Tetrabarium Zirconium(IV) Triruthenate(IV), Ba$_4$ZrRu$_3$O$_{12}$, a Rietveld Refinement of Neutron Powder Diffraction Data

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Abstract. $M_r = 1135 \cdot 87$, rhombohedral, $Z = 3$, $R\bar{3}m$. At room temperature: $a_{hex} = 5 \cdot 7884$ (2), $c = 28 \cdot 7764$ (14) Å, $V = 835 \cdot 00$ (8) Å^3, $D_x = 6 \cdot 777$ (1) Mg m^{-3}. At 4·2 K: $a_{hex} = 5 \cdot 7769$ (2), $c = 28 \cdot 7375$ (15) Å, $V = 830 \cdot 55$ (9) Å^3, $D_x = 6 \cdot 813$ (1) Mg m^{-3}, $\mu R = 0 \cdot 38$. The structure has been refined by Rietveld analysis of neutron powder diffraction data recorded at room temperature and at 4·2 K [$\lambda = 2 \cdot 5904$ (3) Å, $R_I = 2 \cdot 82$, 2·61, $R_P = 7 \cdot 36$, 7·61, $R_{wP} = 8 \cdot 86$, 8·69%, respectively, both for 69 reflections]. The structure at both temperatures is of a rhombohedral, 12L type. BaO$_3$ layers are stacked $(hhcc)_3$ resulting in strings of three face-sharing octahedra, which share corners with single octahedra.

Introduction. In a programme to investigate compounds with perovskite or related structures for their properties as a host lattice for nuclear waste, we investigated the existence of compounds in the system BaZrO$_3$/BaRuO$_3$.

Donohue, Katz & Ward (1966) reported that Zr could not be introduced into the 9L structure of BaRuO$_3$, but that substantial substitution of Zr by Ru occurred in BaZrO$_3$ with the perovskite structure, causing distortion from the cubic structure.

Our investigations showed the existence of the, until now, unknown compound Ba$_4$ZrRu$_3$O$_{12}$. Neutron powder diffraction studies were carried out in order to determine its structure.

Experimental. AR starting materials BaCO$_3$, ZrO$_2$ and Ru were thoroughly mixed in an agate mortar in the appropriate ratios. The mixtures BaZr$_x$Ru$_{1-x}$O$_3$ ($x = 0 \cdot 2, 0 \cdot 4, 0 \cdot 6, 0 \cdot 8$) were heated at 1073 K for 1 d and at 1273 K for 3 d, both in air. After grinding, the products were sealed in Pt capsules and heated at 1673 K for two weeks. X-ray powder diffraction patterns were obtained with a Philips PW 1050 diffractometer. From the diffraction patterns it was deduced that a new compound, with $x \simeq 0 \cdot 25$, exists. Further investigations (other values of x) showed a phase BaZr$_{0 \cdot 25-x}$Ru$_{0 \cdot 75+x}$O$_3$ with positive x. All lines of the new phase could be indexed with a hexagonal cell with rhombohedral absences. This result is in accordance with electron diffraction data (Siemens Elmiskop

102 electron microscope, double tilt, lift cartridge, 100 kV).

The stability in water at 573 K and 0·2 GPa for 1 d was tested; it was found that Ba$_4$ZrRu$_3$O$_{12}$ was stable under these conditions.

Taking into account the thickness of BaO$_3$ layers (2·24–2·45 Å), the hexagonal lattice parameters suggest an $(hhcc)_3$ sequence of the layers (Katz & Ward, 1964) with space group $R\bar{3}m$ (No. 166). Models which meet these requirements are Ba$_4$Re$_2$MgO$_{12}$ (Longo, Katz & Ward, 1965) and Ba$_4$$MRu_3O_{12}$ (M = Nb, Ta) (Greatrix & Greenhouse, 1980).

Further heating at 1873 K showed the structure to change into a 6L BaTiO$_3$ type.

