Crystal structure of rubidium niobium tungsten bronzes, $Rb_xNb_yW_{1-y}O_3$ ($x \approx 0.3$; $y = 0.13, 0.19$)

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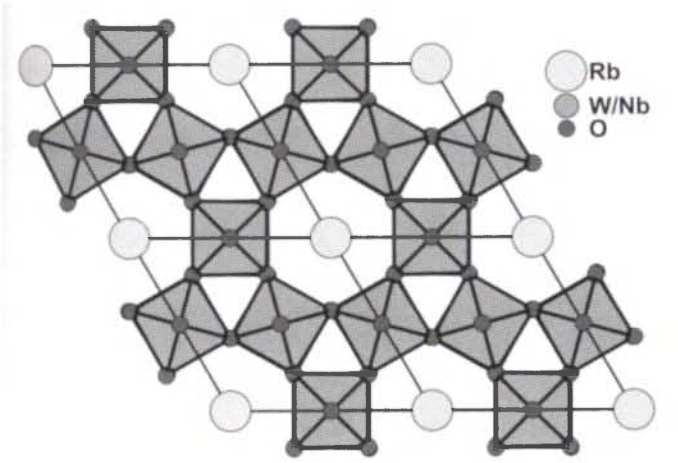

Abstract

$Nb_{0.13}O_3Rb_{0.31}W_{0.87}$, hexagonal, $P6_3/mcm$ (No. 193), $a = 7.3984(3)$ Å, $c = 7.5594(2)$ Å, $V = 358.3$ Å^3, $Z = 6$, $\rho_m = 6.840$ g·cm^{-3}, $R(wP) = 0.032$, $R(P) = 0.025$, $R(I) = 0.007$, $R(F) = 0.005$, $T = 293$ K.

$Nb_{0.19}O_3Rb_{0.30}W_{0.81}$, hexagonal, $P6_3/mcm$ (No. 193), $a = 7.389(2)$ Å, $c = 7.562(1)$ Å, $V = 357.5$ Å^3, $Z = 6$, $\rho_m = 6.689$ g·cm^{-3}, $R(wP) = 0.049$, $R(P) = 0.037$, $R(I) = 0.031$, $R(F) = 0.017$, $T = 293$ K.

Source of material

The starting materials were K_2WO_4, Rb_2WO_4, WO_3, WO_2 and Nb_2O_5 (high quality reagent grade). Samples were prepared according to the chemical reaction:

$x/2\ Rb_2WO_4 + (1-x-y/2)\ WO_3 + (x-y)/2\ WO_2 + y/2\ Nb_2O_5$
$Rb_xNb_yW_{1-y}O_3$ ($x = 0.2$; $y = 0.1$ or 0.2).

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 a period of 5 days and quenched to room temperature. After this reaction single phase black powder remained for both phases.

Discussion

The crystal structures of hexagonal tungsten bronze type (HTB) can be described as built up of WO_6 octahedra sharing corners with the neighboring octahedra forming a three dimensional network. The homogeneity range of HTB phases M_xWO_3 with M = K, Rb, Cs using similar preparation conditions was found to be mostly restricted on x between 0.19 and 0.33 [1]. The formula of tungsten bronzes can be rewritten as $M_x(W_y^{5+}W_{1-y}^{6+}O_3)$ indicating a presence of formally pentavalent tungsten ions. The present structure investigations show that tungsten can be substituted by niobium according to $Rb_xNb_yW_{1-y}O_3$ here with $y = 0.13$ ($x = 0.31$) and $y = 0.19$ ($x = 0.30$) which is in reasonable agreement with the preceding nominal composition.

Mattes et al. [3] reported for a HTB-type structure with a c-lattice parameter of 3.862 Å. However, the present structure refinement leads to a double c-lattice parameter due to the shift of W and O(2) as given in Table 2 and Table 4.

1. Rubidium niobium tungsten bronze, $Rb_{0.31}Nb_{0.13}W_{0.87}O_3$

Table 1. Data collection and handling.

Powder:	black
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	4.61 cm^{-1}
Diffractometer:	STOE STADI P, transmission, Debye-Scherrer mode
$2\theta_{max}$, stepwith:	59.98°, 0.02°
$N(points)_{measured}$:	2500
$N(hkl)_{refined}$:	214
$N(param)_{refined}$:	30
Program:	Rietan-94 [2]

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

Atom	Site	Occ.	x	y	z	B_{iso}
Rb	2*b*	0.93(2)	0	0	0	3.9(3)
Nb	6*g*	0.13(1)	0.4792(2)	0	1/4	0.12(6)
W	6*g*	0.87	0.4792	0	1/4	0.12
O(1)	6*f*		1/2	0	0	1.9(3)
O(2)	12*j*		0.421(2)	0.206(3)	1/4	1.9

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2. Rubidium niobium tungsten bronze, $Rb_{0.30}Nb_{0.19}W_{0.81}O_3$

Table 3. Data collection and handling.

Powder:	black
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	4.62 cm^{-1}
Diffractometer:	STOE STADI P, transmission, Debye-Scherrer mode
$2\theta_{max}$, stepwith:	59.98°, 0.02°
$N(points)_{measured}$:	2500
$N(hkl)_{refined}$:	214
$N(param)_{refined}$:	30
Program:	Rietan-94 [2]

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

Atom	Site	Occ.	x	y	z	B_{iso}
Rb	2*b*	0.89(4)	0	0	0	1.3(7)
Nb	6*g*	0.19(3)	0.4800(9)	0	1/4	0.16(9)
W	6*g*	0.81	0.4800	0.	1/4	0.16
O(1)	6*f*		1/2	0	0	1.9(3)
O(2)	12*j*		0.377(4)	0.161(5)	1/4	1.9

References

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