

## BRIEF COMMUNICATION

# Synthesis and Crystal Structure of a New Ruthenium Silicophosphate: $\text{RuP}_3\text{SiO}_{11}$

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A new ruthenium silicophosphate  $\text{RuP}_3\text{SiO}_{11}$  was obtained and the structure was determined by single-crystal X-ray diffraction. It crystallizes in the trigonal space group  $R\bar{3}c$  with  $a = 8.253(3)\text{\AA}$ ,  $c = 39.317(4)\text{\AA}$ ,  $V = 2319(2)\text{\AA}^3$ ,  $Z = 12$ ,  $R = 0.029$ , and  $R_w = 0.026$ . The structure is composed of  $\text{RuO}_6$ ,  $\text{Si}_2\text{O}_7$ , and  $\text{P}_2\text{O}_7$  units. The  $\text{Si}_2\text{O}_7$  unit shares the six oxygen atoms with six  $\text{P}_2\text{O}_7$  units, while the  $\text{P}_2\text{O}_7$  unit shares the six oxygen atoms with two  $\text{Si}_2\text{O}_7$  units and four  $\text{RuO}_6$  octahedra. The anionic part forms an infinite three-dimensional network of silicophosphate.  $\text{RuP}_3\text{SiO}_{11}$  is isotopic with  $\text{MoP}_3\text{SiO}_{11}$ . © 1996

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Silicophosphates are the compounds having the condensed  $\text{SiO}_4$  and  $\text{PO}_4$  tetrahedra. These tetrahedra are further connected with metal polyhedra. Recently, many silicophosphates were discovered in the  $M\text{-P-Si-O}$  systems,  $M = \text{Cd}$  (1),  $\text{V}$  (2),  $\text{Mo}$  (3–7),  $\text{Ti}$  (8),  $\text{Sn}$  (8),  $\text{Si}$  (9), and  $\text{Ge}$  (10). In their structures,  $\text{PO}_4$  is connected with  $\text{XO}_4$  and  $\text{MO}_6$  (or  $\text{M}_2\text{O}_9$ ) units. On the other hand,  $\text{SiO}_4$  is connected only with  $\text{XO}_4$  tetrahedra.

In the present paper, we describe the preparation and structure of a new ruthenium silicophosphate  $\text{RuP}_3\text{SiO}_{11}$ . It contains  $\text{Si}_2\text{O}_7$  units with  $D_{3d}$  symmetry and  $\text{P}_2\text{O}_7$  units. In the chemistry of phosphate, ruthenium has been less studied than in the case of molybdenum or other transition metals. Only two ruthenium phosphates have been reported (11), and  $\text{RuP}_3\text{SiO}_{11}$  is the first silicophosphate of ruthenium.

Single crystals of  $\text{RuP}_3\text{SiO}_{11}$  were accidentally obtained at first from a system containing niobium by the following method. The mixture of ruthenium chloride hydrate and 85% phosphoric acid in a mole ratio of 1:3 was heated at  $350^\circ\text{C}$  for 1 week under  $\text{N}_2$  gas, and a brown powder of an amorphous ruthenium phosphate  $\text{H}_2\text{RuP}_3\text{O}_{10}$  (11) was obtained. The powder precursor was mixed with  $\text{Nb}_2\text{O}_5$

(metal ratio:  $\text{Nb}/\text{Ru} \approx 0.5$ ) and was sealed in a silica ampoule. The ampoule was heated at  $950^\circ\text{C}$  for 5 days and then slowly cooled at  $5^\circ\text{C} \cdot \text{hr}^{-1}$  to  $850^\circ\text{C}$ , and the furnace was turned off. Large yellow crystals of  $\text{RuP}_3\text{SiO}_{11}$  were obtained as the main product. Though the crystals of  $\text{RuP}_3\text{SiO}_{11}$  have very good quality, they are mixed with a black powder of  $\text{Nb}_2(\text{PO}_4)_3$  (12) and chemical analysis of the crystals was impossible.

