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Lead Tungsten Bronzes[1]

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A series of crystalline lead tungsten bronzes, Pb_xWO_3 ($x \leqslant 0.35$), has been prepared. The lead-rich members of the series exhibit metallic electronic properties. The chemical and physical properties indicate that this system of nonstoichiometric compounds is analogous to the alkali metal tungsten bronzes. A method of oxygen analysis for these compounds is reported.

Tungsten trioxide is known to form solid solutions or "tungsten bronzes" with all of the alkali metals. These nonstoichiometric ternary compounds, M_xWO_3 (M an alkali metal and $0 < x < 1$), characteristically show metallic electronic properties, such as luster and high electrical conductivity. The chemical properties are essentially similar to those of WO_3 itself. Reports of tungsten bronzes containing metals other than the alkali metals are exceedingly few. Only a thallium bronze reported by Sienko[3] and possibly a barium bronze[4] exhibit the typical bronze properties. This paper reports the preparation and properties of a series of solid solutions of lead in WO_3, which series shows many similarities to the alkali metal tungsten bronzes.

Experimental

Materials.—Tungsten trioxide (TO-2 grade) and tungstic acid (TA-2 grade) were obtained from the Sylvania Tungsten and Chemical Division. Tungsten metal was obtained from A. H. Thomas Co. as 99.9% purity powder, and carbon in the form of spectrographic electrodes was obtained from National Carbon Co. All other chemicals used in this work were of reagent grade.

Preparation of $PbWO_4$.—$PbWO_4$ was prepared by making a water slurry of $(PbCO_3)_2 \cdot Pb(OH)_2$ (77.6 g., 0.1 mole) and H_2WO_4 (75 g., 0.3 mole) and, with constant stirring, evaporating the slurry to dryness on a steam bath. The product was washed with hot water, dilute aqueous NH_3, again with hot water and dried at 120°. The final product was a white powder which melted above 1200°. The powder X-ray pattern corresponded to that tabulated for $PbWO_4$ in the A.S.T.M.-N.B.S. file.

Preparation of WO_2.—Tungsten metal powder and WO_3 were mixed together in a molar ratio of 1:2, sealed *in vacuo* in a Vycor tube and heated to 1150° for 2 hr. The product was a brown powder, the powder X-ray pattern of which established it as WO_2.

Preparation of Pb_xWO_3.—Three methods were successful. Method 1: A 1:1 molar mixture of $PbWO_4$ and WO_3 was heated with graphite in a covered porcelain crucible at 1200° for 15 minutes, then cooled to 400° at the rate of 6°/hr. These reactions were carried out in air, since the use of inert atmosphere produced no significant improvement in product or yield. Apparently, oxidation of graphite to CO_2 in the melt provided an inert blanket.

Method 2: Mixtures of $PbWO_4$, WO_3 and WO_2 of various proportions were heated in evacuated, sealed Vycor tubes to 1150°, then cooled to 400° at a rate of 6°/hr. At this point the furnace power was cut off, and the sample was allowed to cool to room temperature overnight Lower cooling rates also were employed, as low as 2°/hr., without significant effect on the compositions or crystal size of the products.

Method 3: Mixtures of $PbCO_3$, WO_3 and WO_2 of various proportions were heated to 1200° in covered porcelain crucibles under an atmosphere of CO_2 for 2 hr., then cooled to room temperature in about 4 hr.

After each preparation the products were purified by the procedure to be described. The solidified reaction mixture was broken up in a mortar and treated for ten-minute periods alternately with 50% HNO_3 and 20% KOH solutions at the boiling point, until further treatment with HNO_3 gave no evidence of H_2WO_4 precipitation. The crystalline product was allowed to remain under aqueous 48% HF for 15 hr. at room temperature. Successive treatment at the boiling point with 28% NH_3, 50% HNO_3, 20% KOH, again 50% HNO_3 and water followed. The crystals were dried for 12 hr. at 110°.

Recrystallization.—It was found possible to increase the size and perfection of the lead bronze crystals by recrystallization in contact with excess $PbWO_4$. The procedure was an adaptation of that of Straumanis.[5] Crystals of Pb_xWO_3 were mixed with a large excess of $PbWO_4$, heated to 1150° *in vacuo* or under CO_2 and cooled at 2°/hr. to 400°, at which point the furnace power was cut off This technique produced crystals, usually of slightly higher lead content than the original crystals, up to 3 mm. in length and 1 mm.^{2} in cross section. Most of the crystals employed in the measurement of electrical conductivity were grown by this method.

All of the above high-temperature preparations were carried out in electric crucible furnaces controlled by a Wheelco Chronotrol temperature regulator.

