Impurity Effects in Sodium Tungsten Bronzes: Niobium and Tantalum Doping*

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Sodium tungsten bronze crystals of composition $Na_{0.8}WO_3$ were doped with varying concentrations of Nb and Ta. The cubic perovskite crystal structure typical of sodium bronzes was found for all samples containing less than about 10% Nb or Ta; lattice constants increased with dopant content. No crystal structure changes were indicated between 300 and 800°K by either thermal or x-ray measurements. Crystal resistivities were increased from about 3×10^{-5} to about 5×10^{-3} Ωcm by the addition of about 7% Nb to $Na_{0.8}WO_3$. An explanation of this large resistivity increase involves more than assuming acceptor behavior for Nb^{5+} substituting at a W^{6+} lattice site.

Introduction

Sodium tungsten bronzes are nonstoichiometric oxides with the general chemical formula Na_xWO_3, where $0 < x < 1$. When $0.3 \leqslant x < 1$, the sodium bronzes have the cubic perovskite crystal structure, vary in color from violet to gold with increasing x and are excellent metallic-type electrical conductors (*1*). The high conductivity appears to arise from the donation of essentially one free electron by each Na atom to a conduction band of the tungsten bronze (*2–4*). The composition of this conduction band has been the subject of several proposals (*3, 5–7*).

In this investigation a cubic sodium tungsten bronze of nominal composition corresponding to $Na_{0.8}WO_3$ was doped with varying amounts of niobium or tantalum. The effects on the structural, thermal, and electrical properties of the sodium bronze by substituting Nb or Ta at W sites were studied. Observed increases in crystal resistivity with increasing dopant concentration, within the cubic perovskite crystal structure, were found to be too large to be explained by assuming acceptor behavior for Nb^{5+} or Ta^{5+} substituted at a W^{6+} lattice site. Alternative causes are proposed and discussed in relation to the existing band theories of the tungsten bronzes.

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Experimental

Crystal Preparation

Crystals of $Na_{0.8}WO_3$ containing Nb or Ta were grown in air at about 725°C, controlled to ±5°C, by electrolyzing a melt of reagent grade $Na_2WO_4 \cdot 2H_2O$ and WO_3 contained in porcelain crucibles. Platinum wire electrodes were used with a current density of about 0.03 amp/cm² at 1.0–1.5 V for a period of 24 hr (*8*). In all preparations, the Na/(W + dopant) atom ratio was held constant at 1.2. Niobium and tantalum dopants were added as Nb_2O_5 and Ta_2O_5 with the dopant concentration reported as the per cent of W atoms replaced by Nb or Ta, e.g., a Nb/W atom ratio of 1/100 in the sample mixture is reported as 1%-Nb doping. Most products were analyzed for Na, W and Nb, or Ta. Sodium was determined by flame emission photometry[1]; W, Nb, and Ta were determined gravimetrically by precipitating and weighing WO_3, Nb_2O_5, or Ta_2O_5, after separating Nb or Ta from W (*9*). The dopant concentrations added to the sample charge, and present in the melt, were found to be somewhat different from actual concentrations present in the grown cyrstals.

Structure Determination

X-ray powder diffraction patterns were run on all samples using a Norelco x-ray diffractometer with Ni filtered Cu $K\alpha$ radiation and glass sample slides.

[1] The flame emission data for Na were kindly furnished by Professor E. Kostiner of Cornell University.

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Variable temperature x-ray powder patterns were obtained for the samples $Na_{0.8}WO_3$, $Na_{0.8}WO_3:1\%$ Nb, $Na_{0.8}WO_3:2\%$ Nb, $Na_{0.8}WO_3:3\%$ Nb and $Na_{0.8}WO_3:4\%$ Nb in the temperature range 300 to 800°K using an MRC Model X-86-N3 variable temperature camera attachment and associated proportional temperature controller.

