JOURNAL OF SOLID STATE CHEMISTRY 1, 210–214 (1970)

# Thermal and Electrical Properties of Sodium Tungsten Bronze

BARRY E. TAYLOR AND PAUL F. WELLER

*Department of Chemistry, State University College, Fredonia, New York 14063*

Received July 28, 1969

Differential thermal analysis measurements on $Na_{0.8}WO_3$ crystals, run between 300 and 770°K, indicate sample heat capacity changes near 420 and 730°K. Specific heat changes for $Na_{0.8}WO_3$ were found near these same temperatures, with values ranging around the 90.7 J/g-at.wt determined at 330°K. Small irregularities in the temperature dependence of the resistivity of $Na_{0.8}WO_3$ crystals were observed near 420 and 730°K and apparently correspond to the changes in the thermal properties of the crystals.

## Introduction

The sodium tungsten bronzes are nonstiochiometric compounds of the form $Na_xWO_3$. Although their resistivities have been reported to be linear with respect to temperature, for $0.25 < x < 0.90$, over a wide range of temperatures (200–1000°K) (*1*), we have found that there is a small change in the slope of the "resistivity versus $T$" curve near 420°K. This change in slope corresponds to a small, but observable, heat capacity change and to thermal conductivity changes observed by Shanks and Redin (*2*), and a change in thermal expansion observed by Takamori and Tomozawa (*3*).

## Experimental

### Crystal Preparation

Crystals with $x$ values equal to 0.8 were grown in air at 750°C by electrolyzing a melt of reagent grade sodium tungstate dihydrate and tungstic oxide contained in porcelain crucibles. Platinum wire electrodes were used with a current density of about 0.03 A/cm$^2$ at 1.0–1.5 V for a period of 24 h (*4*).

### Resistivity Measurements

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 250 mA was supplied by an Electro model D-612 $T$ filtered dc power supply and monitored directly using a Westinghouse multiscale ammeter. A Keithley 155 Null Detector-Microvoltmeter served as measuring device for the emf. Temperatures were sensed with a chromel-alumel thermocouple, which lay adjacent to the crystal in the crystal holder assembly, and were recorded by a Leeds and Northrup Speedomax H AZAR recorder. Thermal equilibrium of the crystal and crystal holder assembly was established in all cases before any electrical measurements were made.

### Thermal Measurements

All thermal measurements were made on a Perkin-Elmer Differential Scanning Calorimeter, model DSC-1B, in a dry $N_2$ atmosphere in the temperature region 300–773°K. Crystal sections of $Na_{0.8}WO_3$, ranging in size from 5–45 mg, were used in all cases. Experiments using both covered and uncovered sample and reference pans (both of aluminum) were run. While many different combinations of sensitivity, scan speed and baseline slope were used, most of the data reported here were taken with a chart span range of 8 mcal/sec, a scan speed of 40°K/min and a slope of about 720.

Two different types of thermal data were observed. The first was the usual differential thermal analysis (DTA) thermogram in which sample heat changes are indicated as endothermic or exothermic peaks or baseline slope changes on a differential power (or temperature) versus temperature plot. The second type of measurement involved the determination of the specific heat of $Na_{0.8}WO_3$ between 330 and

