JOURNAL OF SOLID STATE CHEMISTRY 27, 383–388 (1979)

Composition Dependence of Elasticity in Na_xWO_3

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Received April 24, 1978; in final form June 24, 1978

Single crystal Na_xWO_3 elastic constants have been measured for $x = 0.522, 0.628, 0.695$, and 0.74 using Brillouin light scattering. The elasticity of Na_xWO_3 is found to be similar to that of ReO_3. Calculations indicate that an observed decrease in c_{11} with increasing sodium concentration results from perturbation associated with an increasing lattice constant of strong, covalent W–O bonds.

Introduction

Brillouin light scattering was recently found to yield single crystal elastic moduli values for ReO_3 in adequate agreement with ultrasonic measurements if local heating of the scattering volume was taken into account (*1*). The optical measurements have been extended to the non-stoichiometric sodium tungsten bronze system, Na_xWO_3. Determining the influence of the sodium atoms on lattice cohesion is of interest since this could provide an explanation of the soft mode instability thought to be responsible for superconductivity in Na_xWO_3 at low x-values (*2*). Although the sodium bronze system has been studied intensively with respect to its bulk thermal, optical, electronic, and superconducting properties as well as its surface catalytic behavior, there has been little work on the elasticity of the system. The first single crystal elastic moduli measured as a function of composition for $x = 0.522$, 0.628, 0.695, and 0.74 are reported.

Experimental Measurements

The Na_xWO_3 crystals were grown by fused salt electrolysis (*3*), and the sodium concentrations (x-values) were determined from Debye–Scherrer X-ray-derived lattice constants and the relationship between x-values and lattice constants obtained by neutron activation analysis (*4*). Mass spectrographic studies revealed no impurities in excess of 100 ppm (*5*).

The Brillouin light scattering technique used to determine elastic moduli values has been described in detail with respect to the study of ReO_3 (*1*). Briefly, using a five-pass Febry–Perot spectrometer, the Doppler shift experienced by laser radiation scattered by intrinsic acoustic lattice vibrations or thermal phonons was determined. This shifted frequency along with the measured index of refraction of the sample, determined the

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0022-4596/79/030385-06$02.00/0

propagation velocity of the phonons, the velocity of sound. The refractive index values at the excitation wavelength, 0.488 μ, of the crystals studied were determined by modulation ellipsometry. (*6*). Defining the angle δ as the deviation of the probed phonon wavevector from the [100] crystallographic direction in the $(hk0)$ plane, measured longitudinal and transverse velocities, v_L and v_T, as a function of δ were simply related to the cubic elastic constants by:

$$\rho v_{L,T}^2 = \tfrac{1}{2}[c_{11}+c_{44}] \pm \tfrac{1}{2}[(c_{11}-c_{44})^2 \cos^2 2\delta + (c_{12}+c_{44})^2 \sin^2 2\delta]^{1/2} \quad (1)$$

where the positive sign refers to the longitudinal acoustic (LA) mode, the negative to the transverse acoustic (TA) mode, and ρ is the crystal density (*7*). The elastic constants for Na_xWO_3 with $x = 0.522$, 0.628, and 0.74 were determined from a least squares fit of measured (v_L, δ) and (v_T, δ) and (v_T, δ) ordered pairs to Eq. (1). As discussed below, the $Na_{0.695}WO_3$ data were better described by assuming acoustic propagation in the XY plane of a crystal of the tetragonal classes 4, $\bar{4}$, or $4/m$. For these symmetry classes, the required elastic constants and measured velocities were related by (*7*):

$$\rho v_{L,T}^2 = \tfrac{1}{2}[c_{11}+c_{66}] \pm \tfrac{1}{2}[(c_{11}+c_{66})^2 - 4C]^{1/2} \quad (2)$$

where, again, the positive and negative signs refer to LA and TA modes, respectively. The value of C is given by:

$$\begin{aligned} C = {} & [c_{11}\cos^2\phi + c_{66}\sin^2\phi \\ & + c_{16}\sin 2\phi][c_{11}\sin^2\phi + c_{66}\cos^2\phi \\ & - c_{16}\sin 2\phi] \\ & - [c_{16}\cos 2\phi + (c_{12}+c_{66})\sin\phi\cos\phi]^2. \end{aligned} \quad (3)$$

The angle ϕ is defined with respect to the [100] direction so that $0° < \phi < 90°$.

