

# Syntheses, Crystal Structures and Magnetic Properties of $\text{Rb}_2\text{RuO}_4$ and $\text{K}_2\text{RuO}_4$

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Potassium and rubidium oxoruthenates,  $\text{A}_2\text{RuO}_4$ , were synthesized from the alkali peroxides/hyperoxides and ruthenium dioxide. Both compounds crystallize in the orthorhombic space group *Pnma* (no. 62), ( $\text{K}_2\text{RuO}_4$ :  $a = 7.673(2)$ ,  $b = 6.153(2)$  and  $c = 10.564(3)$  Å,  $Z = 4$ , 796 unique reflections,  $R = 3.5\%$ ;  $\text{Rb}_2\text{RuO}_4$ :  $a = 8.106(2)$ ,  $b = 6.270(1)$  and  $c = 11.039(2)$  Å,  $Z = 4$ , 889 unique reflections,  $R = 3.6\%$ ). The crystal structures, as determined from single crystal data, are of the  $\beta$ - $\text{K}_2\text{SO}_4$  type. Magnetic measurements reveal that both compounds are paramagnetic down to temperatures of around 60 K and further exhibit antiferromagnetic transitions, at around  $T_N = 9$  K for  $\text{Rb}_2\text{RuO}_4$ , and two transitions with  $T_N = 14$  K and 4 K for  $\text{K}_2\text{RuO}_4$ . The magnetic moments as determined applying Curie-Weiss law for both compounds are  $2.68 \mu_B$ , thus confirming the oxidation state +6 of ruthenium.

**Key words:** Potassium and Rubidium Oxoruthenates, Ruthenium, Crystal Structure, Magnetic Properties

## Introduction

Ruthenates crystallize in a rich variety of structure types ranging from pyrochlores and hollandites to perovskite type phases, and exhibiting interesting magnetic and electronic properties. However, only a few alkali oxoruthenates of the type  $\text{A}_2\text{RuO}_4$  (where A = alkali metal) were explored up to now. More than a decade ago we reported the crystal structure of  $\text{Cs}_2\text{RuO}_4$  [1], and last year, including us, two groups reported the crystal structure and magnetic properties of  $\text{Na}_2\text{RuO}_4$  [2, 3]. Recently, many compounds of ruthenium have been studied which exhibit interesting electronic properties, especially due to the unusual behaviour of electrons in these ruthenium based oxides in which the local magnetic moment character for ruthenium is lost due to the hybridization of the Ru *4d* and O *2p* states [4].  $\text{Na}_2\text{RuO}_4$  displays antiferromagnetic behaviour at around 35 K with the ruthenium atom five-fold coordinated by oxygen atoms forming ladders of trigonal bipyramids [3].  $\text{K}_2\text{RuO}_4$  and  $\text{Rb}_2\text{RuO}_4$ , however, are similar to  $\text{Cs}_2\text{RuO}_4$ , containing isolated  $\text{RuO}_4$  tetrahedra and crystallising in the  $\beta$ - $\text{K}_2\text{SO}_4$  type of structure [5]. Here we report on

the syntheses, crystal structure and magnetic properties of  $\text{K}_2\text{RuO}_4$  and  $\text{Rb}_2\text{RuO}_4$ .

## Experimental Section

### Syntheses

$\text{K}_2\text{RuO}_4$  was synthesised from potassium peroxide and ruthenium dioxide in the molar ratio 2 : 1 at 780 °C in a platinum crucible kept in a quartz ampoule for 45 days, and also by heating the mixture at 720 °C in a silver container sealed in a quartz ampoule for 46 days.  $\text{Rb}_2\text{RuO}_4$  was synthesised from  $\text{RbO}_{1.6}$  and ruthenium dioxide in the molar ratio 2.1 : 1 at 650 °C (platinum crucible, sealed in supremax glass ampoule) for 62 days. The crystals obtained are dark green and blackish in colour. Both compounds are hygroscopic [5]. Single crystals suitable for X-ray diffraction studies were selected in dry paraffin oil and sealed into glass capillaries.

