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Syntheses and Structural Characterization of New Mixed-Valent Tellurium Oxides, $A_4[Te_5^{6+}Te_3^{4+}]O_{23}$ (A = Rb and K)

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Two new isostructural mixed-valent tellurium oxides, $A_4[Te_5^{6+}Te_3^{4+}]O_{23}$ [A = Rb (**1**) and K (**2**)], have been synthesized by solid-state reactions and characterized by X-ray diffraction and infrared spectroscopy. Compound **1** could be prepared by hydrothermal reaction as well. These compounds, as determined from the single-crystal X-ray structure of **1**, consist of corrugated $[Te_6O_{23}]$ layers, built from corner-connected TeO_6 octahedra and TeO_5 square pyramids. These layers are connected to one another by tetravalent telluriums, having square-pyramidal and disphenoid geometries. Both compounds crystallize in the orthorhombic space group $Pna2_1$ (33) with $Z = 4$ and have the following unit cell parameters: For **1**, $a = 19.793(4)$, $b = 14.664(4)$, and $c = 7.292(4)$ Å. For **2**, $a = 19.573(3)$, $b = 14.448(2)$, and $c = 7.273(8)$ Å.

Introduction

As a part of our research on low-temperature synthetic routes for new oxide materials, we have previously explored the quaternary A/M/Te/O (A = alkali metals, NH_4; M = Mo or W) systems and succeeded in the isolation, by a hydrothermal method, and structural characterization of a number of tellurites with varied and interesting formulations.[1−5] These compounds possess a variety of structures, having discrete molecular anions and extended anionic frameworks, with Te^{4+} exhibiting one or more of the three coordinations, namely, pyramidal TeO_3, disphenoid TeO_4, and square-pyramidal TeO_5. For example, $A_2Mo_3TeO_{12}$ (A = NH_4, Cs) and $A_4Mo_6Te_2O_{24}\cdot 6H_2O$ (A = Rb, K) have[1], respectively, layered and discrete molecular anions with the same empirical formula, $[Mo_3TeO_{12}]^{2-}$. There has been an upsurge[6−9] of interest in the solid-state chemistry of tellurites, owing to their structural diversity and potential use as second-harmonic-generating (SHG) materials. Furthermore, some of these tellurites, such as $Cs_2Mo_3TeO_{12}$, could be prepared by a solid state-reaction as well. Thus, hydrothermal and solid-state reactions have been found to be suitable for the synthesis of various tellurites, including the tungsten analogues,[5] $A_2W_3TeO_{12}$.

These interesting results have prompted us to undertake a similar exploratory synthetic and structural investigation of the A/Te/O system for oxides with tellurium in both 6+ and 4+ oxidation states. Moreover, there are only two such mixed-valent oxides, $A_2[Te_3^{6+}Te^{4+}]O_{12}$ (A = Cs, K), known,[10,11] and all other compounds, such as $K_2Te_4O_9\cdot 3.2H_2O$, $K_4[Te_2O_6(OH)_4](H_2O)_{7.3}$, $K_2[Te_4O_8(OH)_{10}]$, and $(NH_4)_2[Te_3O_8(OH)_4]$, reported[7,12−14] in this system contain tellurium exclusively in either the 6+ or 4+ oxidation state. $Cs_2Te_4O_{12}$ has been prepared by the solid-state reaction of TeO_2 and Cs_2CO_3 at 640 °C in an argon atmosphere, whereas $K_2Te_4O_{12}$ has been synthesized by the hydrothermal reaction of TeO_2 and K_2CO_3 at 550 °C and under 1 kbar of pressure. $Cs_2Te_4O_{12}$ has a pyrochlore framework of $[Te_4O_{12}]^{2-}$ with all the telluriums charge-delocalized and octahedrally coordinated. $K_2Te_4O_{12}$ is a three-dimensional compound, with

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hexagonal-tungsten-oxide (HTO) layers of $[Te_3O_{12}]$ connected to one another by square-pyramidal Te^{4+}. These two compounds are compositionally similar to, but structurally different from, $A_2M_3TeO_{12}$ (M = Mo, W) phases.[1,5] We have become interested in the synthesis, by both methods, and characterization of $A_2[Te_3^{6+}Te^{4+}]O_{12}$ (A = Cs, Rb, K, Na) compounds to examine structural variations, if any, dependent on the size of A or the method of synthesis. Our synthetic efforts in this direction did not yield the intended products. It is during these attempts that we have isolated new mixed-valent oxides, $Rb_4Te_8O_{23}$ and $Na_3Te_{10.5}O_{28}$ with three-dimensional frameworks. Our work on $A_3Te_{10.5}O_{28}$ (A = K, Na) compounds will be published elsewhere. In this paper, the syntheses and characterization, by X-ray diffraction and spectroscopy, of $Rb_4Te_8O_{23}$ and its isostructural potassium analogue are described. These two compounds could be represented by the formulas $A_4[Te_5^{6+}Te_3^{4+}]O_{23}$ [A = Rb (**1**), K (**2**)], to indicate the fractional contents of hexa- and tetravalent telluriums.

