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The Sodium Tungsten Bronzes[1,2]

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The formation of the sodium tungsten bronzes (Na_xWO_3; $1 \geqq x > 0$) from mixtures of sodium tungstate, tungsten(VI) oxide and tungsten has been studied in the temperature range 500–750°, where all of the reactants remain solid. Extremely long reaction times are required to effect complete reaction, which, as shown by X-ray studies, checked at a few points by chemical analysis, occurs only within the range from $Na_{0.30}WO_3$ to $Na_{0.85}WO_3$ under these reaction conditions. The end member of the series, $NaWO_3$, cannot be prepared by this method, but a new value of about 3.866 Å. is suggested for the lattice constant of this compound by extrapolation of the X-ray data from the region in which complete reaction has occurred. A study of the absorption spectra between 3350 and 12,500 Å. has been made by diffuse reflectance methods, and the absorption peak wave length shows a linear shift to shorter wave lengths with increasing sodium content over the range where a single cubic phase is present. Single crystals, up to 12 mm. on an edge, have been grown by cathodic reduction of tungstate melts.

Since the first reported preparation of the sodium tungsten bronzes by Wöhler,[3] using hydrogen reduction of a sodium tungstate melt, this material has been prepared with tin, zinc, iron or phosphorus as the reducing agent,[4,5] or by an electrolytic reduction of molten sodium tungstate–tungsten(VI) oxide solutions.[6,7] These methods, however, did not yield a product whose composition could be predetermined. More recently, Straumanis[8] reported a preparation of these materials from a melt of sodium tungstate and tungsten(VI) oxide, using tungsten metal as the reducing agent. This reaction is based on the equation

$$3xNa_2WO_4 + (6 - 4x)WO_3 + xW \rightleftarrows 6Na_xWO_3 \quad (1)$$

The products of the reaction represented by equation 1 do not have compositions corresponding to the stoichiometric composition of the melts throughout the cubic range. Brimm, *et al.*,[9] report that this reaction produced bronzes which varied in x from 0.2 to a maximum of 0.6, even when calculated for $x = 1.00$, the preparations being made at 800 to 1000°. These authors, as well as Straumanis,[8] state that large excesses of sodium tungstate must be present in order to obtain bronzes of higher sodium content.

The present work was initiated to determine the composition range wherein bronzes would be formed under conditions such that the starting materials enter completely into the reaction. For this purpose, it was considered necessary, in order to minimize attack on the container, to carry out the reaction at temperatures below the melting point of sodium tungstate. Under these conditions, extremely long periods of heating were required to ensure complete reaction. It was also desired to attempt the preparation of the end-member of the series, $NaWO_3$, and to study the conditions necessary for the growth of large single crystals suitable for physical measurements.

Measurements of reflection spectra of powdered bronzes were made in the hope of using these spectra to supplement the use of lattice constant determinations as a means of characterizing the bronzes, and for the purpose of obtaining further basic information about the metallic properties of these compounds.

Experimental

1. **Materials.**—Reagent grade sodium tungstate dihydrate was dried at 110° and ground to a fine powder before use. Tungsten metal, approximately 300 mesh, was reported to be 99.99% pure. An X-ray pattern showed the presence of α-tungsten with a trace pattern of an additional phase. Because of the small spacings, it was assumed that this additional phase was β-tungsten. Tungsten(VI) oxide, reported to be 99.9% pure, was a bright canary-yellow color. A powder pattern did not show the presence of any extraneous material.

2. **Sample Preparation.**—Weighed amounts of sodium tungstate, tungsten(VI) oxide and tungsten were taken in accordance with equation 1. These materials were ground intimately to a fine powder and placed in Pyrex or Vycor tubes. The sample tubes were then evacuated, flushed with argon to remove traces of oxygen and sealed *in vacuo*. The samples were heated in a Nichrome-wound constant temperature furnace. Five series were prepared with the following heating times and temperatures: 520° for 140, 240 and 500 hours; 675° for 500 hours; and 750° for 500 hours.