The polycrystalline samples on which the magnetic measurements were carried out were synthesised under similar conditions from  $\text{KO}_2$  and  $\text{RuO}_2$  in the molar ratio 2 : 1 for  $\text{K}_2\text{RuO}_4$  and from  $\text{RbO}_2$  and  $\text{RuO}_2$  in the molar ratio 2 : 1 for  $\text{Rb}_2\text{RuO}_4$ . These mixtures were placed in gold ampoules which were flame sealed at one end and mechanically closed at the other. The reactions were carried out under an oxygen flow at 625 °C for 2 days and subsequent cooling to room temperature at a rate of 20 °C per hour.

Compound	Rb <sub>2</sub> RuO <sub>4</sub>	K <sub>2</sub> RuO <sub>4</sub>
Crystal system	orthorhombic	orthorhombic
Space group (no.)	<i>Pnma</i> (no. 62)	<i>Pnma</i> (no. 62)
Lattice parameters (Guinier – data)	$a = 8.106(2) \text{ \AA}$ $b = 6.270(1) \text{ \AA}$ $c = 11.039(2) \text{ \AA}$	$a = 7.673(2) \text{ \AA}$ $b = 6.153(2) \text{ \AA}$ $c = 10.564(3) \text{ \AA}$
Formula units (Z)	4	4
Cell volume / $\text{\AA}^3$	561.02	498.75
X-ray density / $\text{g}\cdot\text{cm}^{-3}$	4.00	3.20
Crystal form	columnar, dark green	cuboid, dark green
F (000)	600	456
Diffractometer	four circle Siemens AED 2	four circle Siemens AED 2
Wavelength	Mo-K $\alpha$ , ( $\lambda = 0.71073 \text{ \AA}$ )	Mo-K $\alpha$ , ( $\lambda = 0.71073 \text{ \AA}$ )
Monochromator	graphite	graphite
Intensity correction	Polarisations and Lorentz factor	Polarisations and Lorentz factor
Linear absorption Coeff., $\mu$ , Mo-K $\alpha$ , $\text{cm}^{-1}$	194.9	42.9
Data collection mode	Omega-scan, Profile fit method [9]	Omega-scan, Profile fit method [9]
Scan region $\rho$	$3^\circ < \theta < 30^\circ$	$3^\circ < \theta < 30^\circ$
No. of measured reflections	6556	5875
No. of unique reflections	889	796
No. of omitted reflections	6	4
No. of free parameters	40	40
Structure solution	Direct method and Differential Fourier-Synth.	Patterson and Differential Fourier-Synth.
Structure refinement	Full matrix least-squares; anisotropic displacement parameter	Full matrix least-squares; anisotropic displacement parameter
$R(\text{obs})$	3.6 %	3.5 %
$R_w(\text{obs})$	2.3 %	2.5 %
Weighing scheme	$2.3814/\sigma(F_o)^2$	$2.0470/\sigma(F_o)^2$

Table 1. Crystallographic data and details on the structure determination of Rb<sub>2</sub>RuO<sub>4</sub> and K<sub>2</sub>RuO<sub>4</sub> [5] at 298 K.

Atom	Rb <sub>2</sub> RuO <sub>4</sub>			Atom	K <sub>2</sub> RuO <sub>4</sub>		
	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
Ru	0.2208(1)	1/4	0.4209(1)	Ru	0.2864(1)	1/4	0.5830(1)
Rb1	0.6619(1)	1/4	0.4166(1)	K1	0.3362(1)	1/4	0.9270(1)
Rb2	0.4932(1)	1/4	0.7940(1)	K2	0.4932(1)	1/4	0.2895(1)
O1	0.3048(6)	1/4	0.5692(4)	O1	0.1736(5)	1/4	0.4402(3)
O2	0.5065(6)	1/4	0.0764(5)	O2	0.0039(5)	1/4	0.9440(4)
O3	0.2981(5)	0.4789(5)	0.3469(3)	O3	0.2782(5)	0.5236(5)	0.1684(3)

Table 2. Atomic coordinates of Rb<sub>2</sub>RuO<sub>4</sub> and K<sub>2</sub>RuO<sub>4</sub> with standard deviations in parentheses.