Resistivity Measurements

Variable temperature resistivity measurements were made in a dry N_2 atmosphere employing four pressure probes, two probes of chromel wire for measuring resistance and two adjustable aluminum plate current probes. Constant dc current of about 250 mA, supplied by an Electro model D-612T filtered dc power supply and monitored with a Westinghouse multiscale ammeter, was passed through the crystal and the resulting potential difference measured with a Keithley 155 null detector–microvoltmeter. Crystal temperatures were sensed with a chromel–alumel thermocouple and were recorded with a Leeds and Northrup Speedomax H AZAR recorder. Thermal equilibrium of the crystal and crystal holder assembly was established prior to any electrical measurement, as indicated by the temperature record. Resistivity measurements above or below room temperature were corrected for a small but detectable thermal emf.

Thermal Measurements

All thermal measurements were made on a Perkin–Elmer Differential Scanning Calorimeter, model DSC-1B, in a dry N_2 atmosphere between 300 and 773°K. Crystal sections of Nb and Ta doped $Na_{0.8}WO_3$ of 10–30 mg were used as samples. Differential thermograms were run using both covered and uncovered aluminum sample and reference pans at a chart span range of 8 mcal/sec, a scan speed of 40°K/min and a slope setting between 700 and 800. Typical differential thermal analysis (DTA) thermograms were obtained in which sample heat changes were indicated as endothermic or exothermic slope changes, away from a baseline, on a differential power (or temperature) versus temperature plot.

Results

Crystal Preparation

The size and quality of the crystal and the amount of sodium bronze formed during electrolysis were very dependent on the dopant concentration and the preparation temperature (8). Melt temperatures below about 750°C were necessary at Nb doping levels above 2%; at higher temperatures there was no tungsten bronze formation. The data in Table I indicate the dependence of crystal growth on the amount of Nb present in the sample charge. (The presence of Ta seemed to reduce crystal, but not product, formation more effectively than did Nb.) No tungsten bronze product formation could be obtained, at any preparation temperature, for Nb concentrations greater than 4% Nb in the Na_2WO_4–WO_3 sample charge. However, if NaF–WO_3 melts were used, Nb doped crystals could be obtained from sample charges containing over 7% Nb, as indicated in Table II. Crystals prepared from fluoride melts have slightly different properties from those prepared using tungstate melts.

Chemical analysis yielded a composition corresponding to $Na_{0.8}WO_3:y\%$ Nb or Ta for the samples studied. The percentage of Nb or Ta found in the tungsten bronze products was higher than that added to the sample, as is shown in Table II.

TABLE I

DEPENDENCE OF PRODUCT AND CRYSTAL
FORMATION ON DOPANT CONCENTRATION

Sample Designation	% Nb in Sample	Preparation Temperature, °C	Product Yield, g	Crystal Quality
PF-2	None	750	12	Good
PF-A	2.0	705	12	Good
PF-7	3.0	715	12	Good
PF-9	4.0	735	7	Fair
PF-C	5.0	720	None	None
PF-10	6.0	750	None	None

TABLE II

DOPANT CONCENTRATION IN SAMPLE CHARGE
VERSUS
DOPANT CONCENTRATION FOUND IN PRODUCT

Sample Designation	% Nb in Sample	% Nb in Product	Sample Designation	% Ta in Sample	% Ta in Product
9 NaW	1.0	1.1	7 NaW	1.1	5.0
23 NaW	2.0	5.4	17 NaW	1.7	7.0
JM-14[a]	5.2	8.3	20 NaW	2.2	8.0
JM-15[a]	7.3	10.0	8 NaW	9.1	20.0

[a] These two high-Nb-content products were prepared using a NaF–WO$_3$ melt.

Crystal Structures

The x-ray powder diffraction data indicated that all of the samples had the cubic perovskite crystal structure, typical of the sodium tungsten bronzes, except for the $Na_{0.8}WO_3$:10% Ta sample in which extra diffraction lines (weak) were present. Lattice constants determined for undoped sodium bronzes corresponded (10) to the $Na_{0.8}WO_3$ formula given by chemical analysis. Table III lists d spacings for the strongest lines of Nb doped $Na_{0.8}WO_3$ crystals at 300°K. There appears to be an increase in lattice constant with increasing Nb or Ta concentration, as indicated by the increases in d spacings. For Nb doped crystals, the lattice constant increases from

