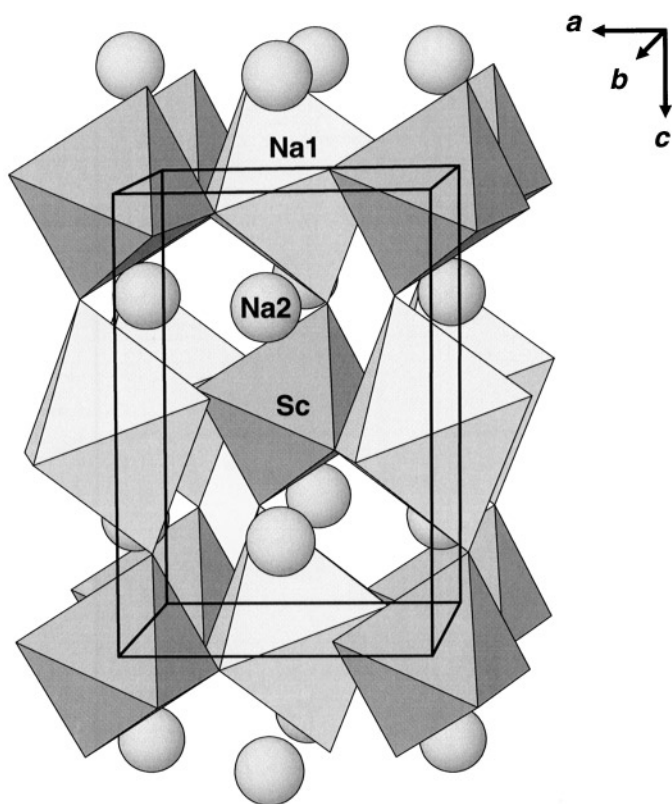


FIG. 1. Diagram of the Na₃ScF₆ structure viewed roughly along [010]. Dark octahedra represent the fluoride coordination polyhedra around the scandium atoms, light octahedra indicate the coordination polyhedra around Na1, and Na2 atoms are shown as spheres.

diamond culet diameters of 600 μm (Diacell Products; Type DXR-5). Preindented stainless steel gaskets (SS 142331-44, 400 μm thick) with mechanically drilled gasket hole diameters of 300 μm were used. A mixture of methanol: ethanol: water (16:3:1) was used as the pressure-transmitting medium.

The high-pressure single-crystal X-ray intensity data were collected with a four-circle diffractometer (Siemens P4/RA), using graphite-monochromatized MoK α radiation ($\lambda = 0.71073\text{\AA}$). The rotating-anode generator was operated at 5.0 kW (50 kV and 100 mA) for a filament size of 0.3×3 mm and a collimator with the diameter $\phi_i = 350\ \mu\text{m}$. Single-crystal X-ray diffraction data collection was performed with ω - 2θ scans for those reflections with $2\theta < 80^\circ$, expected to allow transmission of the incident and scattered radiation through the DAC. The azimuthal angles (ψ values) used were those that would minimize the absorption and shadowing of the beams by the DAC. To achieve this, computer programs (5) have been developed that generate optimal setting angles ($\omega_\psi, \theta_\psi, \varphi_\psi, \chi_\psi$) of all possible reflections directly from the orientation matrix of the crystal. To partially overcome limitations imposed by the Siemens dif-

fractometer software (viz., XSCANS), single-point “ Ψ data collections” had to be made for the angular settings at the best $\Psi = 0^\circ$ value, modulo 30° . The diffraction data were corrected for background, Lorenz, polarization, and absorption effects.

Pressure calibration was performed using the ruby R_1 fluorescence method (6). A small ruby crystal (about 20 μm), placed close to the single crystal in the pressure cell, was irradiated with a laser beam (Ar ion laser, 488 nm). The fluorescent light from the ruby was collected with a spectrograph (Oriel Multispec) equipped with a 1024 diode array detector. The observed wavelength shift ($\Delta\lambda$) of the R_1 fluorescence line was then used to calculate the pressure from the linear equation $P = 2.740\Delta\lambda$ (7). The estimated standard deviation of the readout of the wavelength shift is 0.1 \AA , and the estimated error of 0.016 kbar \AA^{-1} in the proportionality constant (2.740) was considered when the e.s.d.’s (σ ’s) for the different pressures were calculated. Pressure determination was performed both before and after the diffraction experiments to secure that pressure changes during periods of data collection were negligible.