Analysis of Lead Tungsten Bronzes.—Two methods of analysis were employed. In Method 1, a finely powdered sample was fused with a mixture of $NaNO_3$ (67%) and Na_2CO_3 (33%) in a porcelain crucible. The cooled melt was dissolved in water, and the solution was made acid with HCl to dissolve lead oxide, then made basic (0.6 *M*) with NaOH to dissolve $PbWO_4$. Lead was then determined electrolytically as the metal deposited on a platinum gauze cathode, and tungsten was determined gravimetrically as tungstic acid, employing the tannin–cinchonine precipitation.[6] On samples of known composition, this procedure yielded lead values which were about 0.5% high.

Method 2 was developed to provide a direct determination of each element in the bronze. Finely powdered 0.2–0.5 g. samples were reduced with purified hydrogen gas at *ca.* 800° until no further loss of weight could be observed. The water produced was absorbed in Dehydrite and weighed. Oxygen was thus determined both on the basis of weight lost by the sample and weight of water produced. The reduced sample, a mixture of lead and tungsten, was then heated in a stream of pure oxygen at 800° for 15 hr. The oxidation products, as established by the powder X-ray diffraction pattern, were $PbWO_4$ and WO_3. From this stoichiometry and the weights of the reduced and oxidized sample, the Pb and W percentages were calculated. On samples of known composition, this method produced results within 1% of theoretical for Pb (high) and W (low) and within 0.5% for oxygen. Where samples as large as one gram were available for analysis, the accuracy of the method was increased approximately fivefold.

Electrical Conductivity Measurements.—Reasonably well-formed prismatic crystals of the tetragonal $Pb_{0.17}WO_3$ were selected for conductivity measurements. The experimental crystal was mounted under spring-loading between indium-faced brass blocks, which served as current contacts, with the long crystal axis (c axis) parallel to the direction of current flow (see Fig. 1). Potential probes, consisting of

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(3) M. J. Sienko, THIS JOURNAL, **81**, 5556 (1959).

(4) L. A. Hallopeau, *Ann. Chim. Phys.*, **19**, 122 (1900).

(5) M. E. Straumanis, THIS JOURNAL, **71**, 679 (1949).

(6) F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1937, p. 226.

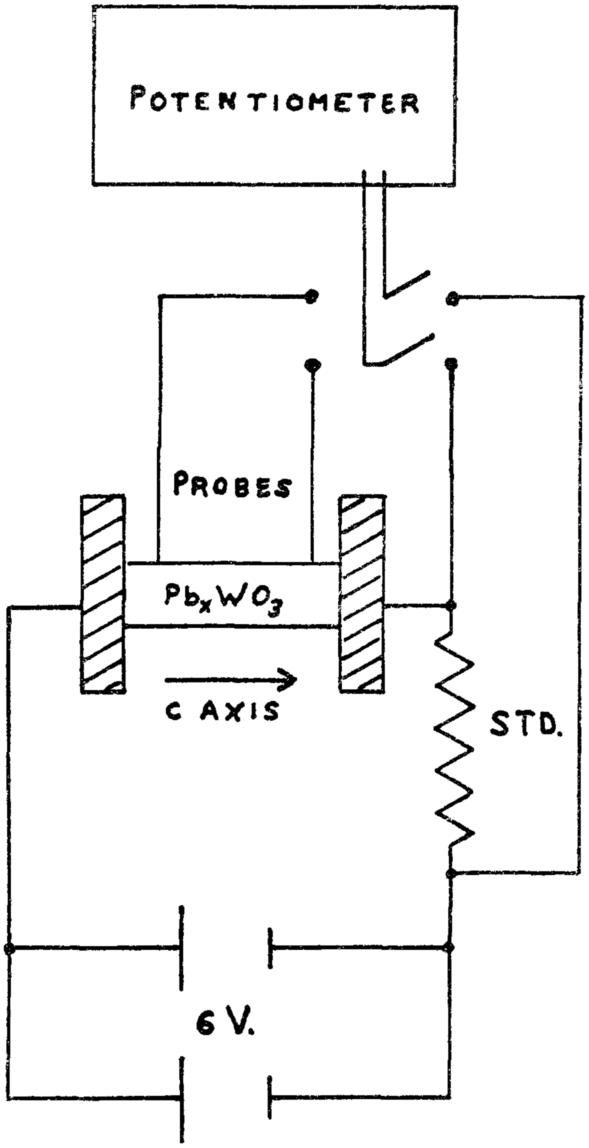

Fig. 1.—Resistivity apparatus.

sharpened 5 mil tungsten wires, were spring-loaded in contact with one crystal face along a line parallel to the c axis. The potential drop across the probes was measured with a Leeds and Northrup Type K-2 potentiometer. The current through the crystal was supplied from lead-acid storage batteries and was monitored by observing the potential drop across a standard resistance in series with the crystal. The crystal and contacts were enclosed in a cylindrical copper chamber which in turn was supported inside of a Dewar flask. Temperature control was maintained by the method of Ure,[7] which employs an electrical resistance heater and liquid nitrogen cooling. The temperature of the crystal was measured with a thermocouple mounted beside it within the copper chamber. During resistance measurements, an atmosphere of dry nitrogen gas was maintained within the chamber. Crystal dimensions were taken with the aid of a microscope fitted with a micrometer eyepiece.