Brillouin spectra from $Na_{0.522}WO_3$, typical of those obtained from metallic Na_xWO_3, are shown in Fig. 1 for two phonon wavevector directions, $\delta = 10.2°$ and 29.3°. The continuous curves result from computer smoothing. A representative fit of the Brillouin velocity data to Eq. (1) is shown in Fig. 2 for $Na_{0.522}WO_3$. The corresponding curve for $Na_{0.695}WO_3$ based on Eq. (2), tetragonal symmetry, is shown in Fig. 3. Calculated Na_xWO_3 elastic moduli along with those for ReO_3 are given in Table I for comparison. Results are included for $Na_{0.695}WO_3$ assuming both cubic and tetragonal symmetry. There was not sufficient data to determine C_{13}, C_{33} and C_{44} for the tetragonal symmetry. Calculated sample temperatures based on the method of Carslaw and Jaeger (*8*) and measured Na_xWO_3 thermal conductivities (*9*) are also included.

Discussion

A fundamental calculation of the elastic constants of the Na_xWO_3 system is beset with numerous difficulties including the random occupation of lattice sites by the sodium atoms, the sodium concentration dependent free electron density, and the predominantly covalent nature of the W–O bond. However, some insight into the character of the Na_xWO_3 lattice may be obtained through a simple calculation. By assuming the value of c_{11} is determined only by the strength of the W–O bond and by following Cowley's calculation of elastic constants for the perovskites $SrTiO_3$ and $BaTiO_3$ (*10*), the modulus can be written in terms of a constant, A_2, which describes short range forces acting parallel to the line joining interacting tungsten and oxygen atoms as:

$$c_{11} = [e^2/32r^4]A_2, \quad (3)$$

where r is half the lattice parameter and e is the fundamental unit of charge. The assumed dominance of the W–O bond in determining the values of c_{11} is in agreement with the findings of Pearsall and Coldren concerning

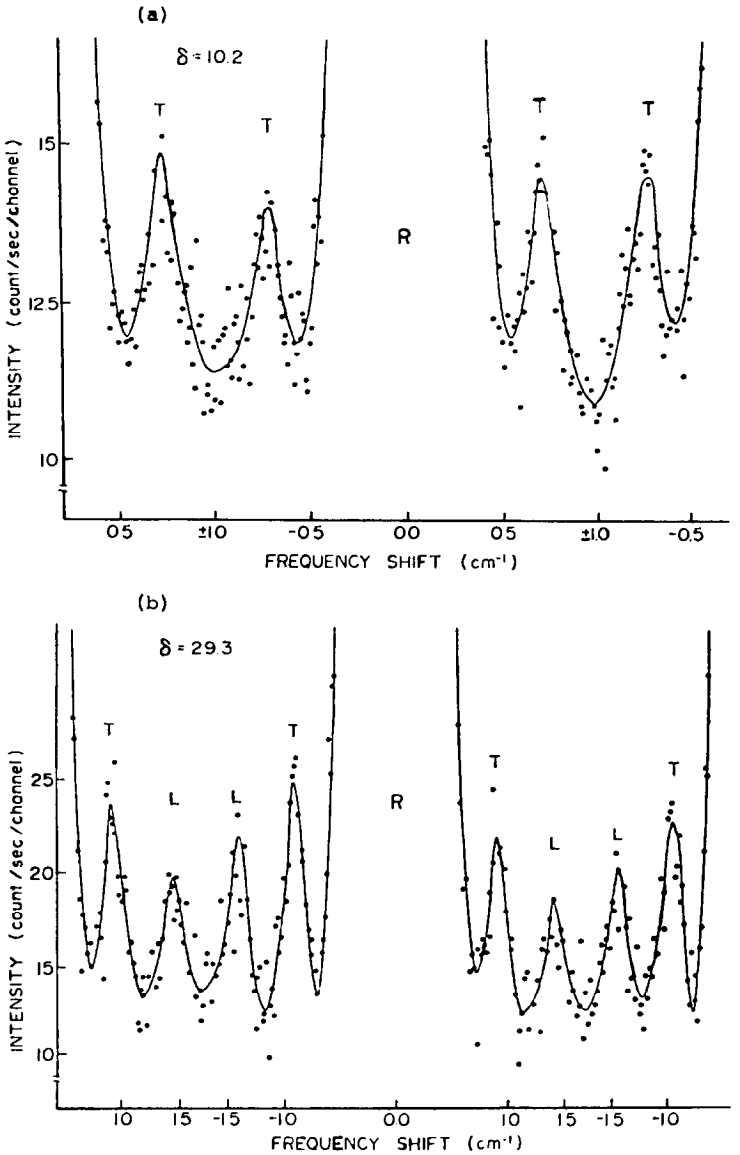

FIG. 1. Brillouin spectra from $Na_{0.522}WO_3$ for two-phonon propagation directions each making an angle δ with respect to [100] in the ($hk0$) plane: (a) $\delta = 10.2°$, (b) $\delta = 29.3°$. The ordinate is the absolute photoelectron count rate in counts per second per channel of the multichannel analyzer. The dots are the accumulated signal. The lines are computer generated smooth curves. *L* and *T* refer to Brillouin shifted signals scattered from quasi-longitudinal and quasi-transverse acoustic phonons, respectively. *R* denotes the parasitic elastic scattering at the laser frequency.