The first series of samples was initially heated at 520° for 70 hours. When the sample tubes were removed from the furnace, the mixtures were visibly inhomogeneous. They were then returned to the furnace for an additional 70 hours at 520°. Since they then appeared homogeneous, the tubes were opened and samples taken for X-ray analysis. As the plot of lattice constant *vs.* nominal composition (see section 4) showed deviations from linearity between $x = 0.75$ and $x = 0.85$, it was decided to extend the range of temperatures and times to determine if complete reaction could be effected over a wider composition range by further increases in temperature or time of reaction. It was found that the linear range could be extended up to $x = 0.83$ by increasing the time at 520° to 500 hours, while an increase to 240 hours had a much smaller effect. Increasing the reaction temperature at 500 hours to 675° extended the linear region up to $x = 0.85$. Further increases in temperature did not seem to give any extension of the range in which complete reaction occurred.

For those compositions which fell on the linear portion of the lattice constant–nominal composition plot (section 4) there was no evidence of extraneous lines in the X-ray powder diagrams. The powder photographs for samples having higher nominal values of "x" showed lines which could be attributed to sodium tungstate and α-tungsten. No tungsten(VI) oxide lines were present, which indicated

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[2] Abstracted in part from Thesis for degree of Master of Science in Chemistry submitted by B. W. Brown to the Graduate School, Polytechnic Institute of Brooklyn, June, 1952.

[3] F. Wöhler, *Ann. chim. phys.*, [2] **29**, 43 (1823).

[4] H. Wright, *Liebig's Ann.*, **79**, 221 (1851).

[5] J. Philipp, *Ber.*, **15**, 499 (1882); *Jahr. Ber. Forts. Chem.*, **28**, 444 (1882).

[6] L. Kahlenberg and H. H. Kahlenberg, *Trans. Am. Electrochem. Soc.*, **46**, 181 (1924).

[7] V. Spitzin and L. Kaschtanoff, *Z. anorg. Chem.*, **157**, 141 (1926); *Z. anal. Chem.*, **75**, 440 (1928).

[8] M. E. Straumanis, THIS JOURNAL, **71**, 679 (1949).

[9] E. O. Brimm, J. C. Brantley, J. H. Lorenz and M. H. Jellinek, *ibid.*, **73**, 5427 (1951).

that all the tungsten (VI) oxide had taken part in the formation of bronzes of lower sodium content than the original reaction mixture. This is borne out by the fact that the lattice constants of these bronzes invariably fall below the extrapolated section of the linear portion of the lattice constant–nominal composition plot (Fig. 1). It is estimated that the strongest line of α-tungsten should be detectable at concentrations of the order of less than one-half of 1% tungsten mixed with the bronze. Since tungsten is present in all cases of incomplete reaction, we estimate that those mixtures where the tungsten lines are absent have undergone essentially complete reaction. For these reasons, it is very probable that the actual compositions of the bronzes in this region are very close to the nominal compositions. We have used the phrase "nominal composition" to mean the composition calculated from equation 1, which would be the actual composition if complete reaction were attained.

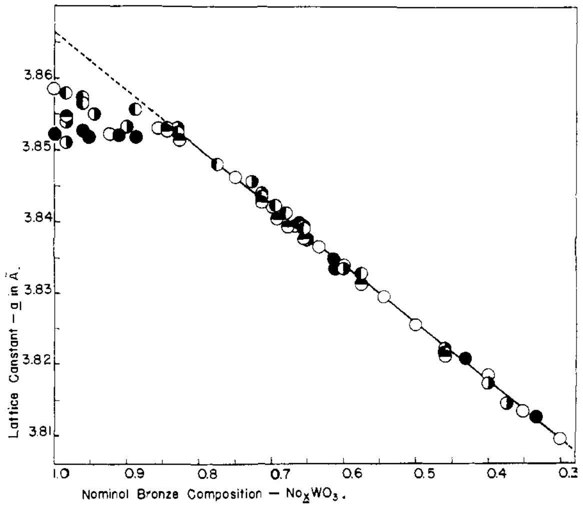

Fig. 1.—Variation of lattice constant with nominal bronze composition: O, prepared at 520° for 140 hours; ●, 520° for 240 hours; ◑, 520° for 500 hours; ◐, 675° for 500 hours; ◒, 750° for 500 hours.