On addition of water or dilute hydrochloric acid, a reaction of the oxoruthenates(VI) takes place, yielding an orange colour in water and a red colour in hydrochloric acid. No further investigation of these products was carried out.

#### X-ray diffraction

Single crystal data were collected on a four circle Siemens AED 2 diffractometer (Mo-K $\alpha$  radiation). Further information concerning the data collection and processing, the crystallographic parameters, as well as details on the structure solution and refinement are given in Table 1\*. Powder pat-

terns were refined on the Guinier-Simon data with Cu-K $\alpha$ 1 radiation. Quartz was used as an internal standard.

#### Magnetic measurements

The magnetisation was recorded using a SQUID-magnetometer (Quantum Design MPMS; 5–330 K, magnetic fields up to 5 T; sample size: 38 mg of K<sub>2</sub>RuO<sub>4</sub> and 46 mg of Rb<sub>2</sub>RuO<sub>4</sub> sealed in quartz ampoules under helium). The susceptibility data were corrected for the core diamagnetic contributions.

## Results and Discussion

Rb<sub>2</sub>RuO<sub>4</sub> and K<sub>2</sub>RuO<sub>4</sub> crystallize in the  $\beta$ -K<sub>2</sub>SO<sub>4</sub> structure [5]. According to single crystal structure analyses [6], in the case of Rb<sub>2</sub>RuO<sub>4</sub> the Ru atom is

\*Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein Leopoldshafen (Germany), on quoting the depository number CSD-415748 for Rb<sub>2</sub>RuO<sub>4</sub> and CSD-415749 for K<sub>2</sub>RuO<sub>4</sub>, and the name of the author(s), and citation of the paper.

Table 3. Anisotropic displacement parameters for Rb<sub>2</sub>RuO<sub>4</sub> (in Å<sup>2</sup>) with standard deviations in parentheses. The  $U_{ij}$  are defined as  $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{12}hka^*b^* + U_{13}hla^*c^* + U_{23}klb^*c^*)]$ .

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Ru1	0.0171(2)	0.0207(2)	0.0200(2)	0	-0.0005(1)	0
Rb1	0.0231(3)	0.0325(3)	0.0387(4)	0	-0.0026(2)	0
Rb2	0.0222(3)	0.0328(3)	0.0244(3)	0	-0.0003(2)	0
O1	0.0416(28)	0.441(28)	0.0269(25)	0	-0.0094(21)	0
O2	0.0186(24)	0.0899(49)	0.0618(40)	0	0.0041(27)	0
O3	0.0522(22)	0.0273(18)	0.0510(24)	0.0127(16)	0.0149(17)	0.0029(17)

Table 4. Anisotropic displacement parameters for K<sub>2</sub>RuO<sub>4</sub> (in Å<sup>2</sup>) with standard deviations in parentheses. The  $U_{ij}$  are defined as  $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{12}hka^*b^* + U_{13}hla^*c^* + U_{23}klb^*c^*)]$ .

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Ru1	0.0161(2)	0.0345(2)	0.0169(2)	0	-0.0005(1)	0
K1	0.0230(5)	0.0651(8)	0.0373(6)	0	0.0020(4)	0
K2	0.0208(5)	0.0660(8)	0.0218(5)	0	-0.0004(2)	0
O1	0.0287(21)	0.1825(63)	0.0238(20)	0	-0.0117(15)	0
O2	0.0206(23)	0.2649(95)	0.0473(29)	0	0.0001(19)	0
O3	0.1248(32)	0.0353(17)	0.0797(25)	0.0070(16)	-0.0653(23)	0.0028(19)