the Re–O bond in ReO_3 (*11*). Using Eq. (3), calculated A_2 values for $ReO_3 = 122$ and for Na_xWO_3, $x = 0.522$, 0.628, 0695, and 0.74, A_2 values are 133, 141, 92, and 103, respectively. Based upon a Raman light scattering study Salje has found A_2 for the W–O bond in WO_3 to be $120 < A_2 < 156$ (*12*). The correspondence A_2 values for ReO_3, Na_xWO_3, and WO_3 suggests that the observed decrease in c_{11} with increasing x-value is

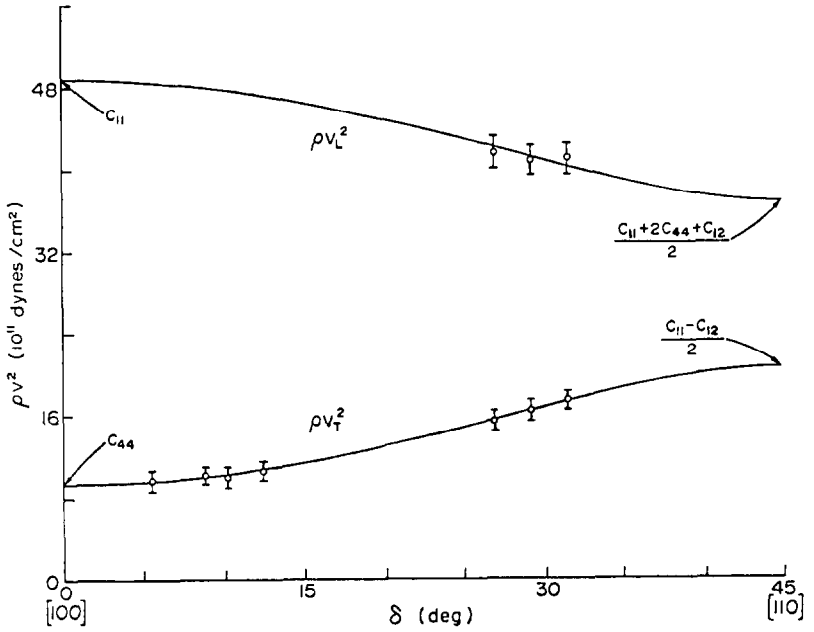

FIG. 2. The variation in the effective elastic moduli of $Na_{0.522}WO_3$ as a function of the angle δ. The form for the longitudinal and transverse acoustic phonons, ρv_L^2 and ρv_T^2, was computed using a best fit to the data points: $c_{11} = 48.8 \times 10^{11}$ dynes cm^2, $c_{44} = 9.29 \times 10^{11}$ dynes cm^2, and $c_{12} = 6.84 \times 10^{11}$ dynes cm^2.

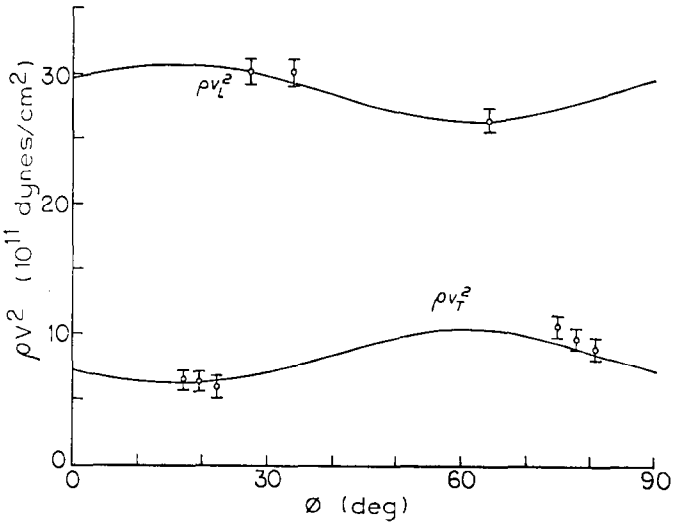

FIG. 3. The variation in the effective elastic moduli of $Na_{0.695}WO_3$ as a function of the angle ϕ. The form for the longitudinal and transverse acoustic phonons, ρv_L^2 and ρv_T^2, was computed using a best fit to the data points: $c_{11} = 29.6 \times 10^{11}$ dynes cm^2, $c_{66} = 7.48 \times 10^{11}$ dynes cm^2, $c_{12} = 10.7 \times 10^{11}$ dynes cm^2, and $c_{16} = 1.9 \times 10^{11}$ dynes cm^2. The results describe propagation in the XY plane of the tetragonal classes 4, 4, and $4/m$.