These preparations, because of the long reaction times at low temperatures, are not strictly comparable to those reported by Straumanis,[8] Brimm, *et al.*,[9] and others, where molten sodium tungstate was present, sometimes in excess, and where the reaction times were much shorter. The resulting bronzes were of uniform color with a particle size of about three microns. There was a definite metallic luster in samples with nominal values of x between 1.00 and 0.25. With samples of lower sodium content, the colors were dull and the samples had a more resinous luster. There was no sintering of the samples even at the highest temperatures studied. The Vycor tubes were partially devitrified at the higher temperatures with samples of high sodium content.

3. **Analytical Procedure.**—In view of the X-ray evidence for complete reaction over the range of "x" values from 0.30 to 0.85, it was not believed necessary to analyze a large number of samples. In the region of "x" values above 0.85, analyses would have been meaningless due to the presence of metallic tungsten. In the range where no extra phases were found by X-rays, four compositions were selected for analysis. The analyses were based on the method of Philipp.[5,10] The finely ground bronze powders were first leached with hot water to remove any unreacted sodium tungstate and then dried. Weighed samples of the dried material were decomposed with ammoniacal silver nitrate, depositing an equivalent of silver metal for each equivalent of sodium in the bronze. The dissolved tungstate was determined as tungsten(VI) oxide, no correction being made for silica. The silver was determined by the Volhard method[11] after dissolving in 0.3 N nitric acid. The sodium was found from the silver and also determined as sodium sulfate. The error in the analyses was such that there was an error of about ±0.02 in the value of x.

The bronze with x greater than 0.70 showed partial decomposition during the leaching process. This was in accord with Straumanis' observation[8] that high-sodium bronzes were decomposed by water containing dissolved oxygen. The extremely small particle size of our samples would tend to accelerate this process. Because of this effect, analysis of these two samples was abandoned. Two samples with lower sodium content were analyzed with these results: x(nominal) = 0.68, x(by analysis) = 0.66; x(nominal) = 0.43, x(by analysis) = 0.42. The deviation is less than the probable error of the analytical method. Because of this agreement and the apparent absence of additional phases in the unleached reaction mixtures, it was concluded that these bronzes had essentially the same composition as the reaction mixtures. The linear dependence of the lattice constant on composition of the reaction mixture for "x" values between 0.30 and 0.85, as discussed in the next section, is taken as further evidence that this is the case.

4. **X-Ray Data.**—Precision lattice constants of the bronzes were obtained by the powder method, employing the Straumanis technique[12] and the Cohen method of analytical extrapolation.[13] Filtered copper radiation was used ($K\alpha_1$ = 1.5405 Å.). Several lattice constants were checked on a Philips X-ray Spectrometer, using a high purity silicon sample as an internal standard. The lattice constants agree with those measured from the films with a maximum error of 0.0005 Å. The data obtained are summarized in Fig. 1. The lattice constants of the bronzes with x between 0.85 and 0.30 depend linearly on nominal composition according to Vegard's Law, the nominal composition being the actual composition only in this region.

The equation for this linear portion was determined to be a (Å.) = $0.0819x + 3.7846$. An extrapolation of this line to $x = 1.00$ suggests that the bronze $NaWO_3$ should have a lattice constant of about 3.866 Å. The average deviation of the measured points from linearity results in an error of less than ±0.0007 in the value of x. Those samples whose lattice constants fall below this line or its extension may be expected to have lower sodium contents than indicated by the stoichiometry of the reaction mixtures. The slope of this line is essentially identical to that of the upper portion of the curve reported by Straumanis.[8] However, we were unable to duplicate the discontinuity in Straumanis' curve at approximately $x = 0.70$. From these data, the compositions of the samples assumed to be $NaWO_3$ by Straumanis[8] and by Brimm, *et al.*,[9] would therefore be about $Na_{0.92}WO_3$ and $Na_{0.95}WO_3$, respectively.