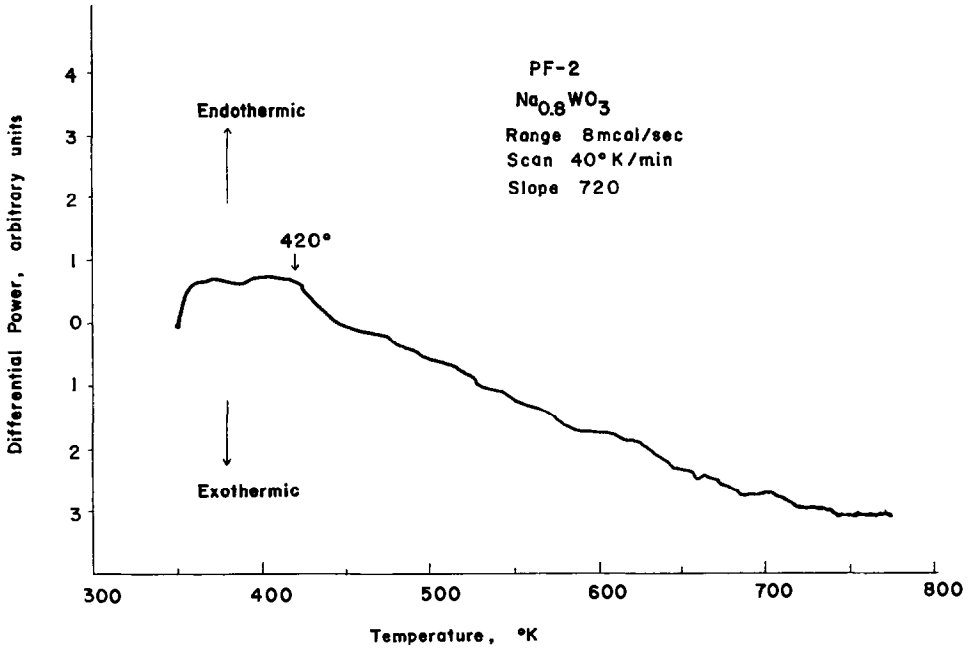


FIG. 1. DTA thermogram taken with covered sample and reference pans. The linear baseline slopes in the exothermic direction, approximately parallel to the sample curve.

770°K. Here, sample deflections versus an empty pan are compared to deflections of a sapphire standard sample of known specific heat versus an empty pan. After correcting the data for blank pan deflections, the unknown sample specific heat is easily calculated.

## Results and Discussion

### Thermal Data

A typical DTA thermogram for a crystal of $Na_{0.8}WO_3$ is presented in Fig. 1. An approximately linear baseline appeared to drift slowly in the exothermic direction; it is not shown in Fig. 1. This DTA curve does not show any distinct peaks but does indicate heat capacity changes in the $Na_{0.8}WO_3$ sample. We interpret Fig. 1 in the following way. The initial slope, between 300 and 400°K, indicates an endothermic change occurring in the sample (which becomes cooler than the reference) and, consequently, an increasing sample heat capacity. At about 420°K, there is a distinct change in the heat capacity behavior of the sample, as shown by the break in the curve. After this change the sample heat capacity appears to remain essentially constant, possibly increasing or decreasing slightly, to about 730°K. There is another break in the DTA curve at this temperature, indicating another heat capacity change.

The heat capacity changes and corresponding transition temperatures can also be determined from plots such as those shown in Fig. 2. The data given in Figs. 1 and 2 are quite comparable but were obtained under slightly different experimental conditions. For Fig. 1 covered sample and reference pans were used; for Fig. 2 uncovered pans. Different slope settings in the two cases cause greatly different base lines. The curves in Fig. 2 give transition temperatures of about 420°K for the low temperature heat capacity change.

To remove uncertainty in the interpretation of the DTA curves, the specific heats of $Na_{0.8}WO_3$ crystals were measured between 330° and 770°K. Data for one of these crystals are shown in Fig. 3. Note that there is an increase in specific heat from 330°–410°K, followed by a slow decrease to about 730°K and, what appears to be, a more rapid decrease between 730 and 770°K. The transition temperatures agree very well with those of the DTA curves, as do the general trends in the specific heat and DTA data. The specific heat value of 90.7 J/g-at.wt (0.0866 cal/g) for the $Na_{0.8}WO_3$ crystal at 330°K is in good agreement with the value of 91.35 J/g-at.wt at 300°K as determined by Gerstein, Klein, and Shanks (5) for $Na_{0.679}WO_3$. (The small difference comes, no doubt, from the values selected for the gram-atomic-weights of the samples.)

