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$Cs_{8.5}W_{15}O_{48}$ and CsW_2O_6 : Members of a New Homologous Series of Cesium Tungsten Oxides

R. J. CAVA, R. S. ROTH, T. SIEGRIST, B. HESSEN,*
J. J. KRAJEWSKI, AND W. F. PECK, JR.

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

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The crystal structures of two new reduced cesium tungsten oxides are reported. Along with the previously reported compound $Cs_6W_{11}O_{36}$, they represent several members of a homologous series of layer compounds between the hexagonal tungsten bronze and pyrochlore structure types. The series formula is [A] $Cs_{2n}W_{4n-1}O_{12n}$, where $n - 1$ is the number of pyrochlore layers. © 1993 Academic Press, Inc.

Introduction

The alkali tungsten oxides with the hexagonal tungsten bronze crystal structure are well known oxide superconductors (see, for instance *1–3*). Superconductors of this type are known for A_xWO_3, where A = K, Rb, and Cs, and $0.16 \leq x \leq 0.33$, with T_c's in the range of 1 to 7 K. Although recent years have seen an explosive growth in the number of known copper oxide superconductors, the number of noncuprate oxide superconductors remains relatively small. We therefore investigated the A_2O–WO_2–WO_3 chemical systems, for A = Li, Na, K, Rb, and Cs, to look for previously unreported phases. In the Cs_2O–WO_2–WO_3 system we found the two new phases $Cs_{8.5}W_{15}O_{48}$ and CsW_2O_6, and we report their crystal structures here. Polycrystalline samples of both compounds were found to be nonsuperconducting down to 1.8 K.

Synthesis

Starting materials for investigation of the Cs_2O–WO_2–WO_3 phase diagram were Cs_2WO_4, WO_2, and WO_3. Single phase Cs_2WO_4 was prepared from $CsNO_3$ and WO_3 in air by heating at 550 and 650°C for 1 hr, with intermediate grindings, and then heating at 775°C overnight. Single phase WO_2 was prepared from WO_3 by heating in forming gas (95% N_2–5% H_2) at 500°C for 2 hr and then 700°C for 12 hr. Cs_2WO_4, WO_3, and WO_2 were then mixed and ground in appropriate proportions in 1.5-g 0.5-in. diameter pellets half of which were wrapped in Au foil, put into a closed ended quartz sleeve, and then into an evacuated quartz tube 4 in. in length, 0.5 in. in diameter. Samples were heated for 16–40 hr at temperatures between 700 and 750°C. Reaction was generally complete after the first 16-hr heating. Frosting of the quartz sleeves indicated that some alkali was lost during the reaction. Twenty compositions were studied for Cs_2O contents of 40% and less. Due to the Cs_2O loss we did not determine the true ternary

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* Present address: Shell Laboratory, Postbus 3003, 1003 AA Amsterdam, The Netherlands.

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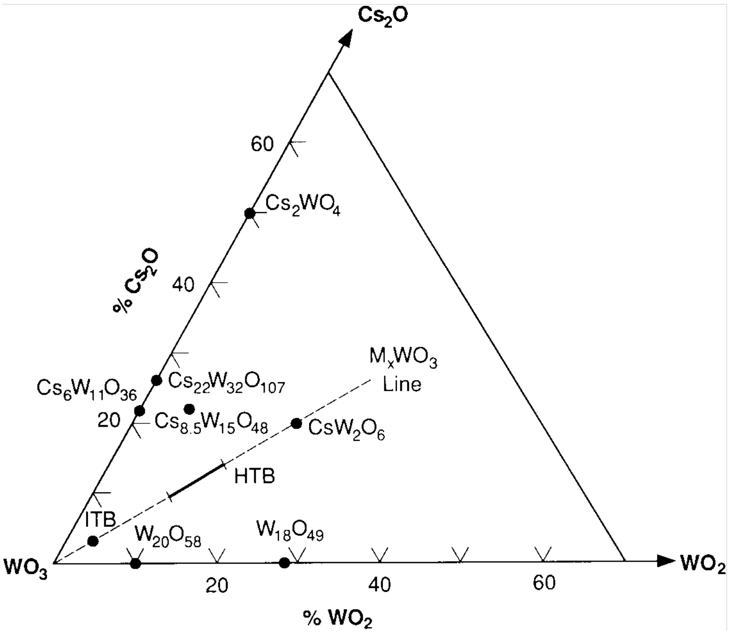