TABLE I

Crystal Cubic	Elastic Moduli (10^{11} dynes/cm^2)			
	c_{11}	c_{44}	c_{12}	$T(K)$
ReO_3	71.7±3.5	7.11±0.25	10.3 ±3.4	354
$Na_{0.522}WO_3$	48.8±1.5	9.29±0.41	6.84±0.82	521
$Na_{0.628}WO_3$	47.7±1.7	8.94±0.52	9.0 ±1.4	508
$Na_{0.695}WO_3$	29.6±3.0	7.48±0.5	10.7 ±3.5	431
$Na_{0.74}WO_3$	32.1±3.0	9.55±0.31	4.8 ±2.9	436
Tetragonal	c_{11}	c_{12}	c_{16}	c_{66}
$Na_{0.695}WO_3$[a]	29.6±3.0	10.7 ±3.5	1.9 ±1.0	7.48±0.5

[a] These results were obtained assuming tetragonal symmetry of the class 4, $\bar{4}$, or $4/m$ with acoustic propagation in the XY plane. The elastic moduli c_{13}, c_{33} and c_{44} were not determined for the tetragonal symmetry.

predominantly a manifestation of an increasing perturbing effect of the sodium ions on the W–O bond rather than the effect of repulsive Na–Na or Na–O interactions. The lattice constant of cubic Na_xWO_3 may be written as: $a_0(x) = 0.0818x + 3.7850$ Å (*13*), and that of ReO_3 is 3.743 Å (*11*).

Goodenough has proposed that the W–O bond results from covalent π-bonding of tungsten $5d$ with oxygen $2p$ orbitals, and that Na–O σ-bonding competes for the p_π orbitals that π-bond with the tungsten atoms as sodium atoms are added to the host WO_3 lattice (*14*). His result explains the increasing lattice constant of Na_xWO_3 with increasing x-values, as well as the observed decreasing value of the modulus c_{11}.

The Brillouin data are not sufficient to evaluate additional atomic interaction constants. An expression similar to Eq. (3) involving only W–O interactions predicts a negative c_{44} value contrary to the stability condition $c_{44} > 0$. Thus, sodium and oxygen interactions must contribute significantly to the value of the shear constant. Large error bars associated with the measurement of c_{12} preclude meaningful interpretation of the experimental values of this constant. However, a Raman scattering study in conjunction with the Brillouin results should permit evaluation of additional atomic interaction constants and a better characterization of the Na_xWO_3 lattice.

Laser heating of the scattering volume and low signal-to-noise ratios are limitations of the Brillouin technique in determining bronze elasticity. While effective sample temperatures can be calculated as above, it would be desirable to isolate the composition dependence by collecting all data at the same sample temperature. This was not done in the present experiments because of access problems associated with the collection optics required for the weak Brillouin components. It was not possible to mount the sample in a cell which could be temperature controlled.

The observed departure from cubic symmetry of the acoustic phonon spectra of $Na_{0.695}WO_3$ can be considered with respect to the recently proposed phase diagram of Na_xWO_3 determined by X-ray studies (*15*). According to this work, a phase transition from tetragonal $C4/mmb$ to cubic $Pm3m$ occurs for Na_xWO_3 $(0.6 < x < 0.74)$ with increasing temperature in the interval $404 < T < 420 \pm 20$ K. Transition temperatures increase with increasing x-values. The Brillouin result that the $Na_{0.695}WO_3$ sample was tetragonally distorted at the measurement

temperature ($T_m = 431$ K) is in general agreement since the transition to cubic might not have occurred and since, owing to increasing thermal conductivity with increasing x-values for fixed laser input power, the higher sodium concentration samples were at lower temperatures during the Brillouin study. The $Na_{0.74}WO_3$ sample might have been tetragonal during the measurements ($T_m = 436$ K), but this was not reflected in the Brillouin data. The results obtained for the $Na_{0.695}WO_3$ crystal appear to be in disagreement with the symmetry proposed by Clarke (*15*) for the higher temperature tetragonal phase but this disagreement is uncertain because of the possible error in the determination of c_{16}. The proposed crystal class, based on X-ray data, has the elastic constant c_{16} equal to zero. The non-zero value of c_{16} determined in this work is consistent only with the tetragonal classes 4, $\bar{4}$, or $4/m$.

Acknowledgment

This work was supported in part by the U.S. Department of Energy, Office of Basic Energy Sciences.

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