In the region above $Na_{0.85}WO_3$, the actual sodium content of the bronze is lower than the nominal composition. This can be ascribed to two factors: (1) as the sodium positions become filled, it becomes increasingly difficult to force the sodium into the available positions, in the absence of large excesses of sodium; and (2) the attack on the Vycor tubes by the sodium tungstate results in a loss of sodium to a level below that calculated from the reaction equation.

In the samples with x less than 0.30, the actual sodium content is frequently greater than the nominal composition. Here, however, new phases are appearing in the powder patterns. These as yet unidentified phases have patterns differing from the tetragonal sodium bronzes[14] and the reduced tungsten oxides.[15,16] The sodium tungstate can react with the excess tungsten(VI) oxide in the reaction mixture to form any of a series of sodium polytungstates. If these phases are composed of reduced tungsten oxides or sodium polytungstates, the net result would be to have a large amount of tungsten unavailable for the formation of the bronze, leaving the resultant bronze with a proportionately higher sodium content. The bronze with the lowest sodium content which still retained the cubic perovskite structure was found to be $Na_{0.26}WO_3$, which is in fair agreement with

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(10) J. Philipp and P. Schwebel. *Ber.*, **12**, 2234 (1879).

(11) F. P. Treadwell and W. T. Hall. "Analytical Chemistry," Vol. II, 9th Ed., John Wiley and Sons, Inc., New York, N. Y., 1942, p. 647.

(12) M. J. Buerger, "X-Ray Crystallography," John Wiley and Sons, Inc., New York, N. Y., 1942, p. 394 *ff.*

(13) M. U. Cohen, *Rev. Sci. Instruments*, **6**, 68 (1935); *ibid.*, **7**, 155 (1936).

(14) A. Magnéli, *Arkiv. Kemi*, **1**, 269 (1949).

(15) A. Magnéli, *Nova Acta Regiae Soc. Sci. Upsaliensis*, [4] **14**, No. 8 (1950).

(16) A. Magnéli, G. Anderson, B Blomberg and L. Kihlborg, in manuscript form, to be published.