TABLE III

VARIATIONS OF d SPACINGS WITH
Nb CONCENTRATIONS IN $Na_{0.8}WO_3$[a]

h k l	Standard NaWO$_3$[b]	0.1% Nb (22 NaW)[c]	1% Nb (9 NaW)[c]	2% Nb (23 NaW)[c]
1 0 0	3.862 (100)	3.834 (100)	3.887 (100)	3.920 (100)
1 1 0	2.730 (77)	2.711 (91)	2.743 (98)	2.773 (86)
1 1 1	2.234 (18)	2.212 (18)	2.235 (13)	2.294 (10)
2 0 0	1.931 (48)	1.916 (29)	1.933 (54)	1.958 (63)
2 1 0	1.728 (29)	1.716 (72)	1.730 (55)	1.746 (64)
2 1 1	1.577 (28)	1.566 (42)	1.576 (32)	1.606 (20)
2 2 0	1.365 (11)	1.357 (9)	1.364 (12)	1.384 (9)
2 2 1	1.287 (15)	1.279 (15)	1.286 (20)	1.300 (25)
3 0 0	1.287 (15)	1.279 (15)	1.286 (20)	1.300 (25)
3 1 0	1.221 (15)	1.213 (15)	1.219 (12)	1.235 (9)
3 1 1	1.164 (5)	1.157 (8)	1.162 (6)	1.176 (5)
2 2 2	1.115 (5)	1.107 (7)	1.112 (3)	1.125 (3)
3 2 0	1.071 (8)	1.064 (8)	1.068 (10)	1.080 (5)
3 2 1	1.032 (10)	1.025 (16)	1.029 (12)	1.038 (10)

[a] Relative line intensities, I/I_1, are given in parentheses after each d spacing, listed in angstroms.

[b] Data taken from E. O. BRIMM et al., *J. Amer. Chem. Soc.* **73**, 5427 (1951).

[c] Sample designation.

TABLE IV

Variations of d Spacings with Temperature
for Sample PF-9, $Na_{0.8}WO_3$:4% Nb[a]

$h\,k\,l$	299°K	398°K	423°K	440°K	586°K	624°K	718°K	808°K
1 0 0	3.932 (100)	3.931 (100)	3.931 (100)	3.934 (100)	3.931 (100)	3.931 (100)	3.946 (100)	3.943 (58)
1 1 0	2.757 (79)	2.761 (75)	2.757 (58)	2.761 (63)	2.761 (84)	2.762 (84)	2.769 (79)	2.771 (100)
1 1 1	2.244 (32)	2.250 (30)	2.247 (21)	2.252 (21)	2.248 (32)	2.251 (26)	2.258 (32)	2.263 (26)
2 0 0	1.943 (79)	1.941 (85)	1.943 (67)	1.945 (71)	1.946 (84)	1.947 (79)	1.948 (79)	1.949 (95)
2 1 0	1.733 (47)	1.732 (45)	1.734 (33)	1.736 (38)	1.737 (42)	1.739 (47)	1.740 (47)	1.743 (37)
2 1 1	1.580 (42)	1.583 (45)	1.583 (33)	1.584 (33)	1.584 (42)	1.585 (37)	1.588 (42)	1.589 (42)
2 2 0	1.366 (21)	1.367 (20)	1.367 (17)	1.368 (17)	1.372 (21)	1.373 (16)	1.376 (16)	1.375 (16)
2 2 1 3 0 0	1.290 (21)	1.290 1.288 (20)	1.290 (17)	1.290 (21)	1.292 (21)	1.293 (26) 1.291 (21)	1.295 (21)	1.296 1.294 (26)
3 1 0	1.223 (16)	1.222 (15)	1.225 1.221 (13)	1.226 1.223 (13)	1.224 (11)	1.226 (16)	1.229 1.227 (11)	1.229 (11)
3 1 1	1.166 (11)	1.167 (10)	1.167 (13)	1.169 1.167 (8)	1.169 (16)	1.169 1.172 (11)	1.172 (11)	1.175 1.172 (11)
2 2 2	1.115 (11)	1.116 (10)	1.116 (8)	1.117 1.114 (8)	1.119 1.118 (11) 1.116	1.119 1.117 (11)	1.118 (11)	1.122 1.119 (5)
3 2 0	1.071 (11)	1.073 (5) 1.070 (10)	1.072 (8)	1.072 1.069 (8)	1.074 (11)	1.074 1.072 (11)	1.076 1.074 (11) 1.072	1.078 (21) 1.075 (16)
3 2 1	1.032 (16)	1.033 (15)	1.032 (13)	1.033 1.030 (13)	1.035 1.033 (16)	1.036 1.033 (11)	1.037 1.034 (16)	1.039 1.036 (11)