Single crystals were obtained also from the system without niobium by the following procedure. The mixture of ruthenium chloride hydrate (Tanaka) and 85% phosphoric acid (Koso-kagaku) in a mole ratio of 1:4 was heated in air for 40 min, and the residue was then heated in platinum boats under  $\text{N}_2$  gas flow at  $350^\circ\text{C}$  for 1 week. The resulted brown powder was amorphous ruthenium phosphate (Ru content 24.2%). It was pressed into a pellet and sealed in an evacuated silica ampoule. The ampoule was heated at  $950^\circ\text{C}$  for 5 days, and yellow thin plate crystals of  $\text{RuP}_3\text{SiO}_{11}$  were obtained with a small amount of  $\text{RuO}_2$ . Silicon in  $\text{RuP}_3\text{SiO}_{11}$  comes from the silica ampoule. The crystals yielded in this reaction were very thin. Even the largest crystal, which was used for single-crystal X-ray study, was only 0.01-mm thick.

The structures of the two crystals, one from the  $\text{Ru-P-Si-O}$  system and another from the  $\text{Ru-Nb-Si-P-O}$  system, have been determined by single-crystal X-ray studies. Atomic parameters were determined by the Patterson method (SHELXS86 (13)) and Fourier techniques (SHELXS76 (14)). A full-matrix least-squares program ANYBLK (15) was used for the final refinement. The crystallographic and experimental data of the two crystals are summarized in Table 1. The comparison of the results shows that they are the same compound. The cell parameters of the two crystals are identical within the normal experimental error. The refined atomic coordinates of the two crystals have only the statistically expected differences, i.e., the maximum value of  $\Delta/(\sigma_1^2 + \sigma_2^2)^{1/2}$  was 2.2. Here,

TABLE 1  
Crystallographic Data for RuP<sub>3</sub>SiO<sub>11</sub>

	Crystal 1 <sup>a</sup>	Crystal 2 <sup>a</sup>
Formula weight	398.07	398.07
Space group	R3c (No. 167)	R3c (No. 167)
<i>a</i> (Å)	8.247(2) <sup>b</sup>	8.253(3) <sup>b</sup>
<i>c</i> (Å)	39.287(4) <sup>b</sup>	39.317(4) <sup>b</sup>
<i>V</i> (Å <sup>3</sup> )	2314(1)	2319(2)
<i>Z</i>	12	12
<i>F</i> (000), electrons	3348	3348
<i>D</i> <sub>calcd</sub> (g · cm <sup>-3</sup> )	3.428	3.421
<i>T</i> (K) of data collection	296	296
Crystal size (mm)	0.12 × 0.10 × 0.01	0.25 × 0.12 × 0.05
Diffractometer	Rigaku AFC-5R	Rigaku AFC-6S
Radiation	MoKα 0.7107Å	MoKα 0.7107Å
(graphite monochromated)		
Scan mode	2θ - ω	2θ - ω
Scan range (degree)	1.10 + 0.3 tan ω	1.26 + 0.3 tan ω
Collection region	0 ≤ <i>h</i> ≤ 12 -12 ≤ <i>k</i> ≤ 12 -55 ≤ <i>l</i> ≤ 55	0 ≤ <i>h</i> ≤ 9 -10 ≤ <i>k</i> ≤ 10 0 ≤ <i>l</i> ≤ 54
2θ limit	5° ≤ 2θ ≤ 60°	5° ≤ 2θ ≤ 60°
No. of measured reflections	4821	2448
No. of unique reflections	908	767
No. of observed reflections	520	611
	<i>F</i> <sub>o</sub>   > 4σ(  <i>F</i> <sub>o</sub>  )	<i>F</i> <sub>o</sub>   > 3σ(  <i>F</i> <sub>o</sub>  )
Linear absorption coeff. μ(cm <sup>-1</sup> )	28.71	28.65
Absorption correction	ψ-scan correct with -6 1-10 reflection	ψ-scan correct with -1 5 0 reflection
Transmission factor	0.7738/0.9725	0.7846/0.9880
No. of variable parameters	50	50
weighting scheme	<i>w</i> = 1/σ <sup>2</sup> (  <i>F</i> <sub>o</sub>  )	<i>w</i> = 1/σ <sup>2</sup> (  <i>F</i> <sub>o</sub>  )
<i>R</i> , <i>R</i> <sub>w</sub>	0.0367, 0.0233	0.0290, 0.0260
Goodness of fit, <i>S</i> <sup>d</sup>	1.50	2.07
Residual density <sup>e</sup> eÅ <sup>-3</sup>	1.04	0.87

<sup>a</sup> Crystal 1 was obtained from the Ru-P-Si-O system and crystal 2 was obtained from the Ru-Nb-P-Si-O system.