Since no single crystals were available we used Rietveld's (1969) method for refinement of neutron powder diffraction data on the powder diffractometer at the Petten High-Flux Reactor; $5° < 2\theta < 163°$ in steps of 0·1°; neutrons at room temperature and 4·2 K from (111) planes of a Cu crystal; pyrolytic graphite with a total thickness of 120 mm as a second-order filter; Soller slits, horizontal divergence 0·5°, placed between the reactor and the monochromator and in front of each of the four ^{3}He counters; sample holder ($\varnothing = 29$ mm) consisted of a V tube, closed with Cu plugs fitted with O-rings. No precautions against preferred orientations. Maximum absorption correction 5%, $\mu R = 0 \cdot 38$ (Weber, 1967). Background determined from those parts in the diagram not containing any contribution from reflections or − for high values of 2θ − only a small contribution, and extrapolation between these points. Statistically expected values of R_{wP} 3·45 and 3·85% respectively.

Sample was slightly contaminated with BaZrO$_3$, most reflections of which coincide with those of Ba$_4$ZrRu$_3$O$_{12}$. BaZrO$_3$ reflections were subtracted from those of Ba$_4$ZrRu$_3$O$_{12}$. Scaling, based on one non-coincident BaZrO$_3$ reflection, resulted in a BaZrO$_3$ percentage of approximately 5%.

The proposed structure of Ba$_4$NbRu$_3$O$_{12}$ (Greatrix & Greenhouse, 1980) was used as a trial model: Ba(1) in 6(c) (0,0,z); Ba(2) in 6(c); Zr in 3(a) (0,0,0); Ru(1) in 3(b) (0,0,$\frac{1}{2}$); Ru(2) in 6(c); O(1) in 18(h) ($x,-x,z$); O(2) in 18(h). 23 parameters in the refinement: a scale factor, three half-width parameters defining the Gaussian line

Table 1. *Fractional atomic coordinates and thermal parameters of* $Ba_4ZrRu_3O_{12}$ *at room temperature and 4·2 K*

	x	z	B (Å^2)
$Ba_4ZrRu_3O_{12}$, room temperature			
Ba(1)	0	0·1291 (2)	0·5 (2)
Ba(2)	0	0·2872 (3)	1·1 (2)
Zr	0	0	−0·3 (2)*
Ru(1)	0	0·5	0·6 (1)
Ru(2)	0	0·4121 (2)	1·7 (1)*
O(1)	0·4893 (3)	0·1229 (1)	0·7 (1)
O(2)	0·4981 (3)	0·2921 (1)	0·9 (1)
$Ba_4ZrRu_3O_{12}$, 4·2 K			
Ba(1)	0	0·1294 (3)	0·6 (2)
Ba(2)	0	0·2875 (3)	0·6 (2)
Zr	0	0	−0·9 (2)*
Ru(1)	0	0·5	0·7 (2)
Ru(2)	0	0·4118 (2)	1·7 (2)*
O(1)	0·4898 (3)	0·1227 (1)	0·2 (1)
O(2)	0·4981 (4)	0·2921 (2)	0·5 (1)

* The thermal parameters of Zr and Ru(2) are strongly correlated.

shape of the reflections, the counter zero error, preferred-orientation parameter (along [001]), an asymmetry parameter below $2\theta = 37°$, the unit-cell parameters, the atomic positional parameters and the isotropic thermal parameters. The coherent scattering lengths used are: Ba 5·25, Zr 7·16, Ru 7·21, O 5·805 fm (Koester, Rauch, Herkens & Schroeder, 1981).

The Rietveld program minimizes the function X^2 $= \sum_i w_i[y_i(\text{obs.}) - (1/c)y_i(\text{calc.})]^2$, where $y_i(\text{obs.})$ and $y_i(\text{calc.})$ are the observed and calculated data points, w_i is the statistical weight $[1/y_i(\text{obs.})]$ allotted to each data point and c is the scale factor. The following R factors were calculated:

$$R_I = 100\sum |I_i(\text{obs.}) - (1/c)I_i(\text{calc.})| / \sum I_i(\text{obs.}),$$
$$R_P = 100\sum |y_i(\text{obs.}) - (1/c)y_i(\text{calc.})| / \sum y_i(\text{obs.}),$$
$$R_{wP} = 100[\sum w_i |y_i(\text{obs.}) - (1/c)y_i(\text{calc.})|^2 / \sum w_i |I_i(\text{obs.})|^2]^{1/2},$$

where $I_i(\text{obs.})$ and $I_i(\text{calc.})$ are the observed and calculated integrated intensities of each reflection. $\Delta/\sigma < 0·3$ in final cycle.

