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The Preparation and Properties of a Barium Tungsten Bronze[1]

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A series of barium tungsten bronzes, Ba_xWO_3 ($0 < x < 0.13$), has been prepared by reaction of $BaCl_2$, WO_2, and WO_3 at 1000°. The chemical and electrical properties are similar to those of the alkali metal bronzes. Structural data indicate a unit cell like that of the tetragonal potassium tungsten bronze. Mixed sodium–barium tungsten bronzes, $Na_xBa_yWO_3$, where $0 < y < 0.16$ and $0 < (x + y) < 0.46$, were prepared by reducing fused mixtures of Na_2WO_4, $BaWO_4$, and WO_3 with W metal or with WO_2 at 900–1100°.

Introduction

Although tungsten bronzes, M_xWO_3 (M is a metal and $0 < x < 1$), containing each of the alkali metals have been prepared, alkaline earth tungsten bronzes have not been reported in the modern literature. Hallopeau[2] reported the preparation of a product resembling a bronze and Engels[3] described some mixed alkali metal–barium metatungstates. All attempts to repeat the Hallopeau procedure, which consists of the reduction of barium paratungstate at "red heat," yielded only mixtures of $BaWO_4$, W metal, and a product similar to the α and β tungsten oxides studied by Magnéli.[4] We now report the preparation of a tetragonal barium tungsten bronze, Ba_xWO_3, by the reaction of $BaCl_2$, WO_2, and WO_3 at 700–1000°. The assumed stoichiometry of the reaction is

$$xBaCl_2 + xWO_2 + WO_3 \longrightarrow Ba_xWO_3 + xWO_2Cl_2(g) \quad (1)$$

In addition a mixed sodium–barium bronze, $Na_xBa_yWO_3$, was prepared by the reduction with W metal or WO_2 of melts containing Na_2WO_4, $BaWO_4$, and WO_3 at *ca.* 1000°.

Experimental

Materials.—The WO_3 was obtained from Sylvania Chemical and Metallurgical Division (Grade TO-2), and tungsten (99.99% powder) was obtained from A. D. Mackay, Inc. All other chemicals were of reagent grade. WO_2 was prepared by the reaction of W and WO_3 at 950° under purified argon. Commercial grade argon was purified by passage through a train consisting of (1) a 50-cm. column of copper deposited on Filter Cel[5] and held at 200° and (2) a 30-cm. column of Linde Type 4A Molecular Sieve.

Preparation of Ba_xWO_3.—Anhydrous $BaCl_2$, WO_2, and WO_3 were ground together in a mortar. The mixture was packed in a recrystallized alumina combustion boat and heated at 900° for 15 hr. under vacuum (10^{-6} torr) or under purified argon. The product consisted of fine needle crystals having a red-violet metallic luster. A yellow-green deposit of the volatile tungsten oxides and oxychlorides was formed on the cold portion of the Vycor combustion tube. The crystals were purified by heating at 90° in a 10% oxalic acid solution for 6 hr. to remove $BaWO_4$ (a 3 *M* H_3PO_4 solution is also effective in dissolving $BaWO_4$), followed by boiling in 6 *M* NH_3 and washing with 48% aqueous HF.

Preparation of $Na_xBa_yWO_3$.—Mixtures of Na_2WO_4, $BaWO_4$, and either W metal or WO_2 were treated at 900–1100° in a manner analogous to the Ba_xWO_3 preparation. The product in each case was a mass of intergrown crystals as large as 5 mm. on an edge. The product was purified in the same manner as the Ba_xWO_3 preparation above.

Analysis.—Both the Ba_xWO_3 and the $Na_xBa_yWO_3$ preparations were analyzed by heating weighed samples in a stream of dry HCl at 550° for 5–6 hr. Under these conditions tungsten and oxygen are volatilized as oxychlorides of tungsten, leaving NaCl and/or $BaCl_2$ as a residue in the combustion boat. The chloride residue was dissolved in water, and barium and sodium were estimated by flame photometric analysis. The standard solution contained, in addition to Na and/or Ba, all of the components of the analysis mixture in concentrations within 0.5% of those present in the unknown. Total chlorine was determined by titration with $AgNO_3$ (Volhard). Tungsten could be estimated by the weight loss of the samples. As an additional check on the barium content, a sample of $Ba_{0.05}WO_3$ was analyzed for barium by fast neutron activation analysis[6] and these results agreed within ±0.2% for the barium content, an agreement within ±0.003 in x for this composition. Because of the extremely low solubility and inertness of $BaWO_4$, solution methods of determining tungsten yielded very poor accuracy.