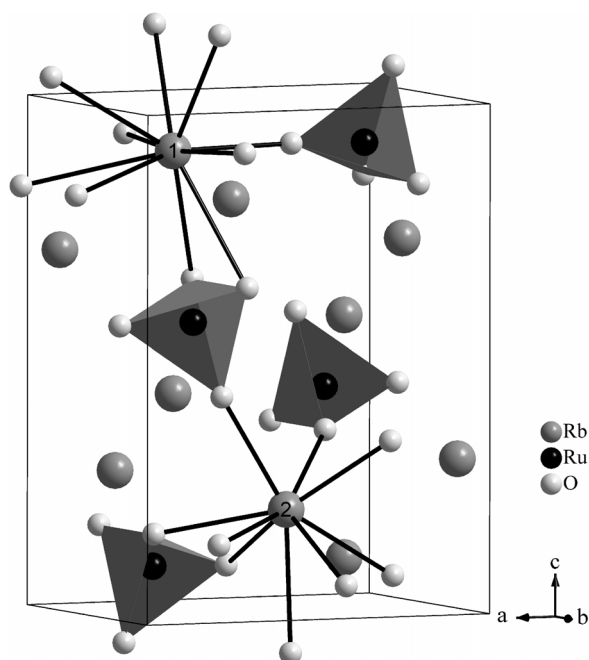
Table 5. Selected interatomic distances in Rb<sub>2</sub>RuO<sub>4</sub> and K<sub>2</sub>RuO<sub>4</sub>.

Rb <sub>2</sub> RuO <sub>4</sub>	Distance (Å)	K <sub>2</sub> RuO <sub>4</sub>	Distance (Å)
Ru-O1	1.773	Ru-O1	1.740
Ru-O2	1.737	Ru-O2	1.693
Ru-O3	1.766	Ru-O3	1.732
Ru-O3	1.766	Ru-O3	1.732
Rb1-O1 × 2	3.151	K1-O1 × 2	3.081
Rb1-O1	3.349	K1-O1	2.944
Rb1-O2	2.794	K1-O2	2.556
Rb1-O3 × 2	3.132	K1-O3 × 2	3.088
Rb1-O3 × 2	3.369	K1-O3 × 2	3.190
Rb1-O3 × 2	3.426	K1-O3 × 2	3.422
Rb2-O1	2.914	K2-O1	2.794
Rb2-O1	2.943	K2-O1	2.924
Rb2-O2	3.119	K2-O2	2.817
Rb2-O2 × 2	3.446	K2-O2 × 2	3.483
Rb2-O3 × 2	2.858	K2-O3 × 2	2.682
Rb2-O3 × 2	2.967	K2-O3 × 2	2.795

Table 6. MAPLE values of A<sub>2</sub>RuO<sub>4</sub> compounds (A = Cs, Rb, K) in kcal/mol.

Atom	Cs <sub>2</sub> RuO <sub>4</sub>	Rb <sub>2</sub> RuO <sub>4</sub>	K <sub>2</sub> RuO <sub>4</sub>
1 Ru	4001.3	3993.5	4084.1
1 A1	100.0	105.9	112.7
1 A2	129.3	139.5	151.4
1 O1	604.9	598.6	611.0
1 O2	631.4	640.7	658.8
2 O3	606.5	599.7	612.0
Σ	6680	6678	6842

tetrahedrally coordinated by oxygen atoms with Ru–O distances ranging from 1.737 to 1.773 Å. The coordination number of Rb2 is nine and that of Rb1 is ten (10 + 1), the eleventh ligand is at a very long dis-

Fig. 1. Schematic view of the unit cell of Rb<sub>2</sub>RuO<sub>4</sub> (ruthenium tetrahedra and coordination spheres of rubidium atoms are shown).

tance of 3.961 Å, see Fig. 1. The atomic positions for both compounds are listed in Table 2. It can be seen from Tables 3 and 4 that for Rb<sub>2</sub>RuO<sub>4</sub> one displacement parameter of the oxygen atom (O2) is somewhat large and that in the case of K<sub>2</sub>RuO<sub>4</sub> the displacement parameters of the oxygen atoms have increased

Table 7. MAPLE values calculated for  $\text{RuO}_3$  from  $\text{A}_2\text{RuO}_4$  compounds ( $\text{A} = \text{Cs}, \text{Rb}, \text{K}, \text{Na}$ ) and  $\text{CsK}_5\text{Ru}_2\text{O}_9$  in kcal/mol.