FIG. 1. The compositions of confirmed phases in the Cs_2O–WO_2–WO_3 phase diagram in the vicinity of WO_3. HTB and ITB are hexagonal tungsten bronze and intergrowth tungsten bronze, respectively. The two compounds found in the present study are $Cs_{8.5}W_{15}O_{48}$ and CsW_2O_6.

phase relations, but present a partial diagram showing the compositions of previously known and new phases in Fig. 1. The previously known W^{6+} phases Cs_2WO_4, $Cs_{22}W_{32}O_{107}$ (*4*), and $Cs_6W_{11}O_{36}$ (*5*) are shown, as are the reduced tungsten oxides $W_{20}O_{58}$ and $W_{18}O_{49}$ and the intergrowth (*6*) (ITB) and hexagonal (*2*) (HTB) tungsten bronzes. For compositions WO_2 rich of the M_xWO_3 line, HTB and CsW_2O_6 are in equilibrium with either WO_2 or W metal depending on whether the temperature is below or above approximately 650–700°C. Due to the alkali loss, it was difficult to prepare single phase polycrystalline samples of the new compounds $Cs_{8.5}W_{15}O_{48}$ and CsW_2O_6, which could only be made as large proportions of samples for 10% or more Cs_2O excess compositions. The compositions of both phases were determined by the crystal structure refinements. The small single crystals of $Cs_{8.5}W_{15}O_{48}$ used in the structure refinements were obtained from a sample of composition $Cs_{16}Ba_6W^{6+}{}_{29}W^{4+}{}_3O_{107}$ ($BaWO_4$ was employed as a starting material) held at 800°C overnight. The presence of Ba enhanced crystal growth but careful examination of the crystals by EDX showed that no Ba was included. Nearly single phase polycrystalline pyrochlore type CsW_2O_6 (5% W metal was present) was obtained by heating a mixture of 3 Cs_2WO_4 + 1 WO_3 + 3 WO_2 at 650°C for 60 hr. The resulting powder, which was a mixture of Cs_2WO_4 + CsW_2O_6 + W, was then washed in H_2O to remove Cs_2WO_4 to yield 95% pure CsW_2O_6. This sample was then employed in an X-ray powder Rietveld refinement to determine the crystal structure of CsW_2O_6.

TABLE I

CRYSTALLOGRAPHIC DATA FOR $Cs_{8.5}W_{15}O_{48}$

Formula	$Cs_{8.5}W_{15}O_{48}$
Space group	$R3m$
Crystal size (mm)	0.12 × 0.12 × 0.01
a (Å) (at 23°C)	7.270(1)
c (Å)	73.63(1)
V (Å^3)	3370(2)
Z	3
D_c (g/cm^3)	6.88
μ (Mo$K\alpha$, cm^{-1})	459.2
Minimum transmission	0.091
Maximum transmission	0.692
Scan type	ω
Reflections measured	2280
Independent reflections	1075
Observed reflections ($I > 2.5\sigma(I)$)	708
Refined parameters	58
R	0.037
R_w ($w = 1/\sigma^2(F_0)$)	0.030
Extinction length (μm)	0.62(5)

