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The Thermal Expansion of Cubic Sodium Tungsten Bronzes*

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The coefficients of thermal expansion of powdered cubic sodium tungsten bronzes (Na_xWO_3; $0{\cdot}9 > x > 0{\cdot}3$) from room temperature to 600° C. have been determined. The expansion coefficients for all compositions studied are constant and essentially identical below transition temperatures (near 200° C.) which vary with sodium content. At the transition temperatures, the expansion coefficients change sharply to lower values which vary with composition, going through a minimum near $x = 0{\cdot}5$. The relation between these changes and a similar change in pure WO_3 is pointed out.

The tungsten bronzes are non-stoichiometric mixed oxides of the general formula M_xWO_3, where M is an alkali metal. For most metals the range of x is relatively small; in the case of sodium, however, compounds have been prepared in which x varies from 0 (pure WO_3) to almost 1 ($Na_{0{\cdot}95}WO_3$) (Hägg, 1935; Straumanis, 1949; Brown & Banks, 1954). When x has a value greater than 0·3 these compounds have the cubic perovskite structure; the unit cell is tetragonal when x is in the range from about 0·1 to 0·3 and monoclinic for values of x less than 0·1 (Magnéli & Blomberg, 1951; Magnéli, 1951). In the cubic range, the compounds (all of which are metallic in appearance) display a shift in color from dark blue through violet, red and orange to yellow, as the sodium content is increased. Magnetic susceptibility (Stubbin & Mellor, 1948; Kupka & Sienko, 1950), resistivity (Huibregtse, Barker & Danielson, 1951; Brown & Banks, 1951; Gardner & Danielson, 1954) and Hall coefficient measurements (Gardner & Danielson, 1954) indicate that the cubic bronzes behave as if sodium atoms were dispersed in the tungsten trioxide structure and ionized into Na^+ and free electrons. The resistivity measurements show a minimum at about $x = 0{\cdot}70$, which has not yet been adequately explained, although a number of suggestions (Juretschke, 1952) have been made. Danielson (Smith & Danielson, 1954) states that ordering of sodium ions and vacancies might account for such a minimum, but reports failure to find evidence for such ordering.

An X-ray diffraction study of cubic sodium tungsten bronzes has been carried out at elevated temperatures to determine whether any order–disorder transformations occur in the temperature range studied. Seven specimens, with values of x (in Na_xWO_3) from 0·3 to $0{\cdot}84_5$, were studied. Irreversible changes in structure occur when these substances are heated in air above 600° C.; the investigation was therefore confined to the range from room temperature to about 550° C. The X-ray diffraction measurements were made using a Norelco Geiger-counter diffractometer adapted for high-temperature studies.

Efforts to detect evidence of structural changes at elevated temperatures by careful measurements of the relative intensities of diffraction lines were inconclusive. Intensity variations due to random and uncontrolled variations in degree and type of preferred orientation were demonstrably greater than the effects which were sought.

Measurements of d spacings did indicate a transformation at about 200° C.; the results of these measurements for three specimens are shown in Fig. 1. All the measurements were reproducible in duplicate runs. The data shown are based on averaged values of

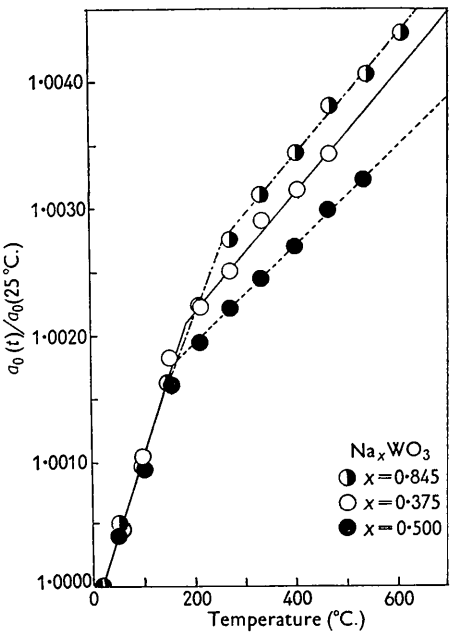

Fig. 1. Thermal expansion of Na_xWO_3.

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a computed from the spacings of five lines in the back-reflection region. All the curves were reversible so long as the specimens were not heated above 600° C.

In all these curves a relatively abrupt change occurs from a low-temperature coefficient of linear expansion of about 12×10^{-6}/°C. to a much lower coefficient above a transition temperature near 200° C. These results are summarized in Table 1.

Table 1

x in Na_xWO_3	'Transition' temperature (°C.)	Slope (below transition temperature)	Slope (above transition temperature)
0·300	210	$12{\cdot}2\times10^{-6}$	$5{\cdot}0\times10^{-6}$
0·375	190	$12{\cdot}0\times10^{-6}$	$4{\cdot}8\times10^{-6}$
0·429	175	12·2	4·0
0·500	165	12·0	4·0
0·678	175	11·4	4·8
0·692	175	11·6	4·6
0·845	250	11·4	4·9–5·0

Within the range of experimental error, the mean low-temperature coefficients of expansion are the same for all samples ($11{\cdot}8\pm0{\cdot}4\times10^{-6}$/°C.). The temperatures at which the slopes change, the 'transition' temperatures, vary with the sodium content of the specimens, going through a broad minimum near $x = 0{\cdot}5$. In all cases, too, the slopes above the transitions varied with composition in much the same manner as did the transition temperatures.

Recently Danielson (Smith & Danielson, 1954) measured the coefficient of expansion of $Na_{0.8}WO_3$ and reported that the data can be represented by a smooth curve over the entire temperature range. Danielson's data do not differ markedly from ours; the differences in interpretation appear to be due to the use of an insufficient number of experimental measurements by Danielson.

It does not appear to be possible to explain the data presented above in terms of an order–disorder transformation. However, we have recently re-measured the coefficients of linear expansion of pure WO_3 and have noted what appear to be significant similarities to the behavior of the sodium tungsten bronzes (Rosen, Banks & Post, 1956). Below about 300° C. all three axes of WO_3 (monoclinic) have approximately equal coefficients of expansion of about 14×10^{-6}/°C.; above 300° C. the monoclinic unit cell appears to become orthorhombic, the coefficients of expansion of the a and c axes change only slightly, but the coefficient of the b axis becomes negative. Similarly, at about 200° C. the coefficients of expansion of the cubic bronzes change, but without any corresponding change in crystal symmetry, from 12×10^{-6}/°C. (below about 200° C.) to about 5×10^{-6}/°C. (above about 200° C.). The exact relationship between this behavior and that of WO_3 is not understood, but it appears likely that the forces responsible for the anisotropy of WO_3 at room temperature are still present even when the lattice has become cubic owing to the addition of sodium atoms. We are now investigating the phase transitions and expansion coefficients in the tungsten bronzes with low sodium content to determine whether this effect extends over the entire composition range.

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