<sup>b</sup> The cell constant refinement is constrained in the trigonal system.

<sup>c</sup>  $R = \sum (|F_o| - |F_c|) / \sum |F_o|$ ,  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$  ( $w = 1/\sigma(F_o)^2$ ).

<sup>d</sup>  $S = [w(|F_o| - |F_c|)^2 / (N_{\text{observns}} - N_{\text{parameters}})]^{1/2}$ .

<sup>e</sup> The highest residual electrons of the final difference Fourier map.

TABLE 3  
Bond Distances and Angles in RuP<sub>3</sub>SiO<sub>11</sub>

	Ru	O2	O2 <sup>#1</sup>	O2 <sup>#2</sup>	O3	O3 <sup>#1</sup>	O3 <sup>#2</sup>
O2		<b>2.040(3)</b>	2.792(5)	2.792(5)	2.967(4)	4.085(4)	2.920(4)
O2 <sup>#1</sup>	86.36(12)		<b>2.040(3)</b>	2.792(5)	2.920(4)	2.967(4)	4.085(4)
O2 <sup>#2</sup>	86.36(12)	86.36(12)		<b>2.040(3)</b>	4.085(4)	2.920(4)	2.967(4)
O3	93.15(12)	91.21(12)	177.55(12)		<b>2.046(3)</b>	2.874(5)	2.874(5)
O3 <sup>#1</sup>	177.55(12)	93.15(12)	91.21(12)			<b>2.046(3)</b>	2.874(5)
O3 <sup>#2</sup>	91.21(12)	177.55(12)	93.15(12)		89.26(12)	89.26(12)	<b>2.046(3)</b>
	Si	O1	O1 <sup>#1</sup>		O1 <sup>#2</sup>		O5
O1		<b>1.608(3)</b>	2.634(5)		2.634(5)		2.588(3)
O1 <sup>#1</sup>	109.96(12)		<b>1.608(3)</b>		2.634(5)		2.588(3)
O1 <sup>#2</sup>	109.96(12)		109.96(12)		<b>1.608(3)</b>		2.588(3)
O5	108.97(12)		108.97(12)		108.97(12)		<b>1.571(2)</b>
	P	O1 <sup>#5</sup>	O2		O3 <sup>#4</sup>		O4 <sup>#3</sup>
O1 <sup>#5</sup>		<b>1.581(3)</b>	2.527(4)		2.494(4)		2.462(5)
O2	111.3(2)		<b>1.479(3)</b>		2.559(4)		2.479(4)
O3 <sup>#4</sup>	108.3(2)		118.8(2)		<b>1.494(3)</b>		2.495(3)
O4 <sup>#3</sup>	101.7(2)		107.52(14)		107.8(2)		<b>1.594(2)</b>

<sup>#1</sup>: -*y*, *x* - *y*, *z*; <sup>#2</sup>: -*x* + *y*, -*x*, *z*; <sup>#3</sup>: -*x* + *y* + 2/3, -*x* + 1/3, *z* + 1/3  
<sup>#4</sup>: -*x* + 2/3, -*y* + 1/3, -*z* + 1/3; <sup>#5</sup>: -*x* + 1/3, -*x* + *y* + 2/3, -*z* + 1/6

angle(P-O1-Si) = 134.7(2)°

angle(P-O4-P) = 127.9(3)°

angle(Si-O5-Si) = 180°

Δ is the difference of the corresponding atomic parameters, and σ<sub>1</sub> and σ<sub>2</sub> are the estimated standard deviations of them. Because the results of the crystal obtained from the Ru-Nb-Si-P-O system have better accuracy, we give them in Tables 2 and 3.