TABLE IIa

ATOMIC POSITIONAL PARAMETERS AND ISOTROPIC TEMPERATURE FACTORS FOR $Cs_{8.5}W_{15}O_{48}$

	x	y	z	B_{iso} (Å^2)	occ
W 1	0	0	0	0.51(6)	
W 2	0.16811(9)	0.83189	0.040618(14)	0.74(3)	
W 3	1/3	2/3	0.08305(3)	0.58(5)	
W 4	0.50378(9)	0.49622	0.123737(14)	0.56(4)	
CS 1	2/3	1/3	0.07138(5)	1.93(10)	
CS 2	2/3	1/3	0.00989(5)	1.83(10)	
CS 3	0	0	0.09231(6)	2.06(11)	
CS 4	0	0	0.15160(5)	2.47(11)	
CS 5	1/3	2/3	1/6	1.0(3)	0.5
O 1	0.8746(17)	0.1254	0.04498(25)	0.9(3)	
O 2	0.7883(18)	0.2117	0.1168(3)	1.1(3)	
O 3	0.2100(16)	0.7900	0.06421(23)	0.6(3)	
O 4	0.1215(17)	0.8785	0.01544(25)	0.9(3)	
O 5	0.4559(15)	0.5441	0.09460(22)	0.3(3)	
O 6	0.2101(16)	0.7899	0.12445(23)	0.6(3)	
O 7	0.4581(19)	0.5419	0.0342(3)	1.5(4)	
O 8	0.5304(18)	0.4696	0.1469(3)	1.1(3)	

Note. B_{iso} is the mean of the principle axes of the thermal ellipsoid.

Structure Refinements

The crystal structure of $Cs_{8.5}W_{15}O_{48}$ was determined on a small single crystal mounted on an Enraf–Nonius diffractometer (graphite monochromated Mo$K\alpha$ radiation) controlled by the NRCCAD program (*7*). The crystallographic cell was found to have rhombohedral symmetry, spacegroup $R3m$. Cell parameters a = 7.270 and c = 73.63 Å were obtained by determining the absolute 2θ values of 24 reflections in the range of 40° to 50° and applying a least squares refinement. The data collection parameters are given in Table I. The refinement converged to a very good agreement index ($R_W = 0.030$ for $I_{hkl} > 2.5\sigma$). Final structural data are presented in Tables IIa and IIb. Metal–oxygen bondlengths are given in Table III. The tungsten–oxygen coordination is octahedral. Note that although there are irregularities in the W–O bondlengths, the deviations of the octahedra from regularity are relatively small.

The crystal structure of $Cs_{8.5}W_{15}O_{48}$ is presented in Figs. 2, 3, and 4. The structure is similar to that of $Cs_8V_{1.1}W_{13.9}O_{48}$, a fully oxidized compound (*8*), with the difference that in the present case an additional 0.5 Cs per formula unit is included in the structure.

Inspection of Fig. 2 shows that in the first layer the WO_6 octahedra are arranged ex-

TABLE IIb

u_{ij} OR U VALUES ×100

	u_{11} (U)	$u33$	$u12$	$u13$
W 1	0.80(7)	0.34(11)	0.40	
W 2	1.03(5)	0.89(5)	0.61(5)	−0.148(20)
W 3	0.78(5)	0.65(8)	0.39	
W 4	0.59(4)	1.02(5)	0.35(4)	−0.034(19)
CS 1	2.32(10)	2.70(18)	1.16	
CS 2	2.31(10)	2.34(17)	1.15	
CS 3	2.49(11)	2.83(19)	1.24	
CS 4	3.81(13)	1.75(17)	1.91	
CS 5	1.6(3)	0.6(4)	0.8	
O 1	1.1(4)			
O 2	1.4(4)			
O 3	0.7(4)			
O 4	1.1(4)			
O 5	0.4(3)			
O 6	0.7(4)			
O 7	1.9(5)			
O 8	1.4(4)			

Note. $u_{22} = u_{11}$, $u_{23} = u_{13}$. Anisotropic temperature factors are of the form $-2\pi^2\,(h^2u_{11}a^* +---+ 2hku_{12}a^*b^* +---)$.

TABLE III

TUNGSTEN–OXYGEN BONDLENGTHS IN $Cs_{8.5}W_{15}O_{48}$ (IN ANGSTROMS)

W1–04	1.91(2) × 6	W3–03	2.08(2) × 3
		–05	1.76(2) × 3
O–W1–O angle range	88.1°–91.9°	O–W3–O angle range	80.5°–98.7°
W2–01	1.93(1) × 2	W4–02	1.92(2) × 2
–03	1.82(2)	–05	2.23(2)
–04	1.94(2)	–06	1.92(1) × 2
–07	1.94(2)		
O–W2–O angle range	87.2°–92.3°	O–W4–O angle range	80.4°–97.6°