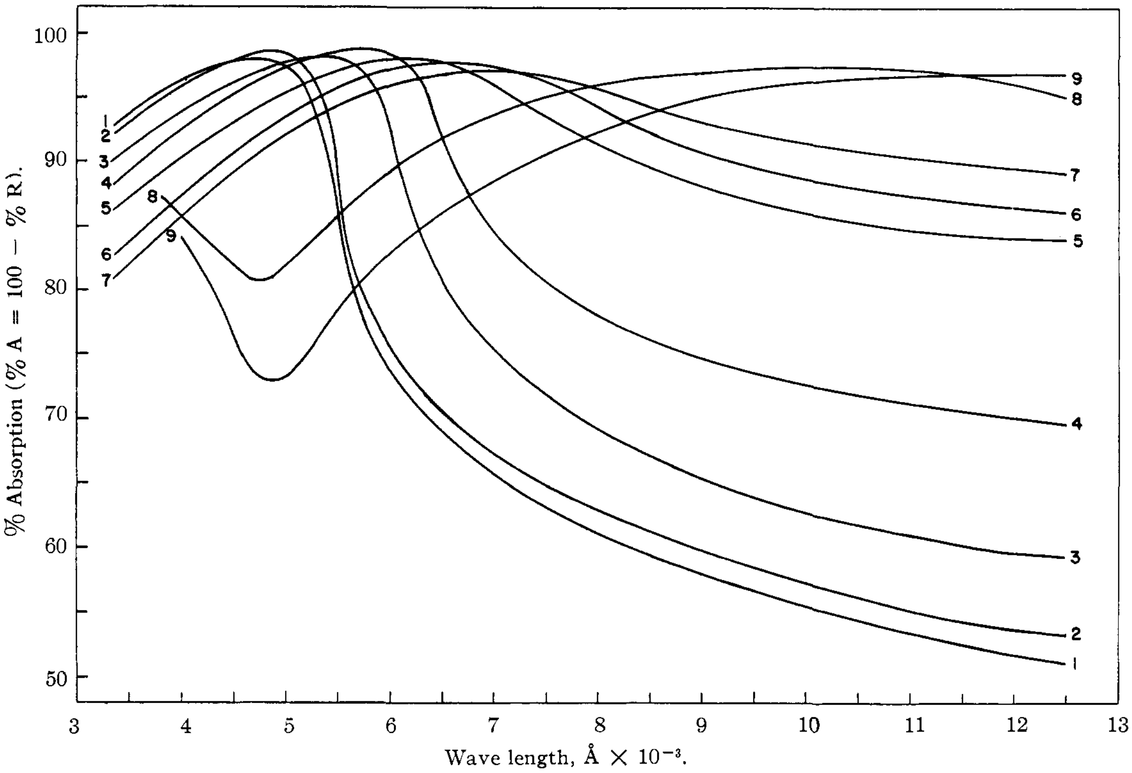

Fig. 2.—Absorption spectra of sodium tungsten bronzes—Na_xWO_3: 1, $x = 0.85$; 2, $x = 0.75$; 3, $x = 0.60$; 4, $x = 0.50$; 5, $x = 0.40$; 6, $x = 0.30$; 7, $x = 0.20$; 8, $x = 0.15$. (nom., WO_3 struct.); 9, $x = 0.10$ (nom., WO_3 struct.).

that reported by Brimm, *et al.*[9] Below $x = 0.15$, the powder patterns appeared identical with that of tungsten(VI) oxide. Although Magnéli[17] has reported tetragonal bronzes of composition near $Na_{0.10}WO_3$, these bronzes were prepared by electrolytic reduction of polytungstate melts,[18] under conditions markedly different from those described here. Therefore, it is not at all surprising that a different result is observed in these experiments.

5. **Absorption Spectra. Sample Preparation.**—The powdered bronzes prepared as described in a previous section were molded into pellets in a press at 35,000 p.s.i. Since the pellets have a tendency to crumble at the edges, a few drops of a dilute collodion solution (USP collodion diluted fifty times with an ethanol–ethyl ether solution) were applied to the edges as a binder. The buttons were cemented to microscope slides with USP collodion. A magnesium carbonate standard was prepared by a similar procedure to correct for any absorption by the collodion in the bronze sample. The pellets were kept in a desiccator to prevent surface discoloration of the samples, which might be due to moisture.

Equipment.—The buttons of sodium tungsten bronze and the specially prepared magnesium carbonate standard were placed in the Diffuse Reflectance attachment of a Beckman quartz spectrophotometer. Measurements of per cent. reflection were made at various wave lengths by comparing the sample with the magnesium carbonate standard.

Examples of the absorption spectra exhibited by the sodium tungsten bronzes between 3350 and 12,500 Å. are shown in Fig. 2. Curves 1 to 7 in this figure show representative spectra for the cubic bronzes. Two points of interest are apparent from these curves: (1) the position of the absorption peaks shifts to longer wave lengths, and (2) the breadth of the peaks increases with decreasing sodium content. Presumably, we could expect the bronze $NaWO_3$ to have an extremely narrow absorption peak. When x has values below about 0.20, the bronzes no longer have a metallic luster, and the absorption spectrum is of an entirely different character (see Fig. 2, curves 8 and 9). With decreasing sodium content, the absorption spectrum rapidly shifts to that of pure tungsten(VI) oxide.