The structure of RuP<sub>3</sub>SiO<sub>11</sub> has a three-dimensional network of silicophosphate ion composed of Si<sub>2</sub>O<sub>7</sub> and P<sub>2</sub>O<sub>7</sub> subunits (Fig. 1). A Si<sub>2</sub>O<sub>7</sub> fragment is illustrated at the center of Fig. 1. The bond lengths and angles are Si-

TABLE 2  
Atomic Parameters for RuP<sub>3</sub>SiO<sub>11</sub> with Standard Deviations in Parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (Å <sup>2</sup> )	<i>U</i> <sub>11</sub> <sup>a</sup>	<i>U</i> <sub>22</sub> <sup>a</sup>	<i>U</i> <sub>33</sub> <sup>a</sup>	<i>U</i> <sub>12</sub> <sup>a</sup>	<i>U</i> <sub>13</sub> <sup>a</sup>	<i>U</i> <sub>23</sub> <sup>a</sup>
Ru	0.0	0.0	0.158752(14)	0.0050(2)	0.56(2)	0.56(2)	0.40(2)	0.278(8)	0.0	0.0
P	0.3715(2)	0.0393(2)	0.11974(3)	0.0062(4)	0.63(5)	0.66(5)	0.55(5)	0.31(4)	-0.01(5)	-0.04(5)
Si	0.0	0.0	0.03997(5)	0.0059(6)	0.66(5)	0.66(5)	0.46(9)	0.33(3)	0.0	0.0
O1	0.0477(5)	0.2035(4)	0.05327(8)	0.0082(13)	1.1(2)	0.6(2)	1.0(2)	0.60(13)	-0.22(13)	-0.06(12)
O2	0.2235(4)	0.0858(4)	0.12695(7)	0.0089(14)	0.80(15)	1.0(2)	0.93(15)	0.49(13)	0.54(12)	0.38(13)
O3	0.1361(5)	0.2309(4)	0.18918(7)	0.0101(13)	1.0(2)	0.9(2)	1.1(2)	0.51(14)	-0.36(13)	-0.47(12)
O4	0.2098(5)	0.0	0.75	0.008(2)	0.9(2)	1.3(2)	0.5(2)	0.64(12)	0.14(9)	0.3(2)
O5	0.0	0.0	0.0	0.014(3)	1.7(2)	1.7(2)	0.8(4)	0.87(12)	0.0	0.0

<sup>a</sup> *U*<sub>*ij*</sub> multiplied by 100.

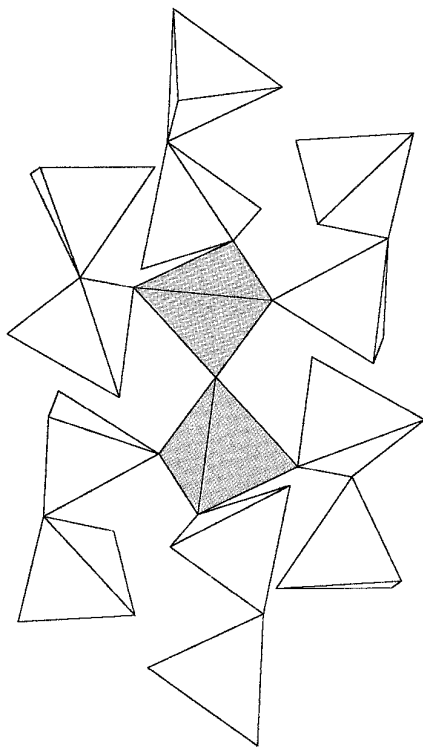


FIG. 1. A partial structure of the silicophosphate ion in  $\text{RuP}_3\text{SiO}_{11}$ . Shaded polyhedra are  $\text{Si}_2\text{O}_7$  units and open polyhedra are  $\text{P}_2\text{O}_7$  units.