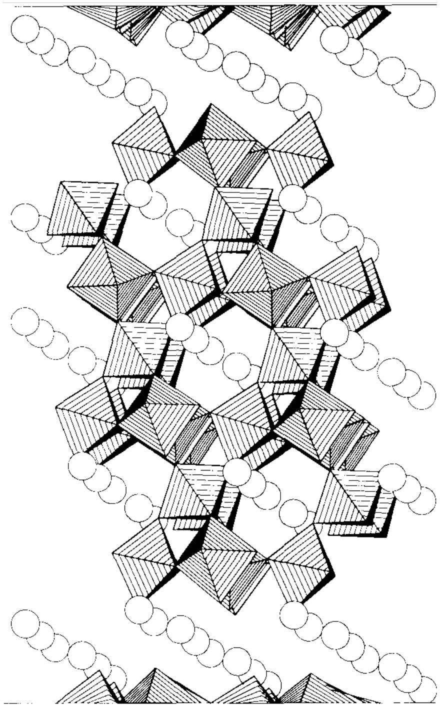

FIG. 3. The crystal structure of $Cs_{8.5}W_{15}O_{48}$ viewed perpendicular to the layers, a few degrees from [100] (to show depth). WO_6 octahedra shown, Cs as large open circles.

actly as they are in hexagonal tungsten bronze, with the familiar alternating hexagonal and triangular openings between corner shared octahedra. That layer is repeated in stacks perpendicular to *c*, displaced with respect to neighboring layers to place some triangular openings above or below triangular openings, and some above or below hexagonal openings. Neighboring HTB type layers are separated by an intermediary layer of octahedra which lie on their faces when viewed parallel to *c* (Figs. 3 and 4), sharing all six vertices with the HTB-like layers above and below. The net effect is to build up a layered fragment of the pyrochlore structure, which is the principle for the homologous series. The cesium atoms occur both inside the pyrochlore-like cavities within the layers and as spacers between the layers (Figs. 3 and 4). One of the cesium sites (the middle one) between layers is only half occupied. No superstructure was observed in the single crystal diffraction patterns. If ordering does occur between filled and empty sites, it is short range in nature; otherwise the sites may be randomly occupied.

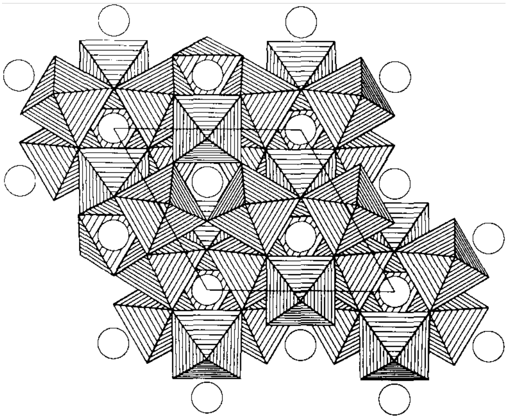

FIG. 2. The crystal structure of $Cs_{8.5}W_{15}O_{48}$ in a partial projection down the *c* axis showing the geometry of the layers. WO_6 octahedra shown, Cs as large open circles.

The conventional powder X-ray diffraction pattern of CsW_2O_6 was easily recognized and indexed on a cubic *F*-centered cell of the Pyrochlore type (Table IV). Pyrochlores are generally of stoichiometry $[AO]AB_2O_6$, where A and B are the large