Attempts to make electrical contacts to the crystals by fusing platinum wires to the faces were unsuccessful. Although the wire appeared to weld to the crystal surface, the region around the weld would always fracture upon cooling. Evaporated silver or platinum films were not adherent to these crystals, and silver or graphite dispersion pastes were found to have too high resistances to be useful as contacts in this work.

Thermoelectric Power Measurements.—The thermoelectric power, or Seebeck coefficient, was determined on two lead bronze preparations of different compositions. A powdered sample was compressed between spring-loaded copper rods 1″ in diameter. A 10° temperature difference was maintained across the sample, and the potential difference across the sample was measured with a Type K-2 potentiometer, employing copper contacts to the crystal. Copper-constantan thermocouples were utilized for temperature measurement. An indication of the accuracy of this procedure is the fact that measurements on samples of powdered semiconductors yielded values within 10% of the single crystal values for the thermoelectric power.

X-Ray Data.—Powder X-ray diffraction photographs were recorded with copper K α radiation using an 11.46 cm. diameter camera. Because of some difficulty encountered in indexing the powder photographs, single crystal photographs were also obtained. Crystals were selected from the preparation of $Pb_{0.17}WO_3$ used in the conductivity measurements, which preparation contained the externally most perfect crystals obtained in this work. Rotation and zero-layer equi-inclination Weissenberg photographs were taken with filtered copper radiation.

Results

Fourteen different solid solutions of lead in tungsten trioxide were prepared and characterized. Table I lists the analysis data for the preparations which were completely analyzed by the hydrogen reduction method. For the other preparations, only lead and tungsten analyses were performed, and their analyses are not included. The substances synthesized in this work varied in Pb:W atom ratio from 0.037:1 to 0.35:1. Oxygen analysis of samples throughout this series indicated a W:O atom ratio of 1.00:3.07 ± 0.04. It is therefore justifiable to formulate these substances as Pb_xWO_3 where $0 < x < 0.35$, in analogy with the alkali metal tungsten bronzes. The products were crystals ranging in color from dark green in the dilute (lead-poor) samples through dark blue, metallic blue and finally to metallic blue-violet in the most concentrated samples. All were quite brittle, with the lead-rich samples appearing to possess greater hardness than the dilute samples. Those crystals having a metallic luster were opaque to visible light, even in very thin sections, whereas the nonlustrous dilute crystals appeared green or blue-green by transmitted light.

Table I

Composition of Lead Tungsten Bronzes

Pb, wt. %	O, wt. %	W, wt. %	Formula
3.7	20.1	76.1	$Pb_{0.043}WO_3$
4.7	19.9	75.4	$Pb_{0.055}WO_3$
4.8	20.1	75.2	$Pb_{0.057}WO_3$
7.9	19.5	72.6	$Pb_{0.095}WO_3$
13.3	18.6	68.1	$Pb_{0.17}WO_3$
13.9	18.8	67.3	$Pb_{0.17}WO_3$
18.6	16.9	64.5	$Pb_{0.26}WO_3$
23.6	16.2	60.2	$Pb_{0.45}WO_3$

X-Ray Studies.—The single crystal and powder data on $Pb_{0.17}WO_3$ indicated tetragonal symmetry with the lattice parameters $a = 12.16_3$ Å. and $c = 3.767$ Å. Using the rather crude pycnometric density of 7.82 g./cc., a unit cell containing ten stoichiometric molecules is indicated for this composition. The powder diffraction patterns of the other compositions indicate that the tetragonal symmetry is maintained over the range of composition $0.16 \leqslant x \leqslant 0.35$. Within this range there is a

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(7) R. Ure, Jr., *Rev. Sci. Instruments*, **28**, 836 (1957).

gradual increase in both lattice parameters with increase in x, the a parameter shifting only slightly from *ca.* 3.77 Å. at $x = 0.17$ to *ca.* 3.78 Å. at $x = 0.35$ and c increasing from *ca.* 12.16 Å. at $x = 0.17$ to *ca.* 12.21 Å. at $x = 0.35$. The lead-poor samples having $x < 0.057$ produced a powder pattern virtually identical with that of pure (monoclinic) WO_3. In the composition range $0.057 < x < 0.16$, a gradual transition of the monoclinic structure to a pseudotetragonal structure was evident. In general, the tetragonal phases exhibited a definitely metallic luster, whereas the monoclinic phases had a much duller cast.