The unit cell parameters of the crystals used for the high-pressure experiments, determined by single-crystal diffraction techniques at ambient pressure, were within 3σ from those reported by Dahlke and Babel (3). To ensure the quality of these single crystals, a structure determination was performed also at ambient conditions. As mentioned earlier, the results did not deviate significantly from those determined by Dahlke and Babel. Therefore, the published structure determination was used as the reference (3).

With the calculated (cf. earlier) best setting angles, the intensities of 787 reflections could be collected at 27.9 kbar. Of these, 144 were unique and had observable ($I > 5\sigma_I$) intensities. The structural model of Dahlke and Babel (3) was refined with these 144 reflections to an R value 0.047 ($wR = 0.055$). To keep the number of parameters used sufficiently low (19) when refining the high-pressure structural model, only isotropic displacement parameters for the atoms were allowed. The isotropic displacement parameters agree well (within 2σ) with the displacement parameters previously determined at ambient pressure. Absorption correction was performed for the single crystal but neglected for the DAC, which possibly might affect the relevance of the displacement parameters.

Compressibility data of the unit cell dimensions versus pressure are given in Table 1, and the relative changes in the unit cell dimensions are shown in Fig. 2. Experimental details for the high-pressure structure determination are given in Table 2, and the resulting fractional coordinates and isotropic thermal parameters are listed in Table 3. All structure refinements were made using the SHELXTL PCTM software package (8). Atomic scattering factors for neutral atoms from the “International Tables for X-Ray Crystallography” (9) were used. Selected bonding distances, angles

TABLE 1
Pressure Dependence of Unit Cell Dimensions of Na_3ScF_6

P (kbar)	a (Å)	b (Å)	c (Å)	β (deg)	V (Å ³)
0.0(3)	5.607(2)	5.816(6)	8.133(4)	90.72(3)	265.2(2)
0.1(3)	5.612(2)	5.821(5)	8.132(2)	90.67(3)	265.6(2)
6.6(3)	5.582(2)	5.799(6)	8.088(2)	90.79(2)	261.8(2)
11.8(3)	5.560(1)	5.783(1)	8.054(2)	90.78(2)	258.93(10)
18.9(3)	5.527(2)	5.763(2)	8.008(2)	90.85(2)	255.05(19)
22.7(3)	5.512(1)	5.755(2)	7.986(2)	90.91(2)	253.32(15)
30.4(3)	5.482(2)	5.737(2)	7.948(2)	90.99(2)	249.64(18)
35.9(3)	5.460(1)	5.724(1)	7.910(1)	91.04(1)	247.16(8)
41.1(4)	5.441(1)	5.711(1)	7.886(1)	91.09(2)	245.00(6)
47.1(4)	5.423(1)	5.703(1)	7.861(1)	91.15(2)	243.05(9)
54.5(4)	5.391(1)	5.687(1)	7.822(1)	91.24(1)	239.75(5)
62.2(5)	5.364(1)	5.678(1)	7.788(1)	91.38(2)	237.14(8)
68.2(5)	5.332(4)	5.673(4)	7.760(5)	91.81(9)	234.6(3)

and polyhedron volumes, calculated with the programs PLATON (10) and VOLCAL (11), are listed in Tables 4 and 5. Packing diagrams of the Na_3ScF_6 structure were obtained by the program ATOMS (12).