$O_{\text{terminal}} = 1.61 \text{ \AA}$ ,  $\text{Si-O}_{\text{bridge}} = 1.57 \text{ \AA}$ , and angle ( $\text{Si-O-Si}$ ) =  $180^\circ$ . Six terminal oxygen atoms of  $\text{Si}_2\text{O}_7$  are bonded to the surrounding six  $\text{P}_2\text{O}_7$  subunits. The P-O bond lengths in the  $\text{P}_2\text{O}_7$  groups are  $1.58 \text{ \AA}$  (with O atoms connected with Si atoms),  $1.48 \text{ \AA}$  (with O atoms connected with Ru atoms), and  $1.59 \text{ \AA}$  (with a bridging O atom). The  $\text{PO}_4$  tetrahedra are smaller than the  $\text{SiO}_4$  tetrahedra, and this is always observed in silicophosphates.

The six  $\text{P}_2\text{O}_7$  units in Fig. 1 are bonded with other  $\text{Si}_2\text{O}_7$  to form an infinite network. Figure 2(a) illustrates the projection of four unit cells of  $\text{RuP}_3\text{SiO}_{11}$  on the  $a$ - $b$  plane. Shaded polyhedra indicate  $\text{SiO}_4$ . Each  $\text{PO}_4$  unit is connected to one  $\text{SiO}_4$  and two  $\text{RuO}_6$  (dotted polyhedra) through three terminal oxygen atoms. Ruthenium atoms exist on threefold axes, and are bonded with the two kinds of oxygen atoms. However, the interatomic distances of Ru-O are  $2.04$  and  $2.05 \text{ \AA}$ , and the  $\text{RuO}_6$  octahedron is almost regular. These distances are similar to those observed in  $\text{Ru}^{\text{III}}\text{P}_3\text{O}_9$  polymorphs ( $2.00 \sim 2.06 \text{ \AA}$ ) (11).

Figure 2(b) shows the projection of  $\text{RuP}_3\text{SiO}_{11}$  along the  $(1\ 1\ 0)$  direction. The crystal structure is constructed from six identical layers as indicated in Fig. 2(b). The layers are built up of  $\text{RuO}_6$ ,  $\text{Si}_2\text{O}_7$ , and  $\text{PO}_4$  units and are stacked along the  $c$  axis sharing the apices of the  $\text{PO}_4$  tetrahedra. The layer is observed in many silicophosphates such as  $\text{AMo}_3\text{P}_6\text{Si}_2\text{O}_{25}$  ( $A = \text{Rb}, \text{Cs}, \text{and Tl}$ )(3, 4),  $\text{Si}_3\text{P}_6\text{O}_{25}$ (9), and

