Compressibilities and high-pressure phase transitions of sodium tungstate perovskites (Na_xWO_3)

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Unit-cell parameters of the sodium tungstate perovskites, Na_xWO_3($x = 0.55$, 0.62, and 0.70), have been determined at a number of pressures to 5.3 GPa with single-crystal x-ray diffraction techniques. Pseudocubic $Na_{0.55}WO_3$ and $Na_{0.62}WO_3$ (probably tetragonal, $C4/mmb$, $c > a$ at room pressure) have compressibilities of 0.0095(1) and 0.0084(1) GPa^{-1}, respectively. The $Na_{0.55}WO_3$ perovskite compresses uniformly with pressure to 4.2 GPa, but $Na_{0.62}WO_3$ transforms reversibly at 1.8(1) GPa to a second single phase (presumably tetragonal, $I4/mmm$) with $c < a$ and compressibility 0.0094(3) GPa^{-1}. A volume change of -0.1% accompanies this reversible, first-order transition. Crystals of $Na_{0.70}WO_3$ (probably tetragonal, $I4/mmm$, $c < a$) have a room-pressure compressibility of 0.0110 (3) GPa^{-1}; however, the compressibility of this phase decreases to less than 0.0070 GPa^{-1} at pressures above 2.5 GPa.

Perovskite-type compounds have been investigated extensively because of their complex phase-transition behavior. The ideal cubic perovskite ABO_3 structure consists of a corner-linked array of regular AO_6 octahedra; a cube of eight octahedra surrounds a large 12-coordinated B cation at the center of each cell. Most perovskites, however, are distorted from the ideal cubic form, by tilting of the corner-linked octahedra, by displacements ("off centerings") of the octahedral cations, or by distortion of these octahedra.[1] Some perovskites, such as those in the system $NaNbO_3$-$KNbO_3$, exhibit remarkably complex transition behavior as a function of temperature and composition, with more than a dozen mixed polyhedral tilting and cation displacement transitions.[2] The phase $NaNbO_3$ displays seven different pseudocubic modifications between -100 and 640 °C.[3]

Perovskite-type compounds, which also undergo displacive phase transitions at high pressure,[4] are of special concern to geophysicists because of recent inferences that magnesium silicate perovskite (a stable form of $MgSiO_3$ at pressures above about 20 GPa) may be the dominant phase in the earth's lower mantle.[5] It has been proposed that magnesium silicate perovskite may experience a series of polyhedral tilt transitions at high pressure.[4] Sodium tungstate, nonstoichiometric $Na_{1-x}WO_3$, is one of the few types of perovskites in which only tilt transitions are known. Sodium tungstate thus provides possible analogs for the very-high-pressure $MgSiO_3$ phase, which is not available in single crystals. Clarke[6] used high-temperature, single-crystal, x-ray photography to identify a sequence of four phases, which he assumed to be related by polyhedral tilting of tungsten octahedra.

Octahedral tilting in perovskites has been systematized by Glazer,[7] who described octahedral orientations in terms of rotations about each of the three pseudocubic unit-cell axes. In untilted perovskite all octahedra are aligned with the orthogonal unit-cell axes. In tilted forms, on the other hand, the arrangement of octahedra may be described in terms of angular rotations about one, two, or all three pseudocubic axes, thus leading to singly, doubly, or triply tilted perovskites. At temperatures above 200 °C sodium tungstates occur in the ideal, untilted cubic structure ($Pm3m$; $a^0a^0a^0$ in Glazer notation[7]). Upon cooling, $Na_{1-x}WO_3$ undergoes a progression of transitions, which were inferred[6] to result from one tilt (tetragonal $C4/mmb$; $a^0a^0c^+$) to two tilts (tetragonal $I4/mmm$; $a^0b^+b^+$) to three tilts (cubic Im^3; $a^+a^+a^+$). Sodium tungstate perovskites were chosen for high-pressure study because sequences of polyhedral tilt transitions observed at high pressure are often identical with those observed on cooling from high temperature.[8]

