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$Rb_4Zr_3Te_{16}$, a one-dimensional zirconium telluride synthesized from molten salt

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A new ternary metal telluride, tetrarubidium trizirconium hexadecatelluride, $Rb_4Zr_3Te_{16}$, has been synthesized through reactions at 698 K using elemental Zr and an Rb_2Te/Te melt as a reactive flux, and characterized by single-crystal X-ray diffraction. Although the structure of this compound is very similar to its $Cs_4Zr_3Te_{16}$ analogue, the compounds crystallize in different space groups, the former in C_{2h}^6 –$C2/c$ and the latter in C_{2h}^5 –$P2_1/n$. Both compounds consist of infinite one-dimensional chains of $[Zr_3Te_{16}]_n^{4n-}$ separated from each other by Rb^+ or Cs^+ cations. Within the chain, each Zr atom is surrounded by eight Te atoms to give a distorted bicapped trigonal prism polyhedron. There are two unambiguous Te—Te single bonds of 2.758 (2) and 2.765 (2) Å, and four longer Te···Te interatomic distances in the range of 2.9277 (14)–3.0445 (18) Å that indicate weak interactions between the adjacent Te atoms. Because of the wide range of Te···Te interactions, simple formalisms cannot be used to describe the bonding within the chain.

Comment

The reactive flux technique has proved to be an effective method of preparing new ternary polychalcogenides. A series of compounds with the general formula $A_xM_yQ_z$ (A = alkali metal, M = Ti, Zr or Hf, and Q = S, Se or Te) have been reported, such as $K_4Ti_3S_{14}$ (Sunshine *et al.*, 1987), $Na_2Ti_2Se_8$ (Kang & Ibers, 1988), $K_4M_3Te_{17}$ (M = Zr or Hf; Keane & Ibers, 1991) and $Cs_4Zr_3Te_{16}$ (Cody & Ibers, 1994). A survey of the reactions of alkali metal polychalcogenide molten salts to yield new materials with Ti, Cu, Au, Hg and Sn is given by Kanatzidis (1990). Although, in general, substitutions of elements in the same group lead to isostructural compounds, it is found that substitutions in ternary or quaternary chalcogenides containing group IV metals do not just involve simple replacement of one atom for another. For example, substitution of Na for K in the quaternary A/Cu/Zr/Q (A = alkali metal and Q = S, Se or Te) system (Mansuetto *et al.*, 1992, 1993) results in subtle differences in structure, while substitution of Cs for K in the ternary A/M/Te system (A = alkali metal and M = Zr or Hf) even leads to a change in composition from $K_4M_3Te_{17}$ (M = Zr or Hf; Keane & Ibers, 1991) to $Cs_4Zr_3Te_{16}$ (Cody & Ibers, 1994). In the present work, the substitution of Rb for Cs in the above-mentioned ternary system gives the new title compound, $Rb_4Zr_3Te_{16}$, with the same composition but a different space group, C_{2h}^6 –$C2/c$.

As shown in Fig. 1, the crystal structure of the title compound is very similar to that of $Cs_4Zr_3Te_{16}$ (space group C_{2h}^5 –$P2_1/n$). Both crystals have similar cell parameters and contain one-dimensional Zr/Te chains extended along the a direction and separated by alkali metal cations. The M/Te chains of $K_4Hf_3Te_{17}$ (Keane & Ibers, 1991), $Cs_4Zr_3Te_{16}$ (Cody & Ibers, 1994) and $Rb_4Zr_3Te_{16}$ are compared in Fig. 2. With the higher symmetry, there are only two crystallographically unique Zr atoms in $Rb_4Zr_3Te_{16}$. One of them, Zr2, is located on a twofold axis (Wyckoff position 4e) and the other, Zr1, on a general position. Each Zr atom is eight-coordinate and at the center of a bicapped trigonal prism of Te atoms. The Zr—Te bond lengths are in the range 2.890 (2)–3.079 (2) Å (Table 1), which are comparable with those found in $Cs_4Zr_3Te_{16}$ (Cody & Ibers, 1994). Each coordination polyhedron of a Zr atom shares opposite triangular faces with the adjacent Zr polyhedron to form a one-dimensional chain. Zr1 is bridged to Zr2 through atoms Te1, Te3^{i} and Te5, while Zr1 is bridged to Zr1^{ii} through atoms Te7, Te7^{ii} and Te8^{ii} [symmetry codes: (i) $-x, y,$