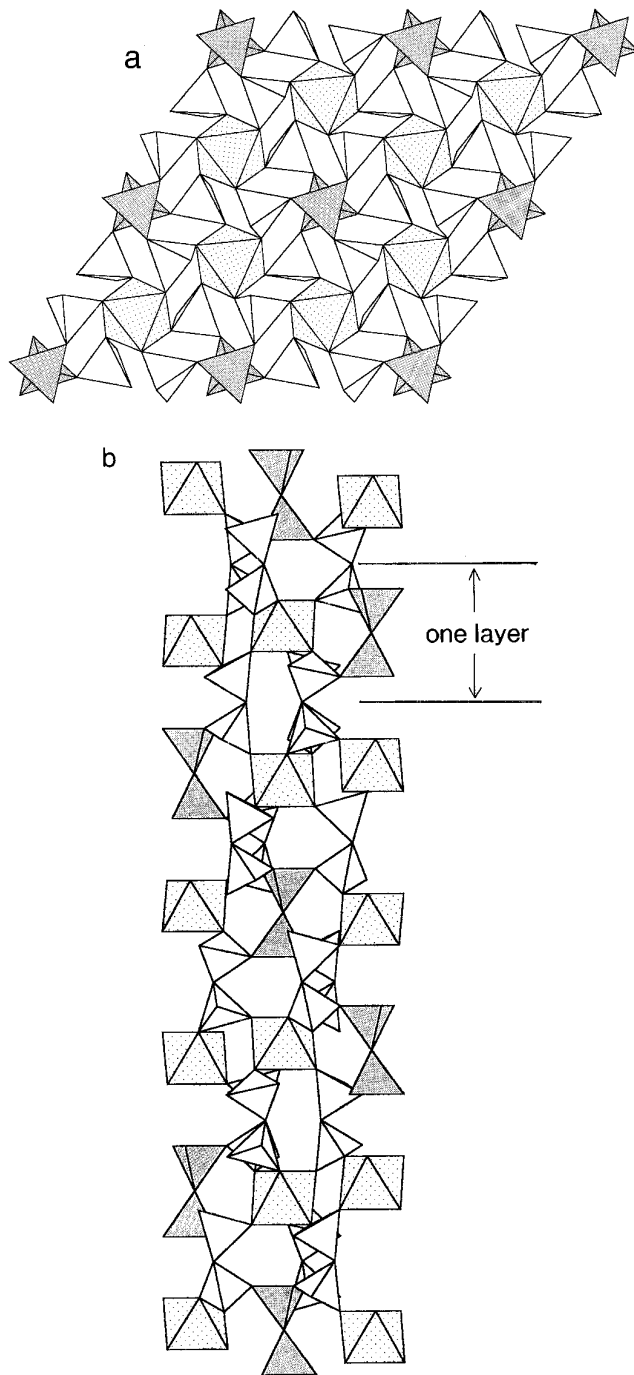


FIG. 2. (a) The structure of  $\text{RuP}_3\text{SiO}_{11}$  projected on the  $a$ - $b$  plane. Four unit cells are seen in this figure. Dotted polyhedra are  $\text{RuO}_6$  and shaded polyhedra are  $\text{Si}_2\text{O}_7$ . Open tetrahedra are  $\text{PO}_4$  units. For the simplification, the figure shows one independent layered substructure (see (b)). (b) The unit cell of  $\text{RuP}_3\text{SiO}_{11}$  projected along the  $(1\ 1\ 0)$  direction. It is constructed of six identical layers. The layers are connected with the oxygen atoms of pyrophosphate units.

MoP<sub>3</sub>SiO<sub>11</sub>(5). While the layers of RuP<sub>3</sub>SiO<sub>11</sub> and MoP<sub>3</sub>-SiO<sub>11</sub> are directly connected with each other, those of AMo<sub>3</sub>P<sub>6</sub>Si<sub>2</sub>O<sub>25</sub> and Si<sub>5</sub>P<sub>6</sub>O<sub>25</sub> are connected through another MO<sub>6</sub> monolayer.

The structure of MoP<sub>3</sub>SiO<sub>11</sub> was described in the monoclinic space group *C2/c*. However, the reported monoclinic unit cell can be converted into a new unit cell with  $a = 8.419 \text{ \AA}$ ,  $b = 8.419 \text{ \AA}$ ,  $c = 39.962 \text{ \AA}$ ,  $\alpha = 90.00^\circ$ ,  $\beta = 90.00^\circ$ , and  $\gamma = 120.02^\circ$ . Here, the cell vectors of the new unit cell are defined by  $\mathbf{a} = 1/2(\mathbf{a}_m + \mathbf{b}_m)$ ,  $\mathbf{b} = 1/2(-\mathbf{a}_m + \mathbf{b}_m)$ , and  $\mathbf{c} = 3\mathbf{c}_m + \mathbf{a}_m$ . The cell parameters suggest the trigonal symmetry. The new atomic coordinates that are obtained by the same basis change followed by a translation of  $(-1/3, -1/6, -1/6)$  show essentially the trigonal symmetry. The deviations of the atomic coordinates from the average structure having the perfect threefold symmetry were less than 1.2 times of the respective standard deviations. Addition of the threefold axis to the space group *C2/c* gives the space group  $R\bar{3}c$ . The new atomic coordinates of MoP<sub>3</sub>-SiO<sub>11</sub> are very close to those of RuP<sub>3</sub>SiO<sub>11</sub>, and the two compounds are isotypic. The cell dimensions of MoP<sub>3</sub>SiO<sub>11</sub> are slightly larger than those of RuP<sub>3</sub>SiO<sub>11</sub>, which is consistent with the larger ionic radius of molybdenum.

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