Specimens of the same material employed in the high-temperature experiments[6] were supplied by Dr. Roy Clarke (Department of Physics, University of Michigan). Unit-cell dimensions of single crystals of $Na_{0.55}WO_3$ and $Na_{0.62}WO_3$ (both tetragonal $C4/mmb$; $Z = 8$; $c > a \approx 7.7$ Å; pseudocubic subcell, $a = 3.83$ Å) and $Na_{0.70}WO_3$ (tetragonal $I4/mmm$; $Z = 8$; $c < a \approx 7.7$ Å; pseudocubic subcell, $a = 3.85$ Å) were examined at pressures to 5.3 GPa with a diamond-anvil pressure cell for single-crystal, x-ray diffraction.[9] An alcohol mixture of 4:1 methanol:ethanol was employed as the hydrostatic pressure medium. Unit-cell parameters were determined with the procedure of King and Finger[10] from the centered positions of 12–20 reflections. All three samples seem to be cubic on the basis of preliminary diffractometry at room pressure and 23 °C, although Clarke[6] reported that the a and c axes differ by approximately 0.1%. High-angle ($2\Theta > 90°$) scans of reflections of classes ($h00$), ($hh0$), and (hhh) revealed splitting of both Mo$K\alpha_1$ and Mo$K\alpha_2$ reflections. Twinning of the tetragonal phase, which often occurs on a very fine scale in pseudocubic perovskites, results in overlap of ($h00$) and ($00l$) reflections along all three orthogonal axes, thus obscuring the true symmetry of the phase. This twinning, furthermore, prevents meaningful analysis of intensity data for three-dimensional structure refinement. The nature of perovskite distortions from cubic symmetry, therefore, usually must be inferred from other physical measurements such as Raman spectra or birefringence.[6]

Unit-cell parameters of a $100 \times 100 \times 30$ μm crystal of $Na_{0.55}WO_3$ were measured at nine pressures to 4.2 GPa (Table I). No discontinuities in lattice parameters or diffraction character were observed over this pressure range; thus, there

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TABLE I. Unit-subcell parameters of $Na_{0.55}WO_3$ versus pressure.[a]

Pressure (GPa)	a_{max} (Å)	a_{min} (Å)	V (Å^3)	V/V_0
0.0001	3.825 (2)[b]	3.822 (3)	55.94 (6)	1.0000
0.20 (5)	3.824 (3)	3.820 (2)	55.88 (5)	0.9989
0.75 (5)	3.818 (1)	3.808 (9)	55.51 (13)	0.9923
1.17 (5)	3.812 (1)	3.809 (11)	55.36 (16)	0.9896
1.62 (5)	3.806 (2)	3.806 (9)	55.15 (13)	0.9859
2.00 (5)	3.804 (1)	3.797 (12)	54.93 (18)	0.9819
3.38 (5)	3.789 (1)	3.779 (7)	54.25 (7)	0.9698
3.75 (5)	3.781 (1)	3.780 (11)	54.05 (17)	0.9662
4.17 (5)	3.781 (2)	3.775 (15)	53.98 (21)	0.9650

[a] Although this material is pseudocubic at all pressures studied, the high-pressure data are consistent with the assignment to tetragonal symmetry of Clarke (see Ref. 6).

[b] Parenthesized figures represent estimated standard deviations in terms of least units cited.

is no evidence for any high-pressure phase transitions in this sodium-poor member of the sodium tungstate perovskites. The bulk modulus K_0 was calculated from regression analysis of P-V data in Table I with a first-order Birch–Murnaghan equation of state in which a value of 4 was assumed for K'.[11] The resultant value of K_0 is 105 $\pm$ 1 GPa, and the compressibility ($\beta = 1/K_0$) of $Na_{0.55}WO_3$ is thus 0.0095 $\pm$ 0.0001 GPa^{-1}.

Unit-cell parameters of $Na_{0.62}WO_3$ were measured at 14 pressures to 5.3 GPa (Table II). Compression is uniform to above 1.7 GPa, with a calculated bulk modulus of 119 $\pm$ 2 GPa ($K' = 4$; $\beta = 0.0084 \pm 0.0001$ GPa.$^{-1}$ A reversible phase transition, characterized by a discontinuous change from $c > a$ to $c < a$ (Fig. 1), is observed between 1.7 and 1.9 GPa. The high-pressure phase, which has diffraction geometry consistent with the doubly tilted tetragonal ($I4/mmm$) perovskite described by Clarke,[6] has a bulk modulus of 106 $\pm$ 3GPa ($\beta = 0.0094 \pm 0.0003$). The greater compressibility of the high-pressure phase is typical of some polyhedral tilt transitions in which the higher pressure phase has a greater number of tilting degrees of freedom.[8]

Unit-cell parameters of $Na_{0.70}WO_3$ were determined at 14 different pressures to 3.8 GPa on two different crystals (Table III). Clarke[6] described this material as tetragonal ($I4/mmm$; doubly tilted $a^0b^+b^+$), but the diffraction maxima are so broad in this specimen that the nature of the pseudocubic lattice distortion could not be confirmed. Compressibility of $Na_{0.70}WO_3$ is greater than that of the other two samples at room pressure ($K_0 = 90.9 \pm 2.5$ GPa; $\beta = 0.0110 \pm 0.0003$ GPa^{-1}) but decreases to less than 0.0070 GPa^{-1} above 2.5 GPa (Fig. 2). Although pressure-volume data do not show clearly whether the change of compressibility is discontinuous with pressure, resolution of the

TABLE II. Unit-subcell parameters of $Na_{0.62}WO_3$ versus pressure.