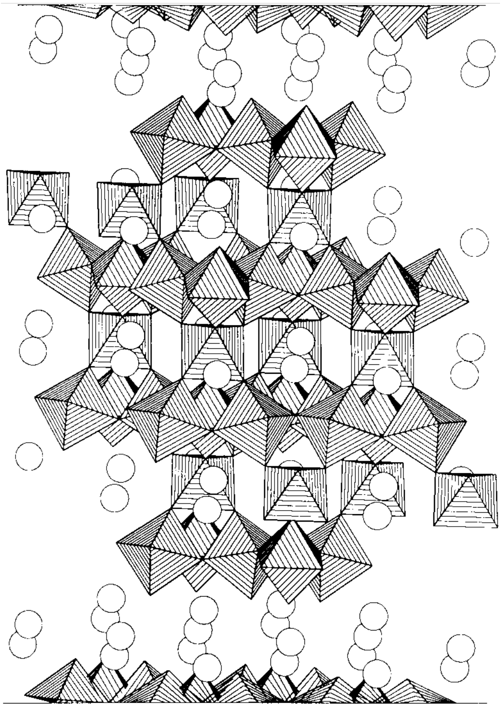

FIG. 4. Crystal structure of $Cs_{8.5}W_{15}O_{48}$ viewed perpendicular to the layers, rotated 30° from Fig. 3, a few degrees from [210]. WO_3 octahedra shown, Cs as large open circles.

and small atom positions respectively (*9*). For Cs based pyrochlores the Cs is expected to occur in the center of the pyrochlore cavity and thus the [*A*O] set of sites (*A* centered in the hexagonal rings) are expected to be vacant, yielding an expected stoichiometry of CsW_2O_6.

The crystal structure of the Cs–W–O pyrochlore was determined by X-ray Rietveld refinement. The data collection and refinement parameters are presented in Table V. As a small amount of W metal was also present in the pattern, the two crystal structures were refined simultaneously. Refinement was carried out by using the GSAS system of programs (*10*).

The crystal structure of CsW_2O_6 is the classical AB_2O_6 pyrochlore type. Cs is found at the center of the large pyrochlore cavity, bonded to 18 oxygens at distances of 3.14 and 3.70 Å. The W_2O_6 array is that of the usual corner shared octahedra, which in this case are quite regular with six W–O bondlengths of 1.97 angstroms. The formal tungsten valence is +5.5. Fully oxidized pyrochlores of stoichiometry $CsM^{5+}W^{6+}O_6$ are known, for M^{5+} = V, Nb, Ta, and Sb (*11, 12*).

The Homologous Series

Comparison of the crystal structures of $Cs_6W_{11}O_{36}$, $Cs_{8.5}W_{15}O_{48}$, and CsW_2O_6 re-

TABLE IV

POWDER X-RAY DIFFRACTION PATTERN OF CsW_2O_6: ($CuK\alpha$) $Fd3m$, a = 10.3287(4) Å

Index	$2\theta_0$	$2\theta_c$	I/I_0
111	14.791	14.843	12
220	24.333	24.353	12
311	28.628	28.639	100
222	29.934	29.942	49
400	34.705	34.710	5
331	37.937	37.938	2
422	42.854	42.856	3
333	45.599	45.598	44
511			
440	49.907	49.903	48
531	52.363	52.359	7
620	56.286	56.282	6
533	58.554	58.551	18
622	59.297	59.296	29
444	62.225	62.217	4
551	64.361	64.358	5
711			
642	67.850	67.843	3
553	69.896	69.893	28
731			
800	73.246	73.252	7
660	78.515	78.511	1
822			
555	80.453	80.456	11
751			
662	81.099	81.101	10
840	83.667	83.673	4
753	85.589	85.593	2
911			
664	88.784	88.784	1

TABLE V

REFINEMENT CONDITIONS AND STRUCTURAL PARAMETERS FOR CsW_2O_6 PYROCHLORE

Refinement	
Radiation	Cu*K*α
Diffractometer	Scintag θ–2θ
Step size	0.02°
Angular range	10°–100° 2θ
Number of structural parameters	1
Total number of parameters	23
R_1	0.0996
R_w	0.0798

Structural parameters	
Space group	*Fd*3*m* (No. 227)
Lattice parameter	10.3287(4)

Atom	Position	Coordinates
Cs	8b	0.375, 0.375, 0.375
W	16c	0.0, 0.0, 0.0
O	48f	0.3209(8), 0.125, 0.125