The heat capacity change for $Na_{0.8}WO_3$ around 420°K, as shown in Figs. 1, 2, and 3, corresponds to

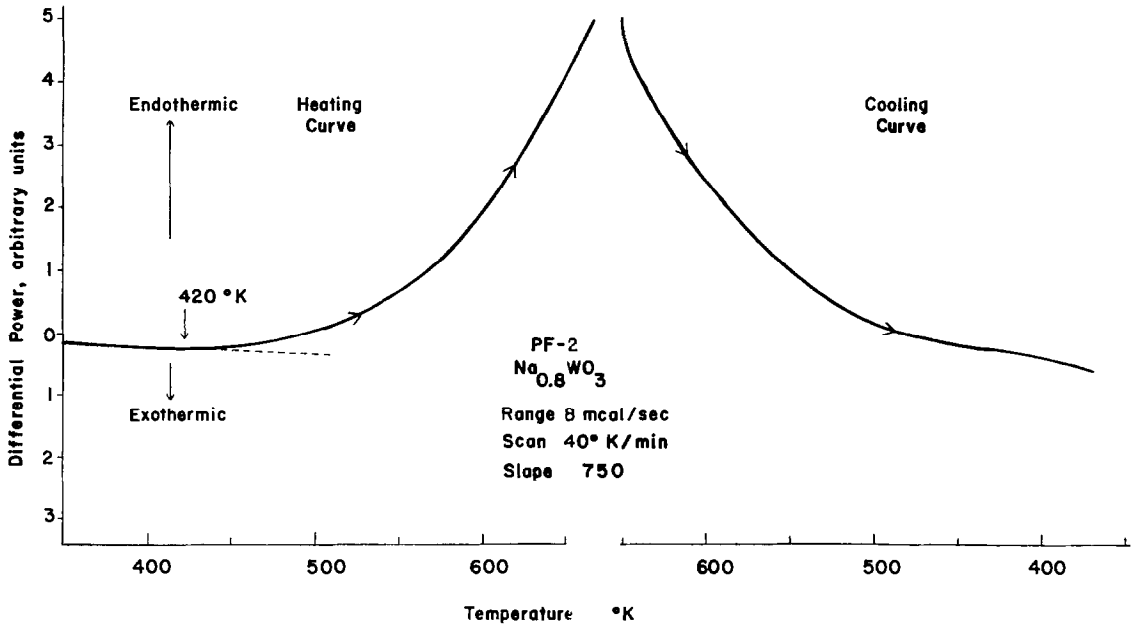


FIG. 2. DTA heating and cooling curves, taken with uncovered pans, of the same sample shown in Fig. 1. Baseline slope is in the endothermic direction.