DISCUSSION

The cryolite-type structure of Na_3ScF_6 has one scandium position, two sodium positions, and three fluorine positions that are symmetry independent in the unit cell (cf. Table 3). The scandium atom is coordinated by six fluorine atoms in a rather ideal octahedral coordination, with bond distances of 2.00–2.01 Å (Table 4). The bond angles deviate by less than 1.8° from 90°. The coordination around Sc^{3+} is largely

TABLE 2
Experimental Details of the High-Pressure Na_3ScF_6 Structure Determination at 27.9 kbar

Pressure	27.9 kbar
Formula	Na_3ScF_6
Formula weight	227.92
Space group symmetry	$P2_1/n$ (No. 14)
Formula units per unit cell, Z	2
Unit cell dimensions	$a = 5.484(1)$ Å $b = 5.732(1)$ Å $c = 7.948(2)$ Å $\beta = 90.96(3)^\circ$
Unit cell volume, V	249.80(10) Å ³
Density (calcd), d_x	3.030(1) g · cm ⁻³
Radiation (rotating anode)	MoK α
Wavelength, λ	0.71073 Å
Temperature, T	293 K
Intensity data collection	ω - 2θ scan
Max of $\sin(\theta)/\lambda$	0.88 Å ⁻¹
Internal R	0.085
Collected reflections	787
Unique reflections	246
Observed reflections	144
Criterion for significance	$F_o \geq 5\sigma_F$
Absorption correction	Numerical integration for the crystal
Crystal size	80 × 80 × 75 μm ³
Linear absorption coefficient	1.77 mm ⁻¹
Transmission factor range	0.77–0.80
Structure refinement	Full-matrix least squares
Minimized function	$\sum w(\Delta F)^2$
Displacement parameters	Isotropic for all atoms
Number of refined parameters	19
Weighting scheme	$(\sigma_F^2 + 0.0005F^2)^{-1}$
R for observed reflections	0.047
wR for observed reflections	0.055
Max of $ \Delta /\sigma$	< 0.001

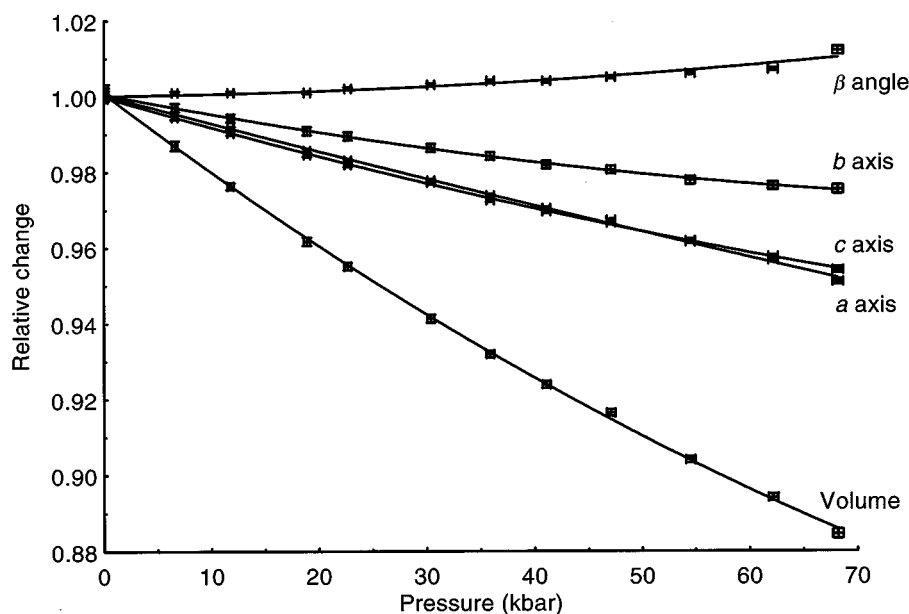


FIG. 2. Relative change in unit cell parameters of Na_3ScF_6 . Error bars indicate two estimated standard deviations.