Bondlengths	
Cs–O bondlengths	3.143(8) × 6 3.697(1) × 12
W–O bondlengths	1.968(3) × 6
O–W–O bond angle range	86.7°–93.3°

veals that they form part of a homologous series of compounds intermediary between the hexagonal tungsten bronze and pyrochlore structure types. The basic structural element is the double layer which is made up of the HTB layer plus the neighboring "lying down" octahedra layer described with reference to Figs. 2, 3, and 4. This double layer, which is a layer of pyrochlore structure, is stacked along *c* in a series of rhombohedral or hexagonal phases, where the number of these pyrochlore layers which is stacked before an alkali oxide layer is encountered is variable. The structural principle is illustrated in Fig. 5, which is a view perpendicular to the layers. The compounds have the formula $[A]_x\text{Cs}_{2n}\text{W}_{4n-1}\text{O}_{12n}$, where $n - 1$ is the number of pyrochlore layers stacked together. $[A]_x$ represents the possibility that an extra layer of alkalis may be included in the separation region between the stacked pyrochlore layers. For $\text{Cs}_{8.5}\text{W}_{15}\text{O}_{48}$, for example, $[A]_x = \text{Cs}_{0.5}$, whereas for $\text{Cs}_8\text{V}_{1.1}\text{W}_{13.9}\text{O}_{48}$ and $\text{Cs}_6\text{W}_{11}\text{O}_{36}$ there is no additional layer $[A]_x$; $x = 0.0$. Note that both $\text{Cs}_8\text{V}_{1.1}\text{W}_{13.9}\text{O}_{48}$ and $\text{Cs}_6\text{W}_{11}\text{O}_{36}$ had been reported with monoclinic cells, but that they can actually be described as rhombohedral, with $a = 7.26$,

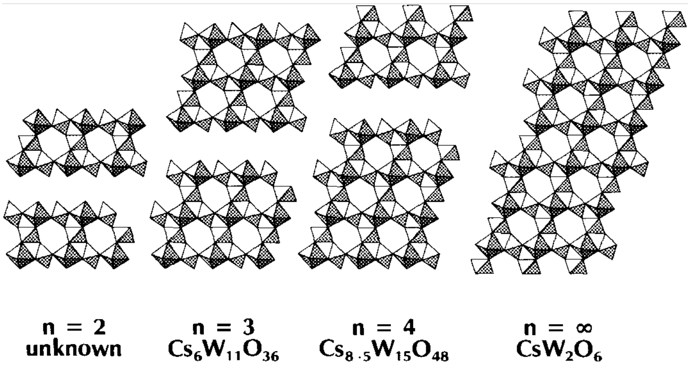

FIG. 5. The principle of the homologous series $[A]\text{Cs}_{2n}\text{W}_{4n-1}\text{O}_{12n}$, where $n - 1$ is the number of pyrochlore layers. Only WO_6 octahedra are shown for clarity. Cs are found inside the pyrochlore cavities and in the region between the stacks of pyrochlore layers, as shown in Figs. 3 and 4.

$c = 73.6$, and $a = 7.26$, $c = 110.6$ Å respectively. The $n = 3$, 4, and ∞ members of the series are now known. Our attempts to synthesize the $n = 5$ member $Cs_xCs_{10}W_{19}O_{60}$ by the techniques described here were not successful. Further work is underway to search for the $n = 2$ and $n = 5$ members of the series in other chemical systems. For the possible $n = 2$ member $[Li]_2Cs_4W_7O_{24}$, synthesized at 650°C in air, a white pyrochlore of composition $Cs_4W_{7.2}Li_{0.8}O_{24}$ was the major phase with a unit cell and powder pattern virtually identical to that of CsW_2O_6.

Conclusions

In our studies of A_2O–WO_3–WO_2 ternary systems we have found two new compounds, of stoichiometry $Cs_{8.5}W_{15}O_{48}$ and CsW_2O_6 (and $Cs_4W_{7.2}Li_{.8}O_{24}$). They are members of a larger homologous series which appears to have never before been described. We have not yet isolated them in the appropriate form to study their resistivities but they may be metallic conductors. Powders of both materials were cooled to 1.8 K in a SQUID magnetometer to check for superconductivity but none was found. Thus although the HTB type Cs_xWO_3 is superconducting, this appears not to be a general characteristic of reduced tungsten oxides. Further work in this series of layered compounds may yet reveal interesting physical properties such as CDW formation or superconductivity.

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