[a] Relative line intensities, I/I_1, are given in parentheses after each d spacing, listed in angstroms.

3.85 to 3.86 to 3.90 Å for 0.10, 1.0, and 2% Nb added to the sample charge. The 3.85 Å value for the 0.10% Nb doped sample was identical to that found for undoped samples, within experimental error. For Ta doping, the lattice constant varied from 3.84 to 3.86 to 3.88 Å for the 1.1, 1.7, and 2.2% Ta samples given in Table II.

If Nb or Ta existed in the tungsten bronze samples studied as occluded Nb_2O_5 or Ta_2O_5, the low dopant concentrations involved would make their detection by x-ray diffraction measurements difficult. On the other hand, occluded oxides (even of similar structure and lattice constant) should not cause the observed increase in sodium bronze lattice constant with increasing dopant concentration. Further, x-ray studies (8) of sodium tungsten bronze crystals containing dopants of quite dissimilar crystal structure, such as WS_2, also show varying lattice constants for the bronze and no apparent impurity diffraction lines. We have, therefore, assumed that the Nb or Ta dopants are dissolved in the $Na_{0.8}WO_3$ crystals, substituting at a W lattice site, and are not present as occluded species.

The variable temperature x-ray powder diffraction data indicated no major structure changes between 300 and 800°K for any of the samples studied, although some of the high angle, low-d spacing, lines appeared to split at the higher temperatures. The lattice constants of all of the bronze samples increased slightly with increasing temperature. Data for $Na_{0.8}WO_3$:4% Nb are given in Table IV; the temperatures were controlled to ±5°K. The most evident changes appear to occur between 423 and 440°K, when several diffraction lines split, and between 718 and 808°K, when significant line intensity changes occur. These are temperature regions in which changes are also observed in the thermal and resistivity properties of the sample. On the other hand, the thermal and resistivity changes observed near 600°K do not seem to be reflected in the x-ray data.