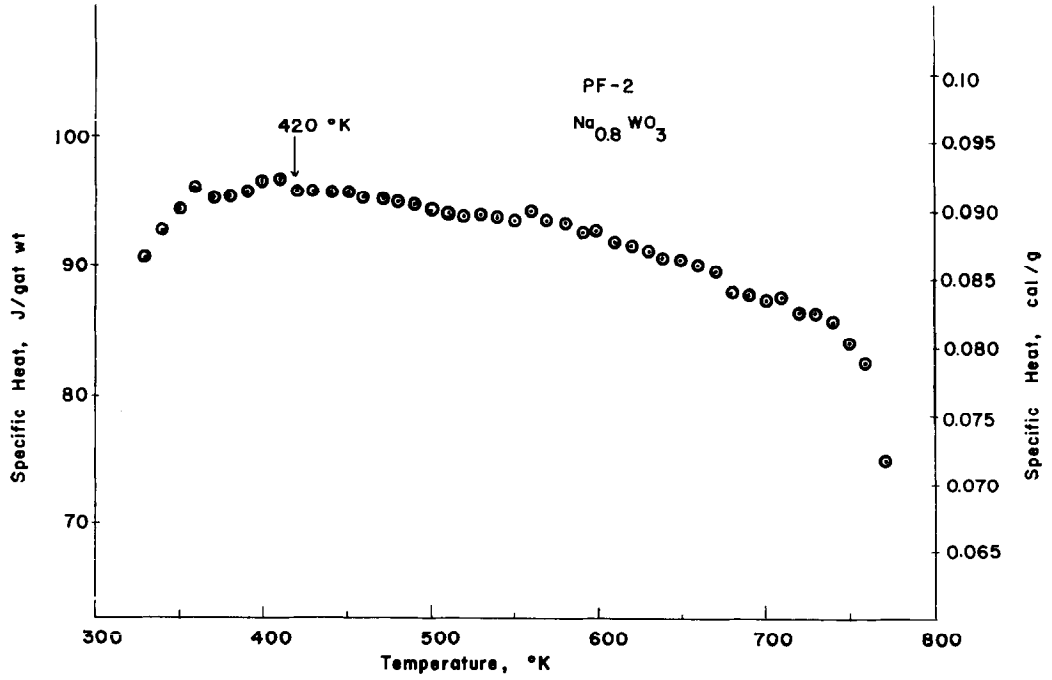


FIG. 3. The variation of the specific heat, in J/g-at.wt and cal/g, of $Na_{0.8}WO_3$ with temperature.

changes noted for the sodium tungsten bronzes in thermal expansion (*3*), in the thermal conductivity (*2*), and in specific heat (*6*). It has generally been assumed [see, for example, (*2*)] that these thermal changes are not reflected in the electrical properties of the sodium bronzes, and, furthermore, that the resistivity of these cubic bronzes is, approximately, a linear function of temperature between 200 and

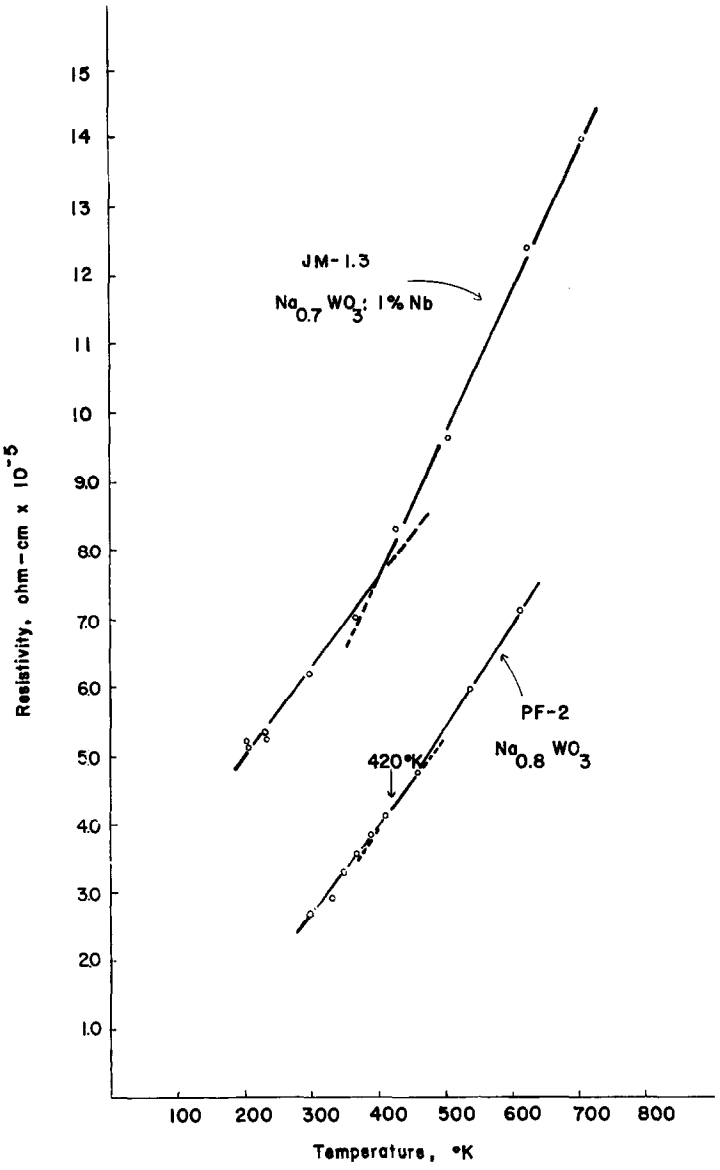


FIG. 4. Resistivity as a function of temperature for pure (PF-2) and Nb doped (JM-1.3) crystals of cubic sodium tungsten bronzes. Thermal changes for the PF-2 sample are shown in Figs. 1–3.