X-Ray Crystallographic Data.—Powder diffraction data were recorded by both photographic and diffractometer methods. Single crystal rotation and zeroth-layer Weissenberg photographs were utilized for initial symmetry determinations. Cu Kα radiation was used throughout. Densities were determined pycnometrically, using water as the fluid.

Electrical Measurements.—Electrical resistivities were measured as a function of temperature by a potential probe method described previously,[7] and Seebeck coefficients were measured under argon with an apparatus similar to that described by Sienko.[8] All measurements were referred to Cu.

Magnetic Susceptibility.—Susceptibilities were measured on powdered samples using the Gouy method. Samples were contained in a double-chambered tube having the lower chamber evacuated, and a nitrogen atmosphere was maintained around the sample during the measurements. $HgCo(SCN)_4$ was employed as the standard.

Results and Discussion

Ba_xWO_3.—Under the conditions of synthesis employed thus far the upper limit of the solubility of barium in the WO_3 lattice corresponds to the composition $Ba_{0.13}WO_3$. The use of an excess of $BaCl_2$ resulted only in the loss of more tungsten as oxychlorides and a smaller yield of bronze. The crystals obtained by this technique are small, averaging about 1 mm. in

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[2] L. A. Hallopeau, *Ann. Chim. Phys.*, **19**, 122 (1900).

[3] E. Engels, *Z. anorg. Chem.*, **37**, 136 (1903).

[4] A. Magnéli, *Arkiv Kemi*, **1**, 223, 513 (1949).

[5] F. R. Meyer and G. Ronge, *Angew. Chem.*, **52**, 637 (1939).

[6] We are indebted for this analysis to Miss Margaret Wechter and Prof. G. C. Danielson of the Ames Laboratory, Iowa State University.

[7] W. McNeill and L. E. Conroy, *J. Chem. Phys.*, **36**, 87 (1962).

[8] M. J. Sienko, *J. Am. Chem. Soc.*, **81**, 5556 (1959).

length and 0.2 mm. in thickness. Compositions corresponding to $0 < x < 0.13$ were produced by equilibrating $Ba_{0.13}WO_3$ with the appropriate amount of WO_3 at 1000° *in vacuo* or under argon. The products range in color from a metallic red-violet luster for larger x values to dark green for the barium-dilute specimens.

The crystallographic data indicate a single phase having a tetragonal unit cell similar to that in the tetragonal potassium[9] and sodium[10] tungsten bronzes. The lattice parameters are reported in Table I. Pycnometric densities of *ca.* 7.12 g./cm.^{3} are consistent with a unit cell containing ten $Ba_{0.12}WO_3$ formula units, similar to the sodium and potassium tetragonal bronzes. The chemical properties of this system of solid solutions are closely similar to those of the alkali metal bronzes, which are notable for their resistance to chemical attack by all common reagents except strong alkali solutions or melts. Boiling H_2SO_4, HCl, HNO_3, or aqua regia produced negligible attack in 4 hr., and no detectable reaction occurred with concentrated NH_3 or 48% HF at room temperature. NaOH (5%) at 100° produced gradual attack and fused NaOH or Na_2CO_3 reacted still more vigorously. Upon heating above 1150° *in vacuo* the bronze decomposes to $BaWO_4$, W, and WO_2. Heating to the same temperature in air yields $BaWO_4$ and WO_3.

TABLE I

UNIT CELL PARAMETERS

Formula	a, Å.	c, Å.	V, Å.^{3}	Ref.
Tetragonal Barium Tungsten Bronzes				
$Ba_{0.12}WO_3$	12.16	3.843	568.4	
$Ba_{0.11}WO_3$	12.15	3.840	566.8	
$Na_{0.33}Ba_{0.10}WO_3$	12.12	3.834	563.2	
$Na_{0.23}Ba_{0.08}WO_3$	12.05	3.819	554.5	
Other Tetragonal Bronzes				
$Na_{0.28}WO_3$	12.094	3.748	548.2	10
$K_{0.48}WO_3$	12.285	3.833	578.5	9
$Pb_{0.35}WO_3$	12.207	3.782	563.6	a

[a] R. A. Bernoff and L. E. Conroy, *J. Am. Chem. Soc.*, **82**, 6261 (1960).