Thermal Properties

The DTA curves for Nb or Ta doped $Na_{0.8}WO_3$ samples contained no distinct peaks between 300 and 773°K but did show slope deviations from the
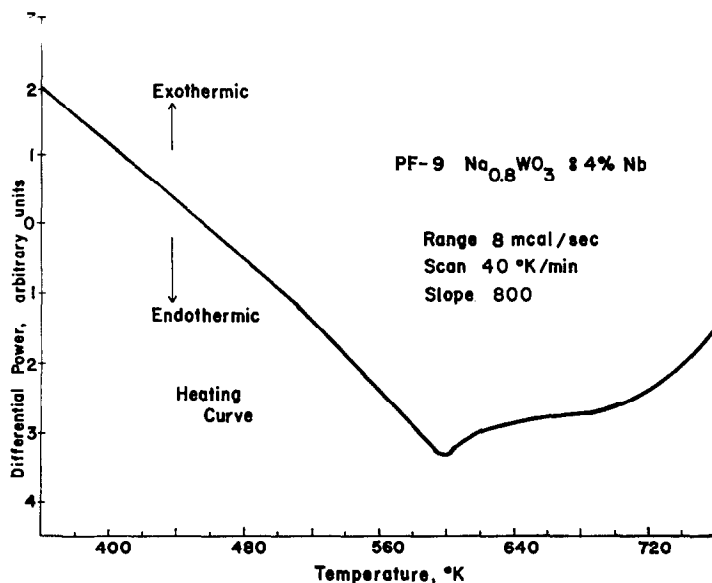
FIG. 1. A DTA thermogram of a $Na_{0.8}WO_3:4\%$ Nb crystal. The baseline slopes in the endothermic direction. A small variation from the baseline occurs near 420°K. Major slope changes occur near 600 and 700°K.
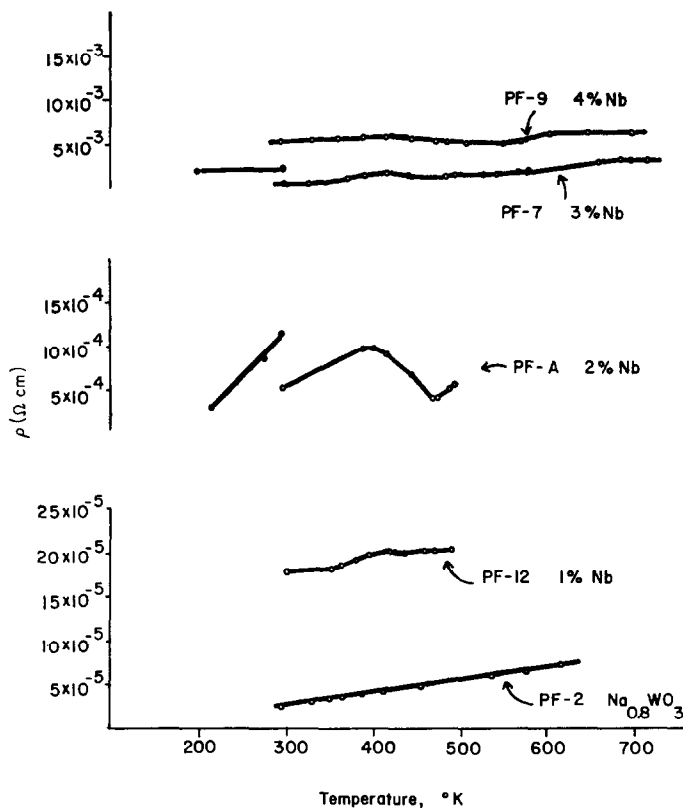

FIG. 2. Resistivity, ρ, as a function of temperature for an undoped sodium bronze crystal, PF-2, and for crystals containing different Nb concentrations. Initial ρ measurements were made during heating. Upon cooling to room temperature, ρ values were slightly higher, as shown for the 2 and 3% Nb samples. Data taken during cooling are designated by filled circles.

baseline indicating variations in sample heat capacities. Similar effects have been observed for undoped sodium tungsten bronzes (11). Some slope changes were gradual while others were rather dramatic, as shown in the DTA curve for $Na_{0.8}WO_3$: 4% Nb given in Fig. 1. In all cases, the changes observed in the DTA curves could be correlated with changes in crystal resistivities, as reported below. For $Na_{0.8}WO_3$:4% Nb, for example, thermal changes were observed near 420 and 605°K. These two temperatures agree quite well with the temperatures at which slope changes occur in the resistivity versus temperature plot given in Fig. 2.

Resistivity Changes

Addition of Nb or Ta to cubic sodium tungsten bronzes changes their electrical properties considerably. Crystal resistivities (ρ) increase rapidly with increasing Nb or Ta concentration as can be seen from the resistivity data given in Table V for Nb doped crystals and a plot of similar data for Ta doping in Fig. 3. Since single crystal preparation was difficult with Ta additions, the data in Fig. 3 were obtained from measurements on pressed pellets.

Not only are the resistivity values increased by doping sodium bronzes with Nb or Ta, but the temperature dependence also changes with varying dopant concentrations, as is shown in Fig. 2. In all cases, hysteresis effects were observed in the resistivity measurements; they become more pronounced at higher doping levels.

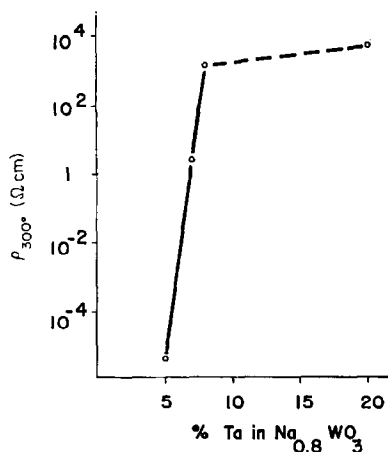In all samples, there appears to be a change in the

ρ versus T plot around 410–420°K, even for undoped crystals (11). Upon addition of a Nb or Ta dopant, this transition is enhanced and other changes in ρ at different temperatures are introduced .