1000°K. We believe, however, that the observed changes in thermal properties, along with their transition temperatures, do correspond to small, but detectable, changes in the resistivity of the bronzes, at these same temperatures.

## Electrical Data

Resistivity, $\rho$, versus temperature data are plotted in Fig. 4 for an undoped $Na_{0.8}WO_3$ crystal (labeled PF-2) and for a $Na_{0.7}WO_3$ crystal doped with 1% Nb [1% Nb indicates a 1/100 ratio of Nb/W atoms in the crystal; Nb was determined gravimetrically, as given in (*4*)]. Notice that the addition of Nb to the tungsten bronze emphasizes the change in slope of the $\rho$ vs $T$ curve, with the transition occurring at about 400°K. But a slope change also appears to be present in the undoped sample, occurring at 420–430°K. This is precisely the same temperature region, within experimental error, at which the thermal transitions occur.

Similar changes in resistivity can be seen in Figs. 1 and 6 in the data of Ellerbeck et al. (*1*). From these

data the following transition temperatures can be approximated: about 520°K for $Na_{0.597}WO_3$, about 435°K for $Na_{0.764}WO_3$ and about 410°K for $Na_{0.851}WO_3$. Apparently the small changes in resistivity-temperature behavior are dependent on the Na content of the crystal. These changes in transition temperature with Na concentration should also be found in the heat capacity data; this is being investigated.

There is another possible correlation between the transition temperatures observed for the heat capacity of $Na_{0.8}WO_3$, given in Figs. 1 and 3, and the electrical data of Ellerbeck et al. (*1*). The break in the DTA and specific heat curves around 730°K appears to agree with a second slope change, occurring near 730°K in the $\rho$ vs $T$ curve in Fig. 1 of Ref. (*1*). This transition seems to be less dependent on Na concentration than the transition occurring near 420°K.

It appears, then, that the resistivity of cubic sodium tungsten bronzes is not a linear function of temperature between 200 and 1000°K, but that two slope changes occur in this temperature region. The temperatures at which these two changes in slope of $\rho$ vs $T$ occur correspond quite well with the temperatures at which distinct changes occur in the specific heat of $Na_{0.8}WO_3$ crystal samples. The changes in thermal properties of the sodium bronzes do seem to coincide with changes in electrical properties, although the electrical characteristics of the samples are not greatly altered. As mentioned above, effects on electrical properties are more pronounced, and more easily correlated, with doped sodium tungsten bronze crystals.

**Acknowledgements**

The authors wish to thank Miss P. Forgnone for assistance with crystal preparations and measurements. This work was supported, in part, by the National Science Foundation under Grant No. GP-8891, by the Research Corporation and by the SUNY Research Foundation.

## References

1. L. D. Ellerbeck, H. R. Shanks, P. H. Sidles, and G. C. Danielson, *J. Chem. Phys.* **35**, 298 (1961).
2. H. R. Shanks and A. D. Redin, *J. Phys. Chem. Solids* **27**, 75 (1966).
3. T. Takamori and M. Tomozawa, *J. Amer. Cer. Soc.* **47**, 472 (1964).
4. P. F. Weller, B. E. Taylor, and R. L. Mohler (to be published).
5. B. C. Gerstein, A. H. Klein, and H. R. Shanks, *J. Phys. Chem. Solids* **25**, 177 (1964).
6. A. H. Klein, H. R. Shanks, and D. H. Dennison, private communication to Shanks and Redin, as reported in (*2*).