TABLE 3
Fractional Atomic Coordinates and Isotropic Thermal Parameters (Å²) with Estimated Uncertainties in Parentheses for the Na₃ScF₆ Structure at 27.9 kbar

Atom	x	y	z	U_{iso}
Sc	0.00000	0.00000	0.00000	0.0114(5)
Na1	0.00000	0.00000	0.50000	0.0172(11)
Na2	0.5158(18)	-0.0595(6)	0.2443(6)	0.0237(9)
F1	0.126(3)	0.0627(8)	0.2349(7)	0.0182(12)
F2	-0.300(3)	0.1788(9)	0.0575(8)	0.0233(15)
F3	0.168(3)	0.2915(9)	-0.0753(9)	0.0245(13)

unaffected by increasing the pressure up to 27.9 kbar. The sodium six-coordinated atom (Na1) has bond distances ranging from 2.23 to 2.34 Å at ambient pressure and from 2.19 to 2.26 Å at 27.9 kbar. The octahedra around Sc and Na form a puckered perovskite arrangement (see Fig. 1). The other sodium atom (Na2) is coordinated by four fluorine atoms at ≤ 2.3 Å in the form of a distorted tetrahedron. If distances up to 2.8 Å are included, the seven fluorines form a monocapped trigonal prism. If even a more distant (about 3.0 Å) fluorine is taken into account, the eight-coordination becomes that of a bicapped trigonal prism. The average decreases in the Na–F bond distances

TABLE 4
Selected Distances (Å) and Angles (Deg) in the Na₃ScF₆ Structure at Ambient Conditions (3) and 27.9 kbar^a

Atoms	Multiplicity	Pressure (kbar)	
		Ambient	27.9
Sc–F1	2	2.013(1)	2.012(8)
–F2	2	1.998(1)	1.998(14)
–F3	2	2.010(1)	2.004(9)
Na1–F1	2	2.335(1)	2.257(7)
–F2	2	2.234(1)	2.187(9)
–F3	2	2.305(1)	2.251(14)
Na2–F1b	1	2.298(1)	2.249(19)
–F3a	1	2.297(1)	2.252(10)
–F2b	1	2.313(1)	2.267(11)
–F1	1	2.356(1)	2.308(8)
–F3c	1	2.632(1)	2.581(14)
–F2	1	2.754(1)	2.661(13)
–F2c	1	2.782(1)	2.743(11)
–F3	1	3.036(1)	2.959(10)
F1–Sc–F2	2	88.55(4)	88.1(5)
F1–Sc–F2a	2	91.45(4)	91.9(5)
F1–Sc–F3	2	88.38(4)	88.6(3)
F1–Sc–F3a	2	91.62(4)	91.4(3)
F2–Sc–F3	2	91.81(4)	91.4(5)
F2–Sc–F3a	2	88.19(4)	88.6(5)

^a The crystallographic symmetry codes are as follows: (a) $-x, -y, -z$; (b) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (c) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.

TABLE 5
Polyhedron Volumes (Å³) and the Relative Change in Volume When the Pressure Is Raised from Ambient Conditions to 27.9 kbar

Polyhedron around	Coordination	Ambient pressure	27.9 kbar	Relative change
Sc	6	10.766(7)	10.91(3)	1.01
Na1	6	15.864(9)	14.70(4)	0.93
Na2	7	20.56(2)	18.83(5)	0.92

when the pressure is increased from ambient to 27.9 kbar are 2.6 and 2.1%, respectively. The relative changes in the volumes (Table 5) of the coordination polyhedra are 1.01, 0.93, and 0.92 for Sc, Na1, and Na2, respectively.

Calculated bond valence sums (bvs) for the structure at 27.9 kbar, using the empirical parameters from Brown and Altermatt (13) and Brese and O’Keeffe (14), agree well with the expected formal charges of the individual atoms. For the Sc³⁺ ion the estimate is 3.1. The bvs values of Na1 and Na2 are 1.3 and 1.0, respectively. The three symmetry-independent fluorine atoms F1, F2, and F3 yield bvs values of 1.1, 1.1, and 1.0, respectively (1.0, 1.0, and 1.0 at ambient conditions). The slight rise of the estimated bvs is of course in accordance with the increasing pressure.