Discussion. Atomic parameters are given in Table 1, atomic distances in Table 2. The agreement between the observed and calculated profile of the data at room temperature is shown in Fig. 1.* In Fig. 2(a) the structure of $Ba_4ZrRu_3O_{12}$ is given. In the structure BaO_3 layers are stacked $(hhcc)_3$ resulting in strings of three face-sharing octahedra which share corners with single octahedra. Because the scattering lengths of Zr

and Ru are almost equal, their positions cannot be distinguished by neutron diffraction. We assume that the Ru atoms are in the face-sharing octahedra as in the structure of $BaRuO_3$ (Donohue, Katz & Ward, 1965) (Fig. 2b), and the Zr atom in the single octahedra. The proposed atomic distribution is in accordance with the ionic radii of Ru^{4+} and Zr^{4+} 0·62 and 0·72 Å respectively (Shannon, 1976) and the atomic distances (Table 2). Also, the Ru—Ru distances in $Ba_4ZrRu_3O_{12}$ are about the same as in $BaRuO_3$, 2·529 (6) (at room temperature) and 2·55 Å respectively. Furthermore, the phasewidth for $BaZr_{0.25-x}Ru_{0.75+x}O_3$ can be understood when Zr is only found in the single octahedra.

Table 2. *Atomic distances* (Å) *at room temperature and coordination numbers*

a (about) equilateral distances.

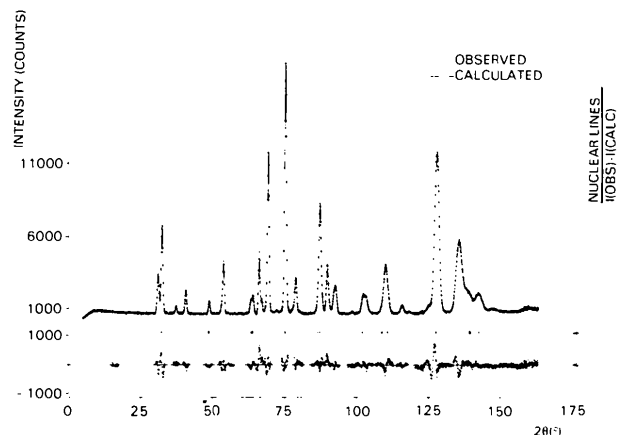| $Ba_4ZrRu_3O_{12}$ (300 K)		$Ba_4ZrRu_3O_{12}$ (4·2 K)		
Ba(1)—O(1)a	2·902 (2)	Ba(1)—O(1)a	2·896 (2)	6×
—O(1)	2·941 (6)	—O(1)	2·929 (7)	3×
—O(2)	3·042 (7)	—O(2)	3·042 (8)	3×
Ba(2)—O(2)a	2·898 (3)	Ba(2)—O(2)a	2·892 (3)	6×
—O(1)	2·836 (7)	—O(1)	2·831 (7)	3×
—O(2)	3·006 (7)	—O(2)	2·998 (8)	3×
The ZrO_6 octahedron				
Zr—O(2)	2·065 (3)	Zr—O(2)	2·062 (4)	6×
O(2)—O(2)a	2·928 (6)	O(2)—O(2)a	2·922 (6)	
O(2)—O(2)	2·911 (6)	O(2)—O(2)	2·911 (7)	
The Ru_3O_9 trioctahedron				
Ru(1)—O(1)	2·009 (3)	Ru(1)—O(1)	2·012 (3)	6×
O(1)—O(1)a	2·708 (5)	O(1)—O(1)a	2·712 (5)	
—O(1)	2·967 (5)	—O(1)	2·971 (6)	
Ru(2)—O(1)	2·013 (4)	Ru(2)—O(1)	2·018 (5)	3×
—O(2)	1·974 (4)	—O(2)	1·964 (5)	3×
O(2)—O(2)a	2·860 (6)	O(2)—O(2)a	2·855 (6)	
—O(1)	2·849 (4)	—O(1)	2·840 (5)	
Ru(1)—Ru(2)	2·529 (6)	Ru(1)—Ru(2)	2·536 (7)	