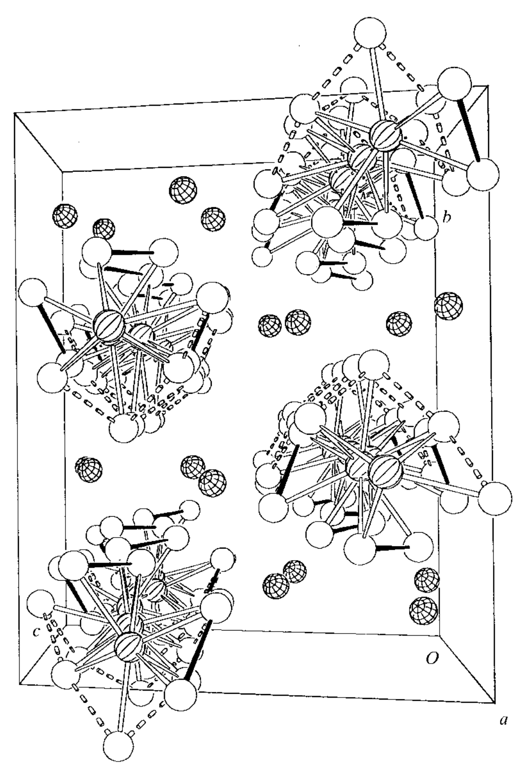

Figure 1
The crystal structure of $Rb_4Zr_3Te_{16}$ along the a direction, with double shaded circles for Rb, single shaded circles for Zr and open circles for Te atoms. The atoms are of arbitrary size.

$\frac{3}{2}-z$; (ii) $-1-x, y, \frac{3}{2}-z$]. A Zr atom coordinated by eight Te atoms in a bicapped trigonal prism has been found not only in ternary *A*/Zr/Te (*A* = alkali metal) systems but also in binary Zr/Te compounds, such as $ZrTe_3$ (Furuseth & Fjellveg, 1991) and $ZrTe_5$ (Furuseth *et al.*, 1973).

As is well known, the tellurides have a greater propensity than do the selenides or sulfides to exhibit $Q-Q$ interactions of intermediate strength between a $Q-Q$ single bond and a $Q^{2-}\cdots Q^{2-}$ van der Waals-type interaction (about 2.76 and 4.10 Å for Te, respectively; Shannon, 1976). While an arbitrary maximum for a Te—Te single bond of 2.94 Å gives $[Hf_3(Te_3)(Te_2)_7{}^{4-}]$ for the Hf/Te chain in $K_4Hf_3Te_{17}$, where each Hf is in the +4 oxidation state, it is somewhat difficult to describe the Te—Te interactions in the Zr/Te chains of $A_4Zr_3Te_{16}$ (*A* = Cs and Rb) and to arrive at a reasonable formal oxidation state assignment for the elements. For $Rb_4Zr_3Te_{16}$, there are two unambiguous Te—Te single bonds with of 2.758 (2) and 2.765 (2) Å, and four somewhat longer Te$\cdots$Te distances in the range 2.9277 (14)–3.0445 (18) Å, which indicates some weak interaction between adjacent Te atoms. The Te—Te single bonds are shown in Fig. 2 as solid lines and other longer Te$\cdots$Te interactions of 3.2 Å or less are shown as broken lines.

The obvious differences between the structures of $Rb_4Zr_3Te_{16}$ and $Cs_4Zr_3Te_{16}$ (Cody & Ibers, 1994) are the coordination environments of the cations. Two unique Rb^+ cations in the former exhibit coordination numbers 12 (Rb1) and 11 (Rb2), with Rb$\cdots$Te distances ranging from 3.614 (2) to 4.316 (3) Å, while the four Cs^+ cations in the latter exhibit coordination numbers 12, 11, 11 and 9, with Cs$\cdots$Te distances ranging from 3.629 to 4.456 Å (Cody & Ibers, 1994).