From Fig. 2, it can be seen that the change in unit cell parameters shows a smooth behavior from ambient pressure to 68.2 kbar. At about 70 kbar the single crystal was crushed, probably by direct contact with the diamond surfaces and not by any dramatic change in the structure. The observed relative change in unit cell volume versus pressure was fit to the Birch type equation of state (15),

$$P = \frac{3}{2} B_0 (x^{-7/3} - x^{-5/3}) (1 - \frac{3}{4} (4 - B'_0) (x^{-2/3} - 1)),$$

where x is the relative volume V/V_0 and P is the pressure. The isothermal bulk modulus at ambient pressure, B_0 , and its derivative with respect to pressure, B'_0 were determined to be 46.0(7) GPa and 3.3(2), respectively. The fact that the compressibility data are well fitted (see Fig. 3) to the Birch equation further confirms that the structure does not undergo any phase transition in the studied pressure range.

The unit cell changes are expected as being predominantly due to features of the packing of the larger, low-charged F⁻ and Na⁺ ions. In Fig. 4 a projection along [010] of these ions is shown, which form layers stacked along $[10\bar{3}]$. The compressibility can be anticipated to be lower in the less densely packed stacking direction. Thus, one would expect that the unit cell parameter changes would be largest for the c axis, smaller for the a axis, and even much smaller for the b axis. If one compares the absolute changes between ambient and 68.2 kbar, the unit cell axes follow this pattern perfectly, the decrease being 0.373, 0.275, and 0.143 Å for c , a , and b , respectively.

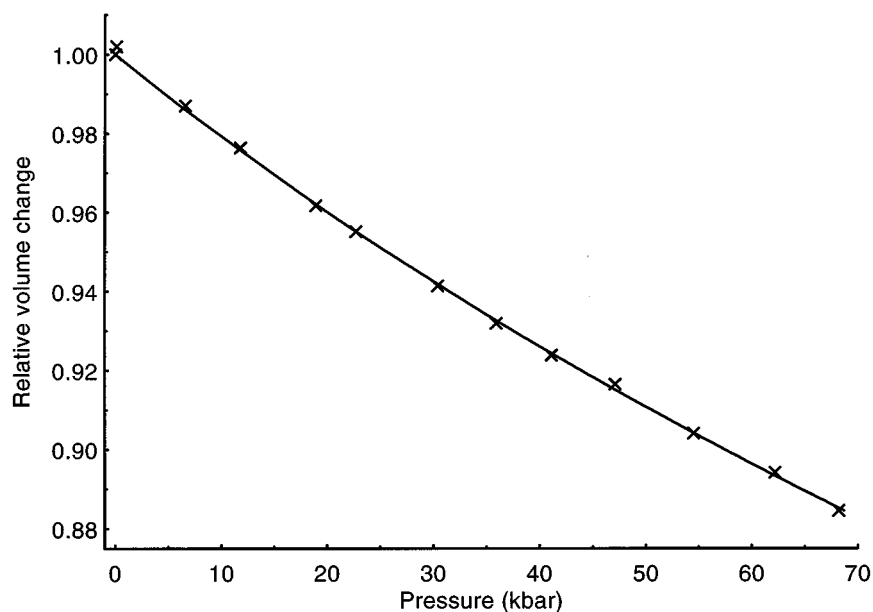


FIG. 3. Relative unit cell volume change calculated with the fitted Birch equation of state (solid line) and the observed volume changes (crosses).

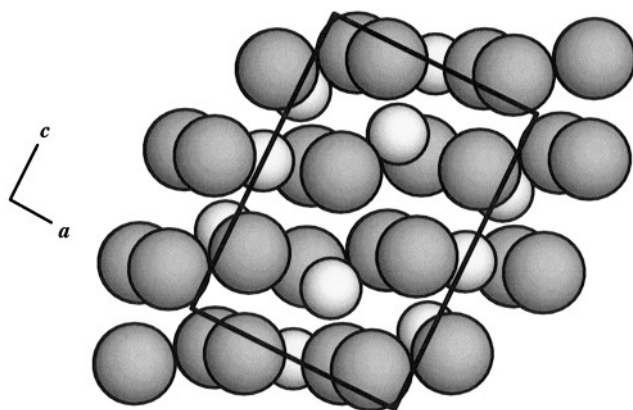


FIG. 4. Packing of F^- and Na^+ ions in Na_3ScF_6 , viewed along $[010]$. The dark gray fluorine ions are drawn with radii 1.0 \AA and the light gray sodium ions with radii 0.75 \AA .

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