Fig. 1. Observed (dots) and calculated (full line) neutron diffraction profile of $Ba_4ZrRu_3O_{12}$ at room temperature; a difference (observed − calculated) curve appears at the bottom of the figure. Tick marks below the profile indicate the positions of the Bragg reflections included in the calculation.

* The numerical intensity of each measured point, as a function of the angle, and the final parameters which are not given in this paper have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39673 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
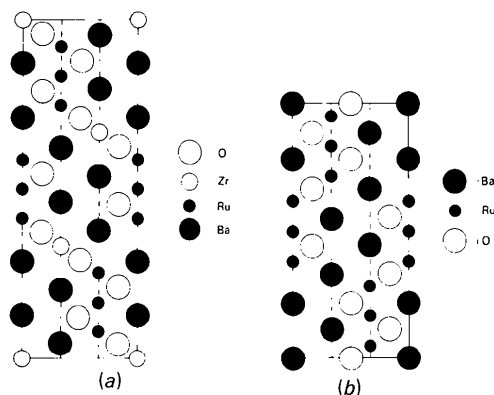
Fig. 2. (a) (110) plane of $Ba_4ZrRu_3O_{12}$ at 4·2 K. (b) (110) plane of $BaRuO_3$.

The 4·2 K neutron diffraction data give no indication of a three-dimensional ordering. The structures at both temperatures are essentially the same (Table 2); the Ru—Ru distances are nearly the same: 2·529 (6) Å at 300 K and 2·536 (7) Å at 4·2 K.

As already mentioned this type of structure is also found in $Ba_4MRu_3O_{12}$ (M = Nb, Ta) (Greatrix & Greenhouse, 1980), in $Ba_4Re_2M\square O_{12}$ (M = Mg, Cd, Co, Zn or Ca) (Longo, Katz & Ward, 1965) and in $Ba_4M_2W\square O_{12}$ (M = Nb, Ta) (Rother, Kemmler-Sack, Treiber & Cyris, 1980). In the last two cases the vacancies ($\square$) are at the centre of the octahedra-string, between the (hh) BaO_3 layers.

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Structure (Neutron) of Room-Temperature Phase III Potassium Iodate, KIO_3

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Abstract. M_r = 214·001, $P1$, a = 7·7436 (4), b = 7·7183 (4), c = 7·7328 (5) Å, α = 108·986 (4), β = 109·449 (4), γ = 109·209 (5)°, V = 359·12 (3) Å³, Z = 4, D_m = 3·89, D_x = 3·96 g cm⁻³, neutron powder diffraction (Rietveld method), λ = 1·9090 (1) Å, $F(000)$ = 320, T = 300 K, R = 7·50% for 716 integrated Bragg intensities. The triclinic structure proposed by Kalinin, Ilyukhin & Belov [*Dokl. Akad. Nauk SSSR* (1978), **239**, 590–593; *Sov. Phys. Dokl.* (1978), **23**, 166–168], from single-crystal X-ray diffraction, is confirmed, thereby resolving previous structural uncertainty.

Introduction. At atmospheric pressure, potassium iodate has been reported to undergo phase transitions with temperature change:

$$\begin{array}{ccccccccc} & 83K & & 255\,K & & 343\,K & & 485\,K & \\ V & \to & IV & \underset{263K}{\overset{}{\rightleftarrows}} & III & \to & II & \to & I \end{array}$$
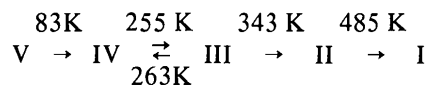
and all phases, except I, are ferroelectric (Herlach, 1961). Attempts to determine the phase III crystal structure have been hindered by a tendency towards twinning and polymorphism, resulting in uncertainty of the true single-crystal nature of specimens used in the