Crystal structure of caesium niobium tungsten bronzes, $\text{Cs}_{0.23}(\text{Nb}_{0.09}\text{W}_{0.91})\text{O}_3$ and $\text{Cs}_{0.29}(\text{Nb}_{0.10}\text{W}_{0.90})\text{O}_3$

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Abstract

$\text{Cs}_{0.23}\text{Nb}_{0.09}\text{O}_3\text{W}_{0.91}$ (1) hexagonal, $P6_3/mcm$ (No. 193), $a = 7.3998(2) \text{ \AA}$, $c = 7.5732(2) \text{ \AA}$, $V = 359.1 \text{ \AA}^3$, $Z = 6$, $wR(P) = 0.062$, $R(P) = 0.044$, $R(I) = 0.023$, $R(F) = 0.012$, $T = 293 \text{ K}$.

$\text{Cs}_{0.29}\text{Nb}_{0.10}\text{O}_3\text{W}_{0.90}$ (2), hexagonal, $P6_3/mcm$ (No. 193), $a = 7.3992(2) \text{ \AA}$, $c = 7.5867(2) \text{ \AA}$, $V = 359.7 \text{ \AA}^3$, $Z = 6$, $wR(P) = 0.080$, $R(P) = 0.057$, $R(I) = 0.028$, $R(F) = 0.014$, $T = 293 \text{ K}$.

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: $x/2 \text{ Cs}_2\text{WO}_4 + (1-x-y)/2 \text{ WO}_3 + (x-y)/2 \text{ WO}_2 + y/2 \text{ Nb}_2\text{O}_5 \rightarrow \text{Cs}_x\text{Nb}_y\text{W}_{1-y}\text{O}_3$ ($x = 0.25$ 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 $\text{Cs}_x\text{Nb}_y\text{W}_{1-y}\text{O}_3$ ($x = 0.23, 0.29$; $y \approx 0.1$) 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 $\text{Rb}_x\text{Nb}_y\text{W}_{1-y}\text{O}_3$ ($x = 0.3$ with $y = 0.13$ and 0.19) [1]. The properties of the present compounds $\text{Cs}_x\text{Nb}_y\text{W}_{1-y}\text{O}_3$ are also observed in close analogy to that reported for $\text{Rb}_x\text{Nb}_y\text{W}_{1-y}\text{O}_3$, revealing decreasing carrier concentration with increasing y and a possible metal insulator transition [2].

Rewriting the formula of tungsten bronzes as $\text{M}_x(\text{W}_x^{5+}\text{W}_{1-x}^{6+})\text{O}_3$ it implies a substitution $\text{Cs}_x(\text{W}_{x-y}^{5+}\text{Nb}_y^{5+}\text{W}_{1-x-y}^{6+})\text{O}_3$. 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, $\text{Cs}_{0.23}(\text{Nb}_{0.09}\text{W}_{0.91})\text{O}_3$

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
$2\theta_{\text{max}}$, stepwith:	115.14°, 0.02°
$N(\text{points})_{\text{measured}}$:	5258
$N(hkl)_{\text{measured}}$:	108
$N(\text{param})_{\text{refined}}$:	29
Program:	Rietan-97 [3]

Table 2. Atomic coordinates and displacement parameters (in Å²).

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

2. Caesium niobium tungsten bronze, $\text{Cs}_{0.29}(\text{Nb}_{0.10}\text{W}_{0.90})\text{O}_3$

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
$2\theta_{\text{max}}$, stepwith:	119.98°, 0.02°
$N(\text{points})_{\text{measured}}$:	5500
$N(hkl)_{\text{measured}}$:	116
$N(\text{param})_{\text{refined}}$:	29
Program:	Rietan-97 [3]

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Table 4. Atomic coordinates and displacement parameters (in Å²).

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

References

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