Discussion

It is evident that the resistivity of the cubic sodium tungsten bronzes of high sodium content, and correspondingly low resistance, can be increased significantly by addition of Nb or Ta impurities. Room temperature resistivities can be varied from about 10^{-5} to about 10^{-3} Ωcm by doping with Nb and possibly to considerably higher values with larger concentrations of Nb or Ta. While additions of Nb or Ta to the sodium bronze, of concentrations up to about 10%, appear to expand the lattice slightly, the crystal structure is not changed from the typical cubic perovskite.

Although substitution of Nb or Ta for W in the tungsten bronzes should produce acceptor centers, since Nb^{5+} or Ta^{5+} can be assumed to replace W^{6+}, the observed increases in resistivity with increasing dopant concentration appear to be much too large to be caused by this mechanism alone. For example, Table V shows that the resistivity increases by more than 100 times between an undoped $Na_{0.8}WO_3$ crystal and one prepared from a melt containing 4% Nb, yielding a crystal of composition $Na_{0.8}WO_3$: 7% Nb. Assuming one conduction electron from each Na in the tungsten bronze (2, 12), there are about 1.4×10^{22} conduction electrons in $Na_{0.8}WO_3$. But only about 1×10^{21} Nb centers are present with 7% Nb doping and, assuming they act as acceptors, about 10^{21} electrons would be trapped and removed from the conduction band. This would cause an insignificant change in the crystal resistivity since the reduction in the number of conduction electrons is, relatively, very small. Then the large increase in resistivity in the doped crystals must be caused by another mechanism.

Increased crystal resistivities with increasing dopant level could be caused by lower charge carrier concentrations, lower carrier mobilities or a combination of these two effects. A lower conduction electron mobility might be expected in Nb or Ta doped bronzes since the crystal lattice expands slightly with increasing dopant content, possibly producing less orbital overlap and a more narrow conduction band. Impurity scattering might also be greater in doped crystals. A different scattering mechanism might be indicated by the crystal resistivities of the 3% and 4% Nb samples shown in Fig. 2 since they appear to be less temperature

FIG. 3. Variation of ρ at 300°K with increasing Ta dopant concentration in $Na_{0.8}WO_3$. Measurements were made on pressed pellet samples. The data plotted correspond to those given in Table II.

TABLE V

INCREASES IN CRYSTAL RESISTIVITY
WITH INCREASING Nb CONCENTRATION

Sample Designation	% Nb in Sample	$\rho_{300°K}$ (Ωcm)
PF-2	None	3×10^{-5}
22 NaW	0.10	3×10^{-5}
PF-12	1.0	2×10^{-4}
PF-A	2.0	5×10^{-4}
PF-7	3.0	1×10^{-3}
PF-9	4.0	5×10^{-3}

dependent than undoped $Na_{0.8}WO_3$ samples. Qualitatively a mobility decrease, such as this, would be consistent with any of the bonding theories now proposed (3, 5–7) because of decreased overlap in conduction-band formation.

On the other hand, if the crystal resistivities increase with dopant concentration because of rather large decreases in the number of conduction electrons, an unusual situation would be present. The Nb or Ta acceptor centers would then appear to be more effective than is ordinarily true, i.e., one acceptor, one Nb^{5+} or Ta^{5+} at a W^{6+} site, would remove more than one free electron from a conduction band state. If this is the case, the idea of a cluster of donor centers being removed from the conduction band states by the addition of a single acceptor would be very attractive. A combination of the bonding theory of Fuchs (6) with those of Sienko (3)

and Goodenough (7) might be useful in explaining the data. It is evident that Hall effect studies are needed to determine the relative contributions of carrier concentration and carrier mobility in determining the resistivities of Nb or Ta doped $Na_{0.8}WO_3$ crystals.

Acknowledgments

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