Attempts to repeat the preparative procedure of Hallopeau,[2] consisting of the reduction of barium paratungstate with hydrogen at 700–1200°, produced only mixtures of products. Powder X-ray photographs of these products showed only the presence of metallic W, $BaWO_4$, and an unidentified product with a structure similar to that of the lower tungsten oxides reported by Magnéli.[4]

Mixed Sodium–Barium Bronze.—Attempts to produce larger crystals of Ba_xWO_3 by chemically reducing melts containing both $BaWO_4$ and Na_2WO_4 resulted instead in the production of a mixed sodium–barium bronze $Na_xBa_yWO_3$, where $0 < y < 0.12$ and $0 < (x + y) < 0.46$. All products exhibited the characteristic metallic luster of the alkali metal tungsten bronzes and ranged in color from orange to red, dependent upon the composition. Individual crystals were typically rectangular solids up to 7 mm. on an edge. Table I lists two of the compositions which were obtained from various mixtures of the sodium and barium tungstates. Crystallographic data on the various products indicated two different phases. Melts in which the Na:Ba atom ratio did not exceed 3:1 produced only a tetragonal phase with lattice parameters not greatly different from those of the other tetragonal bronzes, as can be noted in Table I. This phase apparently corresponds to that reported by Engels.[3] Melts rich in Na_2WO_4 yielded both cubic and tetragonal crystals, and in those melts in which the Na:W atom ratio exceeded 4:1 only a cubic phase resulted. The cubic-phase lattice constant is 3.840 Å., almost identical with that of $Na_{0.7}WO_3$, and the barium content is less than 0.013 atom of Ba per mole of WO_3. Thus barium is present essentially as an impurity in a sodium bronze. This behavior is reminiscent of that reported by Brimm and co-workers[11] for mixed Na–K tungsten bronzes in which case tetragonal crystals containing both sodium and potassium were found, but the cubic phase contained only sodium. As indicated in Table I, both lattice parameters of the tetragonal phase increase with increasing barium content, the c axis showing the greater change.

Electrical and Magnetic Properties.—The plots of ρ *vs.* T (Figure 1) show typically metallic conductivity behavior in both the tetragonal barium bronze (c axis) and the sodium–barium bronze. The data on the barium bronze show more scatter, primarily because of the difficulty of maintaining good current probe contacts on such small crystals. Both samples appeared to be quite homogeneous as measured by the fact that changing the potential probe positions produced no measurable change in the precision of the measurements, so that crystal imperfections, such as were noted by Danielson and co-workers,[12] were not a problem. Typical values at 25° are for $Ba_{0.12}WO_3$ $\rho = 1.53 \times 10^{-4}$ ohm cm. and $1/\rho\ d\rho/dT = 8.0 \times 10^{-4}$, and for $Na_{0.33}Ba_{0.10}WO_3$ $\rho = 2.4 \times 10^{-4}$ ohm cm. and $1/\rho\ d\rho/dT =$

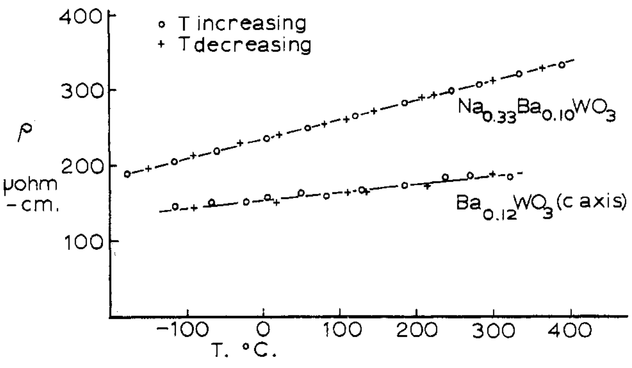

Figure 1.—Electrical resistivity as a function of temperature for a barium tungsten bronze and a sodium–barium tungsten bronze.

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(9) A. Magnéli, *Arkiv Kemi*, **1**, 213 (1949).

(10) A. Magnéli, *ibid.*, **1**, 269 (1949).

(11) B. O. Brimm, J. C. Brantley, J. H. Lorenz, and M. H. Jellinek, *J. Am. Chem. Soc.*, **73**, 5427 (1951).

(12) L. D. Ellerbeck, H. R. Shanks, P. H. Sidles, and G. C. Danielson, *J. Chem. Phys.*, **35**, 298 (1961).