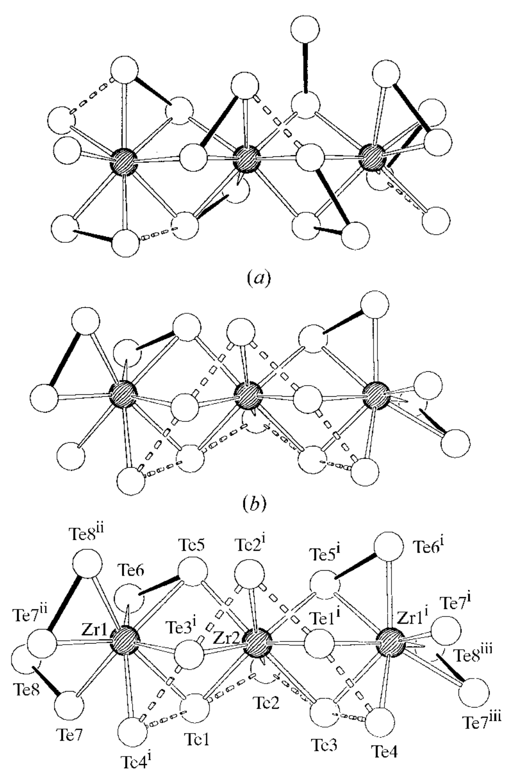

Figure 2
Comparison of the one-dimensional *M*/Te chains of (*a*) $K_4Hf_3Te_{17}$, (*b*) $Cs_4Zr_3Te_{16}$ and (*c*) $Rb_4Zr_3Te_{16}$ with shaded circles for Zr and open circles for Te atoms, black lines for Te—Te single bonds and broken lines for longer Te$\cdots$Te interactions of less than 3.2 Å. The atom-numbering scheme for $Rb_4Zr_3Te_{16}$ is given; symmetry codes are as in Table 1.

Experimental

Rb_2Te was prepared by reactions of rubidium metal (99.5%, Aldrich Chemical Company) and elemental tellurium (99.8%, Strem Chemicals Inc.) in a 2:1 ratio in liquid ammonia. Rb_2Te (0.0746 g, 0.25 mmol), Zr (98%, Aldrich Chemical Company; 0.0228 g, 0.25 mmol) and Te (0.1595 g, 1.25 mmol) were weighed in an inert argon-filled glove box. After thorough mixing, the reactants were transferred to a thin-walled Pyrex reaction tube (9 mm outside diameter). The sample was immediately sealed under a vacuum of approximately 10^{-3} Torr (1 Torr = 133.32 Pa). The reaction vessel was then placed in a furnace and brought up to 698 K over a period of 8 h. After heating at 698 K for 3 d, the container was cooled slowly to 423 K (2 K h^{-1}), followed by natural cooling to room temperature. Upon removal from the furnace, the sample was treated by an isolation procedure. The reaction mixture consisted of the final products embedded in the excess alkali metal polychalcogenide melt. The remaining flux was removed after several washes with *N*,*N*-dimethylformamide in a nitrogen atmosphere. The sample was then washed twice with 95% ethanol and dried with diethyl ether. Black prism-like crystals were isolated after this procedure. Microprobe analysis was performed on selected single crystals using a Jeol JXA-8600 Superprobe and gave an approximate elemental ratio of Rb, Zr and Te in agreement with the crystal data.