The absorption peak wave length shows a linear dependence on the nominal composition throughout the linear region of the lattice constant curve. However, at concentrations above about $x = 0.75$, the scattering of points away from the curve becomes large (see Fig. 3). The determination of the absorption peak positions for bronzes with x below 0.50 becomes increasingly difficult because of the broad ab-

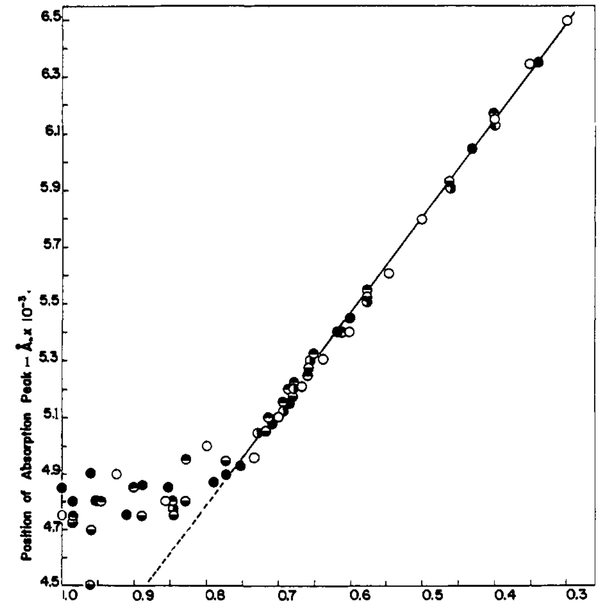

Fig. 3.—Variation of absorption peak position with nominal bronze composition—Na_xWO_3: ○, prepared at 520° for 140 hours; ●, 520° for 240 hours; ◒, 520° for 500 hours; ◓, 675° for 500 hours; ◑, 750° for 500 hours.

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(17) A. Magnéli, *Acta Chem. Scand.*, **5**, 670 (1951).

(18) A. Magnéli and B. Blomberg, *ibid.*, **5**, 372 (1951).

sorption peaks exhibited by these samples. The equation for the linear portion of the curve from these data is: λ (Å.) = − 3387x + 7488, where λ (Å.) is the position of the absorption peak at composition x. The deviation from linearity for measured points in this region results in an error in x of approximately ±0.015. The extrapolation of the linear portion of the line to $x = 1.00$ would indicate that the absorption peak for $NaWO_3$ would lie at 4100 Å., if the linear relationship continues to hold.

Since these bronzes have been considered as solid solutions of tungsten(VI) oxide in the hypothetical $NaWO_3$,[8] attempts were made to treat them as such solutions. We were, however, unable to fit the absorption data to a standard Beer's Law treatment or a reasonable deviation therefrom.

A more recent model of these bronzes is of sodium dissolving in tungsten(VI) oxide with the subsequent formation of sodium ions and an electron gas within the tungsten(VI) oxide lattice. This view is based on the results of magnetic susceptibility,[19,20] Hall effect[21] and conductivity[21,22] measurements. The bronzes have a number of properties similar to those of metals like copper: *viz.*, high conductivity, low magnetic susceptibility, metallic luster and resistance to chemical attack. Considering these similarities, the bronzes were treated as typical metals in an attempt to account for the absorption spectra. In the absorbing region for metals containing perfectly free electrons, the equation: $I_r/I_i = 1\text{-}2(\nu/\sigma)^{1/2}$ will hold,[23] where I_i is the incident light intensity, I_r the reflected intensity, ν the frequency and σ the conductivity (in e.s.u.). The absorption spectra of the bronzes approach the theoretical curve at the limits of measurement in the infrared, but the data are not sufficiently complete to justify the defining of the limits of the true absorption region in this material. It appears that reflectance from the powdered samples is too complex to be simply related to their metallic behavior.