Pressure (GPa)	a (Å)	c (Å)	V (Å^3)	V/V_0
0.0001	3.836 (2)[a]	3.838 (2)	56.47 (2)	1.0000
0.18 (5)	3.833 (1)	3.837 (1)	56.39 (1)	0.9986
0.50 (5)	3.831 (2)	3.832 (2)	56.25 (3)	0.9964
0.71 (5)	3.828 (1)	3.832 (1)	56.16 (1)	0.9945
1.22 (5)	3.824 (1)	3.826 (1)	55.92 (1)	0.9905
1.58 (5)	3.818 (2)	3.823 (1)	55.71 (2)	0.9868
1.71 (5)	3.818 (4)	3.822 (3)	55.69 (8)	0.9862
1.89 (5)	3.817 (1)	3.813 (1)	55.54 (1)	0.9838
2.60 (5)	3.811 (2)	3.806 (2)	55.20 (3)	0.9778
2.80 (5)	3.809 (2)	3.804 (2)	55.13 (3)	0.9765
2.94 (5)	3.806 (2)	3.799 (2)	55.02 (2)	0.9746
3.50 (5)	3.800 (2)	3.794 (2)	54.74 (2)	0.9696
3.87 (5)	3.798 (2)	3.791 (3)	54.66 (2)	0.9682
5.28 (5)	3.779 (2)	3.772 (1)	53.85 (2)	0.9539

[a] Parenthesized figures represent estimated standard deviations in terms of least units cited.

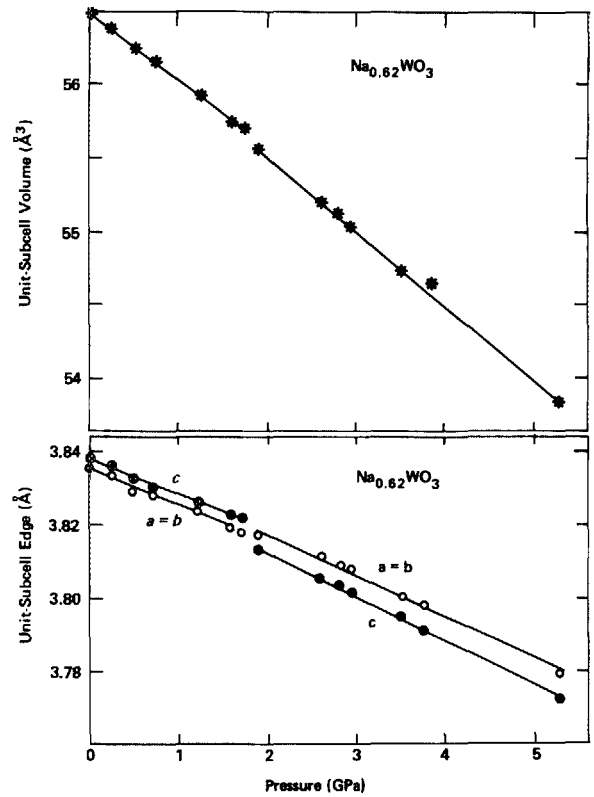

FIG. 1. Unit-subcell parameters of pseudocubic $Na_{0.62}WO_3$ vs pressure. The transition at approximately 1.8 GPa is characterized by a 0.1% volume discontinuity and a change from tetragonal $c > a$ to tetragonal $c < a$.

