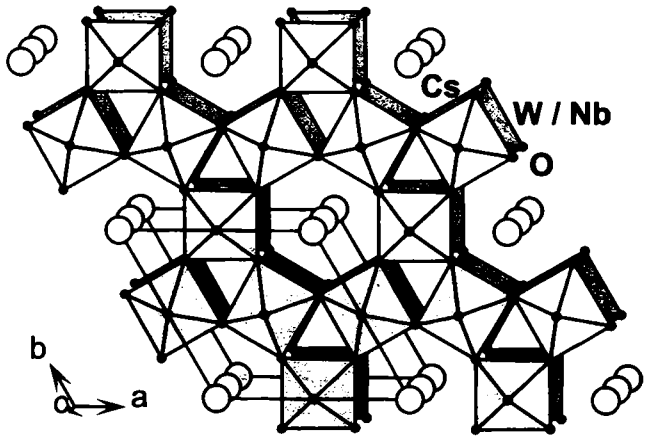
Crystal structure of caesium niobium tungsten bronzes, $Cs_{0.23}(Nb_{0.09}W_{0.91})O_3$ and $Cs_{0.29}(Nb_{0.10}W_{0.90})O_3$

K. R. Dey[I], Th. M. Gesing*[,I], C. H. Rüscher[I] and A. Hussain[II]

[I] Universität Hannover, Institut für Mineralogie, Welfengarten 1, D-30167 Hannover, Germany
[II] University of Dhaka, Department of Chemistry, Dhaka-1000, Bangladesh

Received July 9, 2002, accepted and available on-line September 19, 2002; CSD-No. 409638 and 409639



Abstract

$Cs_{0.23}Nb_{0.09}O_3W_{0.91}$ (1) hexagonal, *P6₃/mcm* (No. 193), $a = 7.3998(2)$ Å, $c = 7.5732(2)$ Å, $V = 359.1$ Å^3, $Z = 6$, $wR(P) = 0.062$, $R(P) = 0.044$, $R(I) = 0.023$, $R(F) = 0.012$, $T = 293$ K.

$Cs_{0.29}Nb_{0.10}O_3W_{0.90}$ (2), hexagonal, *P6₃/mcm* (No. 193), $a = 7.3992(2)$ Å, $c = 7.5867(2)$ Å, $V = 359.7$ Å^3, $Z = 6$, $wR(P) = 0.080$, $R(P) = 0.057$, $R(I) = 0.028$, $R(F) = 0.014$, $T = 293$ K.

Source of material

The starting materials were Cs_2WO_4, WO_3, WO_2 and Nb_2O_5 (high quality reagent grade). Samples were prepared according to the following reaction: $x/2\ Cs_2WO_4 + (1-x-y/2)\ WO_3 + (x-y)/2\ WO_2 + y/2\ Nb_2O_5 \rightarrow Cs_xNb_yW_{1-y}O_3$ ($x = 0.25$ and 0.30; $y = 0.1$). The reactants were mixed intimately in an agate mortar, taken into silica tubes, evacuated at room temperature for 2 – 3 hours, sealed, then heated in a Muffle furnace at a temperature of 1073 K for 7 days and quenched to room temperature. Both samples reveal single phase products of bluish black colour.

Discussion

The crystal structures of $Cs_xNb_yW_{1-y}O_3$ ($x = 0.23$, 0.29; $y \approx 0.1$) are of hexagonal tungsten bronze type (HTB). Tungsten is substituted by niobium according to the predicted chemical reaction. A similar result was also obtained for the analogous $Rb_xNb_yW_{1-y}O_3$ ($x = 0.3$ with $y = 0.13$ and 0.19) [1]. The properties of the present compounds $Cs_xNb_yW_{1-y}O_3$ are also observed in close analogy to that reported for $Rb_xNb_yW_{1-y}O_3$, revealing decreasing carrier concentration with increasing y and a possible metal insulator transition [2].

Rewriting the formula of tungsten bronzes as $M_x(W_x^{5+}W_{1-x}^{6+})O_3$ it implies a substitution $Cs_x(W_{x-y}^{5+}Nb_y^{5+}W_{1-x-y}^{6+})O_3$. According to this, the number of charge carriers may be counted by the number of W^{5+} states, decreasing with decreasing x and increasing y.

1. Caesium niobium tungsten bronze, $Cs_{0.23}(Nb_{0.09}W_{0.91})O_3$

Table 1. Data collection and handling.

Powder:	bluish black
Wavelength:	Cu K_α radiation (1.54059 Å)
μ:	10.98 cm^{-1}
Diffractometer:	Stoe STADI P, transmission, Debye-Scherrer mode
$2\theta_{max}$, stepwith:	115.14°, 0.02°
$N(points)_{measured}$:	5258
$N(hkl)_{measured}$:	108
$N(param)_{refined}$:	29
Program:	Rietan-97 [3]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	B_{iso}
Cs	2*b*	0.679(5)	0	0	0	1.7(1)
Nb	6*g*	0.09(1)	0.4766(1)	0	1/4	0.48(3)
W	6*g*	0.91	0.4766	0	1/4	0.48
O(1)	6*f*		1/2	0	0	1.7(2)
O(2)	12*j*		0.418(1)	0.211(1)	1/4	1.7(2)

2. Caesium niobium tungsten bronze, $Cs_{0.29}(Nb_{0.10}W_{0.90})O_3$

Table 3. Data collection and handling.

Powder:	bluish black
Wavelength:	Cu K_α radiation (1.54059 Å)
μ:	11.61 cm^{-1}
Diffractometer:	Stoe STADI P, transmission, Debye-Scherrer mode
$2\theta_{max}$, stepwith:	119.98°, 0.02°
$N(points)_{measured}$:	5500
$N(hkl)_{measured}$:	116
$N(param)_{refined}$:	29
Program:	Rietan-97 [3]

* Correspondence author
(e-mail: tm.gesing@mineralogie.uni-hannover.de)

Table 4. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	B_{iso}
Cs(1)	2*b*	0.864(5)	0	0	0	1.5(1)
Nb(1)	6*g*	0.10(1)	0.4816(1)	0	1/4	0.36(3)
W(1)	6*g*	0.90	0.4816	0	1/4	0.36
O(1)	6*f*		1/2	0	0	0.9(2)
O(2)	12*j*		0.414(1)	0.205(2)	1/4	0.9(2)

References

1. Gesing, Th. M.; Rüscher, C. H.; Hussain, A.: Crystal structure of Rubidium niobium tungsten bronzes, $Rb_xNb_yW_{1-y}O_3$ ($x = 0.3$; $y = 0.13, 0.19$). Z.Kristallogr. NCS **216** (2001) 37-38.
2. Hussain, A.; Ul-Monir, A.; Murshed, M. M.; Rüscher, C. H.: Synthesis and characterisation of niobium substituted hexagonal tungsten bronzes. Z. Anorg. Allg. Chem. **628** (2001) 416-420.
3. Izumi, F.: In: *The Rietveld Method* (Ed. by R.A. Young), Oxford University Press, Oxford, UK 1993.