Compound	$\text{Cs}_2\text{RuO}_4^*$	$\text{CsK}_5\text{Ru}_2\text{O}_9^{**}$	$\text{Rb}_2\text{RuO}_4^*$	$\text{K}_2\text{RuO}_4^*$	$\text{Na}_2\text{RuO}_4^*$
MAPLE ( $\text{RuO}_3$ )	6148	6209	6106	6242	6131

\*  $\text{A}_2\text{RuO}_4$ ;  $M(\text{RuO}_3) = M(\text{A}_2\text{RuO}_4) - M(\text{A}_2\text{O})$ ; \*\*  $\text{CsK}_5\text{Ru}_2\text{O}_9$ ;  $M(\text{RuO}_3) = [M(\text{CsK}_5\text{Ru}_2\text{O}_9) - 1/2M(\text{Cs}_2\text{O}) - 5/2M(\text{K}_2\text{O})]/2$ .

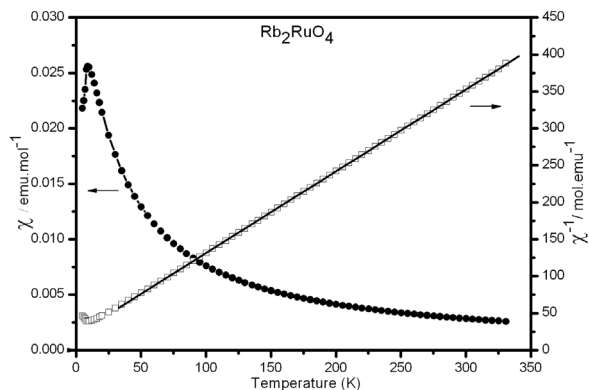


Fig. 2. Magnetic susceptibility of  $\text{Rb}_2\text{RuO}_4$  represented as  $\chi$  vs.  $T$  (circles) and  $\chi^{-1}$  vs.  $T$  (squares) in an applied field of 5000 Oe. The full line represents the linear fit using the Curie-Weiss law.

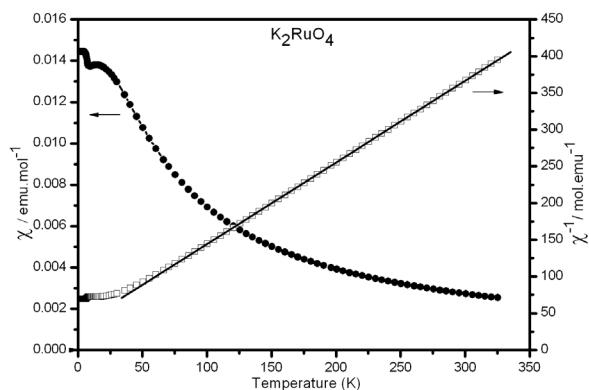


Fig. 3. Magnetic susceptibility of  $\text{K}_2\text{RuO}_4$  represented as  $\chi$  vs.  $T$  (circles) and  $\chi^{-1}$  vs.  $T$  (squares) in an applied field of 5000 Oe. The full line represents the linear fit using the Curie-Weiss law.

further. This can be understood by the arrangement of the ruthenium tetrahedra and the alkali metal cations, which is unfavourable with decreasing size of the alkali metal. The solutions in the acentric space group  $Pn2_1a$ , do not result in better refinement factors. Selected interatomic distances for both compounds are given in Table 5. The tetrahedral coordination for ruthenium is lost already in the case of  $\text{Na}_2\text{RuO}_4$  [3], in which the ruthenium atom adopts five-fold coordination with oxygen atoms forming ladders of trigonal bipyramids

via Ru–O–Ru linkages. Another example is the quaternary mixed alkali ruthenate  $\text{CsK}_5[\text{RuO}_4][\text{RuO}_5]$  [7] which contains isolated  $\text{RuO}_4$  tetrahedra as well as  $\text{RuO}_5$  trigonal bipyramids.

