Structure Refinement of Rubidium Periodate at 297 and 150 K

Danita de Waal* and Klaus-Jürgen Range**

Institute of Inorganic Chemistry,
University of Regensburg, Universitätsstraße 31,
D-93053 Regensburg, Germany

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The scheelite-type structure of rubidium periodate, $RbIO_4$, has been confirmed and refined from single-crystal X-ray data at two temperatures. The compound crystallizes tetragonally, space group $I4_1/a$, with a = 5.897(1), c = 12.876(3) Å at 150 K and a = 5.910(1), c = 13.021(3) Å at 297 K, respectively. Only small changes are observed for the structural parameters at low temperatures, but a significant decrease could be observed in the anisotropic displacement factors.

Refinements of the crystal structures of the room temperature modification of cesium periodate [1] and potassium periodate at two temperatures have recently been reported by us [2] as part of a study of the structures and phase transitions in the alkali metal periodates. For rubidium periodate, $RbIO_4$, a scheelite-type structure (space group $I4_1/a$, Z = 4) was proposed by Beintema [3] by analogy with potassium periodate, KIO_4. This choice was supported by single-crystal polarized Raman spectra of the two compounds [4]. In an X-ray determination of the thermal expansion of $RbIO_4$ the lattice parameters a and c have been determined between 378 and 303 K [5], but other structural details have not been published up to now. In this work the refinement of the structure of rubidium periodate at 297 and 150 K is reported.

Rubidium periodate was prepared by neutralization of orthoperiodic acid (Merck, p.a.) with rubidium carbonate (Fluka, p.a.). The precipitated white solid was repeatedly recrystallized from water. Single crystals were grown by slow evaporation from a saturated aqueous solution of $RbIO_4$ at room temperature.

A colourless transparent crystal (approximate dimensions 0.160 x 0.240 x 0.180 mm) was selected for the X-ray investigations. Data collection was performed at 297 and 150 K on a STOE-IPDS Imaging Plate Diffraction System using Mo$K\alpha$ radiation (graphite monochromator in incident beam). The low temperature measurements were made using a cryostat from Oxford Cryosystems. Experimental details and crystallographic data are summarized in Table I.

Calculations were carried out using the programs SHELXS-86 and SHELXL-93 [6]. The structure was solved by Patterson methods, followed by successive difference Fourier syntheses. After the isotropical refinement a numerical correction for absorption was applied to the original data set (Program DIFABS [7]). The final full-matrix least squares refinement on F^2, including anisotropic displacement factors and an extinction factor, converged at $R1$ = 0.0268, $wR2$ = 0.0630 (297 K) and $R1$ = 0.0294, $wR2$ = 0.0711 (150 K). Atomic positions and displacement factors are presented in Table II, derived atomic distances and angles in Table III.+

The results of the present single-crystal study confirm the scheelite-type structure of $RbIO_4$, as proposed by Beintema [3]. $RbIO_4$ is therefore isostructural with $NaIO_4$ [8] and KIO_4 [2] as well as with the analogous perrhenates $NaReO_4$ [9], $KReO_4$ [10] and $RbReO_4$ [11]. The temperature-dependent changes of the structural parameters are relatively small. While I-O distances within the IO_4^- ion remained almost constant, the Rb-O distances became slightly shorter at 150 K (Table III). This is similar to the observation made for KIO_4 [2].

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* Permanent address: Department of Chemistry, University of Pretoria, Pretoria 0002, South Africa.
** Reprint requests to Dr. D. de Waal or Prof. Dr. K.-J. Range.

+ Further details of the crystal structure determination can be obtained from the Fachinformationszentrum Karlsruhe GmbH, D-76344 Eggenstein-Leopoldshafen, by quoting the depository number CSD 59282.

Table I. Crystal data, data collection and refinement parameters for $RbIO_4$ at 297 and 150 K. Standard deviations are given in parentheses.

Formula		$RbIO_4$	
Structure type		Scheelite	
Space group		$I4_1/a$ Nr. 88)	
Z		4	
Crystal size [mm]		0.16×0.240×0.180	
Diffractometer		STOE-IPDS	
Radiation		MoKα (λ = 0.71069 Å)	
Detector distance		80 mm	
Phi movement mode		Oscillation	
Phi increments		0.5°	
Number of exposures		200	
Irradiation/Exposure		3 min	
Measurement temperature [K]	297.0(2)		150.0(2)
Unit Cell dimensions			
a [Å]	5.910(1)		5.897(1)
c [Å]	13.021(3)		12.876(3)
c/a	2.203		2.183
Volume [Å^3]	454.80(3)		447.80(3)
Density (calculated) [g·cm^3]	4.036		4.099
hkl limits	$-5 \leq h \leq 6$		$-5 \leq h \leq 6$
	$-6 \leq k \leq 4$		$-5 \leq k \leq 6$
	$-14 \leq l \leq 14$		$-14 \leq l \leq 14$
$(\sin\theta/\lambda)_{max}$	0.577		0.577
Recorded reflections	711		694
μ [mm^{-1}]	17.56		17.83
Absorption correction		DIFABS	
Unique reflections, R_{int}	169, 0.0690		167, 0.0595
Parameters refined	15		15
Mean shift/esd, max. shift [Å]	0.000, 0.000		0.000, 0.000
Final $R1$, $wR2$, (for all data)	0.0268, 0.0630		0.0294, 0.0711
GooF(S)	1.158		1.389
$(\Delta/\varrho)_{max,min}$ [e·Å^{-3}]	+0.46, −0.57		+0.83, −1.19

Table II. Atomic positional parameters and displacement factors [Å^2] for $RbIO_4$ at 297 K (first row) and 150 K (second row).

Fractional atomic co-ordinates and equivalent isotropic displacement parameters (Origin at $\bar{1}$).

Atom	Position	x/a	y/b	z/c	U_{eq}*
I	4a ($\bar{4}$..)	0	1/4	1/8	0.0229(5)
		0	1/4	1/8	0.0089(5)
Rb	4b ($\bar{4}$..)	1/2	3/4	1/8	0.0277(5)
		1/2	3/4	1/8	0.0109(6)
O	16f (1)	0.1199(4)	0.4646(4)	0.2011(2)	0.0359(8)
		0.8760(4)	0.4637(4)	0.2022(1)	0.0171(8)

* $U_{eq} = 1/3\ (U_{11} + U_{22} + U_{33})$.

Anisotropic displacement factors

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I	0.0230(5)	U_{11}	0.0228(6)	0	0	0
	0.0075(5)	U_{11}	0.0117(7)	0	0	0
Rb	0.0288(5)	U_{11}	0.0255(9)	0	0	0
	0.0098(6)	U_{11}	0.0131(9)	0	0	0
O	0.038(1)	0.036(1)	0.032(1)	−0.0078(9)	−0.0008(10)	−0.009(1)
	0.017(1)	0.017(1)	0.016(1)	−0.0049(9)	−0.0003(9)	0.003(1)

Table III. $RbIO_4$: Selected interatomic distances [Å] and bond angles [°].

IO_4 tetrahedron			
I–O	(4×)	1.759(2)	1.765(2)
O–I–O	(2×)	111.3(2)	111.3(2)
O–I–O	(4×)	108.5(1)	108.5(1)
RbO_8 dodecahedron			
Rb–O	(4×)	2.911(2)	2.886(2)
Rb–O	(4×)	2.979(2)	2.959(2)
Heavy atom distances			
Rb–I		4.179(1)	4.170(1)
Rb–Rb, I–I		4.396(1)	4.365(1)

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