Crystal data

$Rb_4Zr_3Te_{16}$	D_x = 5.382 Mg m^{-3}
M_r = 2657.14	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 25 reflections
a = 11.982 (2) Å	θ = 7.6–12.5°
b = 18.613 (4) Å	μ = 20.781 mm^{-1}
c = 15.078 (3) Å	T = 293 (2) K
β = 102.79 (3)°	Prism, black
V = 3279.3 (11) Å^3	0.12 × 0.10 × 0.10 mm
Z = 4	

Data collection

Enraf–Nonius CAD-4 diffractometer	R_{int} = 0.023
ω scans	θ_{max} = 24.97°
Absorption correction: ψ scan (North *et al.*, 1968)	$h = -14 \rightarrow 13$
T_{min} = 0.094, T_{max} = 0.126	$k = 0 \rightarrow 22$
2991 measured reflections	$l = 0 \rightarrow 17$
2874 independent reflections	3 standard reflections frequency: 120 min
2335 reflections with $I > 2\sigma(I)$	intensity variation: ±2.2%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R(F)$ = 0.041	$\Delta\rho_{max}$ = 3.095 e Å^{-3}
$wR(F^2)$ = 0.086	$\Delta\rho_{min}$ = −2.361 e Å^{-3}
S = 1.940	Extinction correction: *SHELX*97 (Sheldrick, 1997)
2874 reflections	Extinction coefficient: 3.0 (1) × 10^{-4}
106 parameters	
$w = 1/[\sigma^2(F_o^2) + (0.001P)^2 + 5P]$ where $P = (F_o^2 + 2F_c^2)/3$	

The largest residual electron-density peaks were located around the Te and Zr atoms.

Table 1
Selected bond distances (Å).

Zr1—Te6	2.8895 (18)	Rb1—Te2^{v}	3.830 (2)
Zr1—Te3^{i}	2.9528 (19)	Rb1—Te7^{iv}	3.855 (2)
Zr1—Te7^{ii}	2.9420 (17)	Rb1—Te1^{iv}	3.872 (2)
Zr1—Te8^{ii}	2.9547 (18)	Rb1—Te8^{iv}	3.960 (2)
Zr1—Te4^{i}	2.9819 (18)	Rb1—Te5^{vi}	3.994 (2)
Zr1—Te5	2.9861 (17)	Rb1—Te5^{v}	4.115 (2)
Zr1—Te7	3.012 (2)	Rb1—Te2^{iv}	4.148 (3)
Zr1—Te1	3.0794 (17)	Rb1—Te6^{v}	4.190 (2)
Zr2—Te1	2.9326 (15)	Rb1—Te4^{vii}	4.316 (3)
Zr2—Te2	2.9422 (13)	Rb2—Te8^{v}	3.614 (2)
Zr2—Te3	2.9599 (14)	Rb2—Te1	3.616 (2)
Zr2—Te5	2.9936 (18)	Rb2—Te8^{viii}	3.648 (3)
Te1—Te2	2.9277 (14)	Rb2—Te4^{i}	3.695 (2)
Te1—Te4^{i}	2.9889 (15)	Rb2—Te6^{v}	3.724 (2)
Te2—Te3	3.0165 (16)	Rb2—Te2^{iv}	3.725 (2)
Te3—Te4	3.0445 (18)	Rb2—Rb2^{i}	3.968 (4)
Te5—Te6	2.7578 (17)	Rb2—Te6^{ix}	4.045 (2)
Te7—Te8	2.7648 (15)	Rb2—Te3	4.144 (2)
Rb1—Te4	3.710 (2)	Rb2—Te3^{iv}	4.245 (2)
Rb1—Te7^{iii}	4.052 (2)	Rb2—Te5^{ix}	4.281 (2)
Rb1—Te6^{iv}	3.805 (2)		

Symmetry codes: (i) $-x, y, \frac{3}{2}-z$; (ii) $-1-x, y, \frac{3}{2}-z$; (iii) $1+x, y, z$; (iv) $-x, -y, 1-z$; (v) $\frac{1}{2}+x, y-\frac{1}{2}, z$; (vi) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z$; (vii) $1-x, y, \frac{3}{2}-z$; (viii) $-1-x, -y, 1-z$; (ix) $-\frac{1}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z$.

Data collection: *CAD*-4-*PC Software* (Enraf–Nonius, 1992); cell refinement: *CAD*-4-*PC Software*; data reduction: *XCAD*4/*PC* (Harms, 1997); program(s) used to solve structure: *SHELX*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELX*97; molecular graphics: *SCHAKAL*92 (Keller, 1992); software used to prepare material for publication: *SHELX*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1265). Services for accessing these data are described at the back of the journal.

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