TABLE III. Unit-subcell parameters of $Na_{0.70}WO_3$ versus pressure.[a]

Pressure (GPa)	a_{max} (Å)	a_{min} (Å)	V (Å^3)	V/V_0
0.0001	3.847 (1)[b]	3.845 (1)	56.89 (1)	1.0000
0.21 (5)	3.844 (3)	3.842 (2)	56.74 (9)	0.9976
0.66 (5)	3.838 (3)	3.835 (1)	56.46 (6)	0.9927
0.85 (5)	3.833 (2)	3.827 (3)	56.22 (6)	0.9885
1.25 (5)	3.832 (3)	3.829 (2)	56.28 (10)	0.9895
1.40 (5)	3.834 (3)	3.824 (1)	56.06 (5)	0.9857
1.97 (5)	3.821 (2)	3.819 (2)	55.72 (5)	0.9797
2.42 (5)	3.814 (2)	3.814 (3)	55.48 (6)	0.9752
2.52 (5)	3.812 (1)	3.811 (1)	55.38 (4)	0.9737
2.55 (5)	3.813 (1)	3.810 (1)	55.39 (5)	0.9739
2.74 (5)	3.813 (1)	3.812 (1)	55.42 (5)	0.9744
3.03 (5)	3.811 (2)	3.804 (3)	55.27 (7)	0.9715
3.56 (5)	3.808 (4)	3.804 (1)	55.11 (7)	0.9690
3.84 (5)	3.809 (1)	3.802 (2)	55.07 (5)	0.9680

[a] Although this material is pseudocubic at all pressures studied, the high-pressure data are consistent with the assignment to tetragonal symmetry of Carke (see Ref. 6).

[b] Parenthesized figures represent estimated standard deviations in terms of the least units cited.

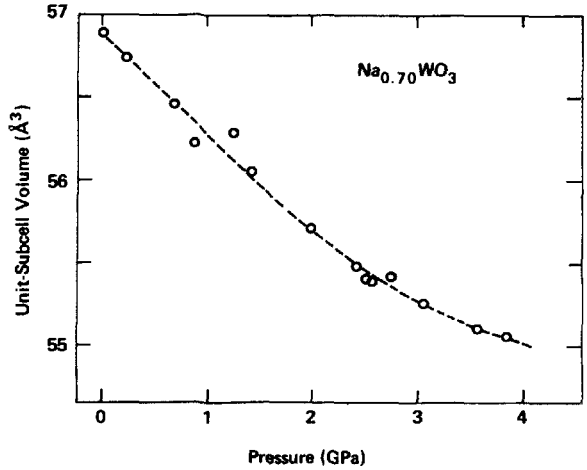

FIG. 2. Unit-subcell volume of $Na_{0.70}WO_3$ vs pressure. The pronounced positive curvature of the pressure-volume relationship is in contrast to the behavior of $Na_{0.55}WO_3$ and $Na_{0.62}WO_3$ over the same pressure range. A discontinuity in the slope at 2.5 GPa is possible but not conclusively demonstrated by these pressure-volume data.

diffraction maxima does change noticeably near 2.5 GPa. Below 2.5 GPa peaks are broad, with no α_1-α_2 resolution; above this pressure Mo$K\alpha_1$ and Mo$K\alpha_2$ components of reflections are resolved. It appears likely, therefore, that $Na_{0.70}WO_3$ undergoes a reversible transition near 2.5 GPa, though the symmetry and structure of the high-pressure phase are not known.

The high-pressure behavior of sodium tungstate perovskites is consistent with the observation of Clarke[6] that these phases undergo a sequence of polyhedral tilt transitions. The least distorted of the three phases, $Na_{0.55}WO_3$, which has been described as a singly tilted tetragonal phase, does not appear to transform below 4.2 GPa. The intermediate composition, $Na_{0.62}WO_3$, which transforms from a singly tilted to a doubly tilted perovskite form at low temperature, appears to undergo the same transition at high pressure. The doubly tilted, high-pressure phase is *more* compressible than the room-pressure phase, probably because of additional degrees of freedom for compression associated with tilting.

The $Na_{0.70}WO_3$ phase, which has been described as a perovskite with a double tilt at room temperature,[6] is the most compressible of the three phases under room conditions, but its compressibility is less by almost 40% at 3 GPa. This difference in compressibility and the increase in resolution of the diffraction maxima may signal a transformation to the triply tilted cubic perovskite phase.

Magnesium silicate perovskite occurs in a highly tilted, orthorhombic structure in its metastable, ambient-conditions modification.[12] Given the complexity of perovskite phase transitions and the dependence of such physical parameters as elastic moduli and thermal expansion on structure, it is not possible at this time to extrapolate equation-of-state parameters for $MgSiO_3$ and other silicate perovskites from room-condition measurements. The variety of behaviors observed for sodium tungstate perovskites at high pressure underscores the need to investigate silicate perovskites, which are thought to exist in the earth's lower mantle, under appropriate conditions of temperature and pressure.

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