6. **Vapor Phase Reaction. Sample Preparation.**—"Y" tubes with arms approximately 3 inches long were prepared from Pyrex or Vycor tubing. Tungsten(VI) oxide or a sodium bronze was placed in one arm, and bright sodium metal was placed in the other. The "Y" tube was then evacuated, flushed with argon, re-evacuated and finally sealed *in vacuo*. The tubes were placed in a constant temperature furnace and heated at 500 to 650° for various lengths of time. The tubes were allowed to cool slowly in the furnace, while distillation of the sodium metal to the arm containing the sample was avoided by placing the tube so the sample was always at a slightly higher temperature than the arm containing the sodium metal.

The solubility of sodium vapor in tungsten(VI) oxide or sodium bronze has been reported, and in fact, has been used to prepare the bronze.[8] Because of the empirical addition of sodium by this method, the temperature and reaction time required for the formation of high sodium content bronzes cannot be determined. This method still remains as the most promising way of obtaining the end member $NaWO_3$.

With the majority of the samples, an X-ray powder pattern indicated the presence of tungsten(VI) oxide, tetragonal bronze or violet cubic bronze (resulting from too little sodium entering the lattice), or else gave the pattern of α-tungsten (complete reduction of tungsten(VI) oxide to the metal). In some cases, however, lines of tungsten(IV) oxide and other reduced tungsten oxides were observed.

One sample, prepared at 520° for 120 hours, resulted in a deep blue product with a bright yellow nodule on top. On opening the tube, this yellow nodule ignited spontaneously on contact with the air. No definite compound could be identified from the powder pattern of the residue, the very broad and diffuse diffraction lines indicating extremely small particle size. It is improbable that this material ignited because it contained free sodium which had distilled over, as the tube was free of any trace of a sodium mirror before opening.

It is possible that the bright yellow compound was a bronze of composition approaching $NaWO_3$, which may be unstable in the presence of moisture or oxygen. Attempts to duplicate this experiment in sealed capillaries, so the products could be subjected to X-ray analysis without exposure to air, have been unsuccessful.

7. **Single Crystal Growth.**—An investigation into the growth of large single crystals of the sodium tungsten bronzes was initiated in order to obtain suitable samples for conductivity measurements.[22] The use of tin metal to reduce a tungstate melt[4] was investigated. For this purpose, tin was placed in a non-porous porcelain tube and covered with a column of sodium tungstate. A layer of tungsten(VI) oxide was added at the top, so it could diffuse slowly to the reaction surface, and the tube placed in a vertical tube furnace at 750°. The largest crystal obtained measured 8.8 × 8.0 × 7.9 mm. However, on cleaving this sample, it proved to be an oriented polycrystal. In general, crystals grown by this method contained occluded material and reduction products such as tin oxide, and the use of this method was discontinued.

The recrystallization of sodium tungsten bronzes from molten sodium tungstate[9] yielded smaller crystals than the tin reduction method. Although the crystals obtained were free of occluded tungstates and tin oxides, they contained some metallic tungsten and had a tendency toward excessive twinning, even with slow cooling from 1100 to 700° over a period of days.

A study of electrolytic reduction methods[7] was made, and suitable crystals up to 12 mm. on an edge were grown. A mixture of sodium tungstate and tungsten(VI) oxide in a porcelain crucible was fused and electrolyzed (platinum electrodes) at an e.m.f. of 4.0 volts, with the cathode at the bottom of the crucible. The ratio of sodium tungstate to tungsten(VI) oxide was varied. The current density at the cathode was varied between 0.025 and 0.76 amp./cm.^{2} and the temperature was kept constant between 750 and 850°. Some qualitative conclusions can be drawn from the data.[24] The sodium content of the resulting bronzes increases with increasing ratios of sodium tungstate to tungsten(VI) oxide. Both the size of the crystals and their perfection seem to be improved with lower current density or higher temperatures.

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[23] F. Seitz. "The Modern Theory of Solids," McGraw-Hill Book Co., New York, N. Y., 1940, eq. (36), p. 640.

[24] This is an extension of the preliminary work done by A. Greenberg, B.S. Thesis, Polytechnic Institute of Brooklyn, 1952, unpublished.