1.1×10^{-3}. Thus both the resistivities and temperature dependences are of the same magnitude as in the sodium tungsten bronzes.[13] The Seebeck coefficients (Figure 2) are negative and of magnitudes typical of other known tungsten bronzes. The magnetic susceptibility for $Ba_{0.12}WO_3$ was $\chi_M = +20.0 \times 10^{-6}$ at 25° and was temperature and field independent over the range 190 to 400°K. and 0 to 12 kgauss. A Pauli–Peierls calculation of an electronic susceptibility per unit volume yields a value of $\kappa = 1.2 \times 10^{-6}$ c.g.s. unit, so that the effective mass ratio $m^*/m_0 \approx 3$, where m_0 is the electron rest mass. Attempts to measure the Hall coefficients of either $Ba_{0.12}WO_3$ or $Na_{0.33}Ba_{0.10}WO_3$ by a d.c. method were unsuccessful, and only an upper limit of the Hall voltage, $V_H < 6 \times 10^{-7}$ volt, could be established. A better evaluation awaits the results of our a.c. Hall voltage measurements.

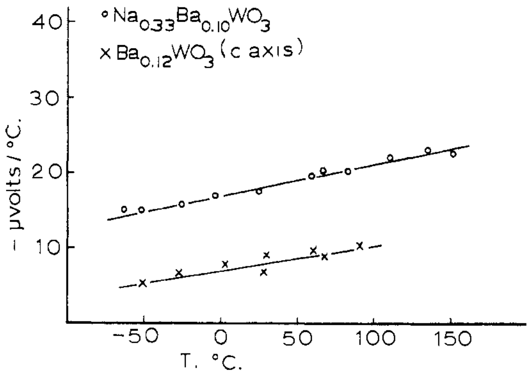

Figure 2.—Seebeck coefficient as a function of temperature for a barium tungsten bronze and a sodium–barium tungsten bronze.

The properties of the barium bronze system are thus in all respects remarkably similar to those of the alkali metal tungsten bronzes. The thallium[14] and lead[15] tungsten bronze systems were earlier evidence that elements other than the alkali metals were soluble in the WO_3 lattice, and it is somewhat reassuring to find that the group II metals, which are so similar in size and ionization potential to the alkali metals, fall into line. The great obstacle in the path of facile synthesis of the alkaline earth solid solutions is the extreme thermodynamic stability of the orthotungstates, MWO_4, of these metals which not only rules out their use as reactants to prepare bronzes, but also strongly favors the production of orthotungstates from almost any combination of tungsten, oxygen, and alkaline earth metal atoms. The halide method perhaps succeeds because an oxidation–reduction reaction occurs first between WO_2 and $BaCl_2$, and then the barium diffuses into the WO_3 lattice. The reaction between Ba metal and WO_3 is very exothermic

$$3Ba + 4WO_3 \longrightarrow 3BaWO_4 + W \quad \Delta H = -419.7 \text{ kcal.} \quad (2)$$

$BaCl_2$ and WO_2 will also react

$$BaCl_2 + 3WO_2 \longrightarrow BaWO_4 + W + WO_2Cl_2(g) \quad (3)$$

and it is this reaction which takes place in the synthesis mixture at temperatures above ~1200° or with a large excess of $BaCl_2$. Both reactions 2 and 3 apparently have high activation energies and can be circumvented by lower temperatures and low concentrations of barium. That this halide method may have more general utility for the preparation of WO_3 solid solutions is indicated by our recent success in preparing solid solutions of strontium in WO_3. There is evidence that the bromides or iodides may be even more convenient for this purpose.

The magnitudes of the resistivity, Seebeck coefficient, and magnetic susceptibility of Ba_xWO_3 indicate mobilities and effective masses characteristic of electrons which are in relatively wide conduction bands. A calculation of the electron mobility in $Ba_{0.12}WO_3$ yields a value of 19.8 cm.^{2} volt^{-1} sec.$^{-1}$ if one conduction electron per Ba atom is assumed and 9.9 cm.^{2} volt^{-1} sec.$^{-1}$ if two conduction electrons per Ba atom are assumed. Both of these values are within the range of mobilities found for the alkali metal tungsten bronzes. Apparently Hall voltage measurement will be necessary to establish the electron : Ba ratio.

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[13] For a summary see M. J. Sienko in "Nonstoichiometric Compounds," R. Ward, Ed., Advances in Chemistry Series, No. 39, American Chemical Society, Washington, D. C., 1961.

[14] M. J. Sienko, *J. Am. Chem. Soc.*, **81**, 5556 (1959).

[15] R. A. Bernoff and L. E. Conroy, *ibid.*, **82**, 6261 (1960).