Chemical Properties.—The chemical properties of lead bronzes are very similar to those of the alkali metal tungsten bronzes and therefore are similar to those of WO_3. The crystals were unaffected by contact with boiling concd. HNO_3 or H_2SO_4 for several hours. Boiling with concd. HCl or H_3PO_4, aqua regia, dilute HNO_3, H_2SO_4, HCl, H_3PO_4 or HF caused only slight (0.2–1.9 %) losses in weight in 2 hr. Boiling aqueous NH_3 produced only slight attack (1% weight loss in 2 hr.), but boiling 3 *M* NaOH or KOH decomposed the crystals within 2 hr., leaving a residue of Pb and a clear supernatant liquid. Fused NaOH, KOH, Na_2CO_3 or K_2CO_3 slowly decomposed the crystals, and fused alkali hydroxides or carbonates mixed with $NaNO_3$ rapidly converted the crystals to lead oxides and the alkali metal tungstates.

Powder X-ray diffraction photographs of samples which had been heated to various temperatures in air indicated that the crystals were unaffected at temperatures up to 620°. At 660° the crystals had partially reacted, and at 690° they were rapidly converted to a mixture of $PbWO_4$ and WO_3. Reaction was indicated by loss of metallic luster and change in color from blue to dull gray-green. Heating to temperatures above 620° *in vacuo* or under argon decomposed the crystals to metallic Pb and WO_3.

Electrical Conductivity.—Electrical resistivity measurements on crystals of $Pb_{0.17}WO_3$ yielded a mean resistivity of $6 \pm 1 \times 10^{-4}$ ohm cm. at 25° and, at temperatures above 0°, showed a linear increase of resistivity with temperature typical of thermal scattering in metals.

Thermoelectric Power.—The thermoelectric power or Seebeck coefficient was found to be -0.014 millivolt per degree for $Pb_{0.26}WO_3$ and -0.135 millivolt per degree for $Pb_{0.055}WO_3$, both values having been corrected for the thermoelectric power of the copper leads and both being referred to copper. (For reference to platinum, both values must be corrected by $+0.0076$ millivolt per degree.)

Discussion

The preparation of this series of non-stoichiometric compounds of lead in WO_3, which exhibits properties typical of the alkali metal tungsten bronzes, is another significant indication that such systems are not confined to the alkali metals or even to the nominally monovalent elements. As in the case of the alkali metal systems, the factors governing the range of solubility of the metal in WO_3 are not at all apparent. Only sodium exhibits complete, or nearly complete, miscibility, the upper limits for x in the potassium system being 0.5–0.6 and in the other alkali metal systems being 0.3–0.4. In all of the known cases, the addition of metal atoms to WO_3 distorts the oxide lattice toward a higher symmetry, as high as cubic in the cases of sodium and lithium, tetragonal or hexagonal in the case of potassium, hexagonal in the cases of rubidium, cesium and thallium and tetragonal in this case of lead.

The unit cell dimensions of the tetragonal lead bronze phases are very close to those of the tetragonal sodium[8] and potassium[9] bronzes, as can be noted from the comparison in Table II.

TABLE II

UNIT CELL PARAMETERS OF SOME TETRAGONAL TUNGSTEN BRONZES

Composition	a (Å.)	a (Å.)	V (Å.^{3})
$Na_{0.28}WO_3$	12.094	3.748	548.2
$Na_{0.38}WO_3$	12.102	3.752	549.5
$K_{0.48}WO_3$	12.285	3.833	578.5
$K_{0.54}WO_3$	12.311	3.840	582.0
$K_{0.57}WO_3$	12.317	3.841	582.7
$Pb_{0.17}WO_3$	12.163	3.767	557.3
$Pb_{0.35}WO_3$	12.207	3.782	563.6

The thermoelectric power and the electrical resistivity behavior of the more concentrated ($x > 0.16$) lead bronzes shows them to be electronic conductors, and the lustrous metallic appearance of the crystals is consistent with such conductivity. Utilizing the observed density for $Pb_{0.17}WO_3$ of 7.82 g./cc. and assuming two conduction electrons per Pb atom, one calculates a mobility for the conduction electrons of 2 cm.^{2}/volt sec., a value of the same order of magnitude as the mobility reported for electrons in the sodium bronzes.[10] The chemical inertness and resistance to thermal decomposition is characteristic of the typical tungsten bronzes and probably can be attributed to a high activation energy for diffusion of lead in the WO_3 lattice.[11]

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(8) A. Magneli, *Arkiv Kemi*, **1**, 269 (1949).

(9) A. Magneli, *ibid.*, **1**, 213 (1949).

(10) W. R. Gardner and G. C. Danielson, *Phys. Rev.*, **93**, 46 (1954).

(11) See J. F. Smith and G. C. Danielson, *J. Chem. Phys.*, **22**, 266 (1954), for the activation energy for diffusion in the sodium tungsten bronzes.