The Madelung Part of Lattice Energy, MAPLE [8], calculated for all the alkali ruthenates as tabulated in Table 6 are satisfactory, it is remarkable however, that the values for  $\text{Rb}_2\text{RuO}_4$  appear to step out of line. This can be explained by the absorption of Mo- $\text{K}\alpha$  radiation in the rubidium ruthenate, which influences the quality of the data set. The MAPLE values obtained for  $\text{RuO}_3$  by subtracting the values of the respective oxides ( $\text{A}_2\text{O}$ , where  $\text{A} = \text{Cs}, \text{Rb}, \text{K}, \text{Na}$ ) from those of the corresponding  $\text{A}_2\text{RuO}_4$  compounds are in good agreement (Table 7). The value obtained for  $\text{RuO}_3$  from  $\text{CsK}_5[\text{RuO}_4][\text{RuO}_5]$ , 6209 kcal/mol, is in between the  $\text{RuO}_3$  values, 6148 kcal/mol and 6242 kcal/mol, obtained for  $\text{Cs}_2\text{RuO}_4$  and  $\text{K}_2\text{RuO}_4$ , respectively. For the same reasons as explained above, here  $\text{Rb}_2\text{RuO}_4$  and  $\text{K}_2\text{RuO}_4$  show again the highest deviations from the average MAPLE value of  $\text{RuO}_3$  which is 6167 kcal/mol.

The magnetic measurements were carried out on polycrystalline powder samples. The plots of inverse susceptibility and susceptibility versus temperature for  $\text{Rb}_2\text{RuO}_4$  and  $\text{K}_2\text{RuO}_4$  are given in Figs 2 and 3, respectively, in an applied field of 5000 Oe. The inverse magnetic susceptibilities obey the Curie-Weiss Law down to about  $T = 60$  K. Fitting the Curie and Weiss constants the values obtained are  $C = 0.9$  emu·K/mol for both compounds, and  $\theta$  around  $-19$  K for  $\text{Rb}_2\text{RuO}_4$  and  $-30$  K for  $\text{K}_2\text{RuO}_4$ . Effective magnetic moments are  $\mu_{\text{eff}} = 2.68 \mu_{\text{B}}$  for both compounds, which is 95% of  $\mu_{\text{SO}} = 2.83 \mu_{\text{B}}$ , the ideal moment for the spin-only  $d^2$  ( $S = 1$ ) configuration, thus confirming the oxidation state +6 for ruthenium. Below 60 K, the inverse susceptibility curves diverge remarkably from the linear behaviour indicating the presence of antiferromagnetic interactions in both compounds, with  $T_{\text{N}} = 9$  K for  $\text{Rb}_2\text{RuO}_4$  and with  $T_{\text{N}} = 14$  K and 4 K (2 transitions) for  $\text{K}_2\text{RuO}_4$ . This can be correlated with the distances between the ruthenium tetrahedra, which are closer for  $\text{K}_2\text{RuO}_4$  than for

Rb<sub>2</sub>RuO<sub>4</sub> giving rise to more pronounced interactions. Also, it can further be related to the case of Na<sub>2</sub>RuO<sub>4</sub> (T<sub>N</sub> = 35 K), in which the tetrahedral coordination of the ruthenium atom is lost and converted into trigonal bipyramids linked *via* oxygen atoms. To evaluate this whole phenomenon in detail we need to carry out further neutron diffraction experiments.

Finally, it would be interesting to know the magnetic properties of Cs<sub>2</sub>RuO<sub>4</sub> and CsK<sub>5</sub>[RuO<sub>4</sub>][RuO<sub>5</sub>], and also the crystal structure and magnetism of Li<sub>2</sub>RuO<sub>4</sub> with the largest and smallest alkali cation, respectively, in order to have a complete overview over the family of these compounds.

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