Experimental Section

Synthesis. Both compounds **1** and **2** were obtained by heating stoichiometric reactant mixtures of appropriate chemicals (>99.5% purity, Sigma-Aldrich), H_6TeO_6, TeO_2, Rb_2CO_3, and K_2CO_3, in air at 500 °C for 8 h and, then, at 550 °C for 36 h, with three intermittent grindings. The colors of **1** and **2** are brick-red and yellow, respectively. $Rb_4Te_8O_{23}$ was also synthesized under hydrothermal conditions, by heating a stoichiometric mixture of Rb_2CO_3 (0.2309 g, 1.0 mmol), H_6TeO_6 (0.5741 g, 2.5 mmol), and TeO_2 (0.2394 g, 1.5 mmol), along with 4 mL of water, in a Teflon-lined acid digestion bomb of 23 mL capacity, at 225 °C for 4 days and then cooling it to room temperature over a period of 1.5 days. The pH of the solution remained unchanged at 6.0 after the reaction. $Rb_4Te_8O_{23}$ was obtained as a single-phase product (0.6457 g, 74.57% yield based on H_6TeO_6). Only polycrystalline products were obtained in our synthetic attempts. To grow crystals, the polycrystalline products, obtained by the solid-state synthetic reactions intended for $A_2Te_4O_{12}$ compounds, were first melted at 675 °C and then cooled to 500 °C at a rate of 2 °C/hour, and finally, the furnace was turned off. Single crystals of $Rb_4Te_8O_{23}$ (**1**) were manually separated from the solidified melts.

Characterization. For both compounds, the ratio of alkali metal to tellurium was ascertained to be correct by an energy dispersive analysis of X-rays (EDAX analysis), using a LEO S440I (Oxford, U. K.) instrument. The Te^{4+} content, in compounds **1** and **2**, respectively, was determined to be 22.4 and 25.6% by conventional chemical analysis[15] as follows. A known weight (~0.1 g) of the sample was digested with 10 mL of hydrofluoric acid and then mixed with 40 mL of a 0.02 N solution of $K_2Cr_2O_7$ and 20 mL of 1:1 H_2SO_4, to oxidize Te^{4+} to Te^{6+}. The excess, unreacted $K_2Cr_2O_7$ was estimated by volumetric titration against a ~0.02 N solution of ferrous ammonium sulfate, using diphenylamine as an indicator. The observed values of Te^{4+} content agree well with the theoretical values.

Powder X-ray diffraction (XRD) patterns were recorded on a Shimadzu XD-D1 Powder X-ray diffractometer using Cu Kα (λ = 1.5405 Å) radiation. Infrared and Raman spectra were recorded on a Bruker 17S 66V FT-IR spectrometer. The samples were ground with dry KBr and pressed into transparent disks for recording infrared spectra (4000−400 cm^{-1}). Thermal analyses, both thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), were carried out on a Perkin−Elmer Delta series TG instrument, under a nitrogen flow, with a heating rate of 20 °C/min.

Single-Crystal X-ray Diffraction Analysis. A block-shaped single crystal, suitable for X-ray diffraction, of the $Rb_4Te_8O_{23}$ (**1**) compound was mounted on a thin glass fiber with glue. An X-ray diffraction data set was gathered on a STOE STADI4 X-ray diffractometer by standard procedures and then reduced by routine computational procedures. The structure solution and refinement were carried out by the SHELXL 97[16] program. The graphic programs ORTEP[17] and ATOMS[18] were used to draw the structures.

The systematic absences of the measured data indicated noncentrosymmetric $Pna2_1$ and centrosymmetric $Pnma$ as the possible space groups for $Rb_4Te_8O_{23}$ (**1**). The structure solutions and refinements were successful in both the space groups. For $Pnma$, values of 0.0559 and 0.1122 were obtained, respectively, for R and R_w by refining 185 parameters. For $Pna2_1$, on the other hand, lower values of 0.0391 and 0.0737 for R and R_w, respectively, were obtained by refining 222 parameters. Both $A_4Te_8O_{23}$ (A = Rb, K) compounds tested negative for a SHG response, as indicated by the nonemission of green light at 532 nm upon exposure to the fundamental line, 1064 nm of a Q-switched Nd:YAG laser (Quanta-Ray). Thus, the lack of a SHG response could not confirm $Pna2_1$ as the correct space group. However, a detailed examination of the relation between the structures in these two space groups revealed, as discussed in next section, that a pseudo center of inversion exists in the structure in $Pna2_1$, leading to an approximate structure solution in $Pnma$. Thus, $Pna2_1$ is concluded to be the correct space group.

Crystallographically distinct tellurium and alkali-metal atoms were located by the direct method. Refinement of their positions and subsequent difference Fourier maps led to the location of the oxygen atoms of the asymmetric unit. All the tellurium and alkali-metal atoms and only some of the oxygen atoms could be refined anisotropically. The peaks with an electron density of >1 e/Å^3 in the final difference Fourier map were found to be the ghosts. The structure refinement for $Rb_4Te_8O_{23}$ (**1**) proceeded smoothly to convergence. The pertinent crystallographic data, the refined positional and thermal parameters, and selected bond lengths of compound **1** are presented in Tables 1−3.

Results and Discussion

Synthetic attempts for $A_2Te_4O_{12}$ (A = Na, K, Rb, Cs) compounds, by both hydrothermal and solid state reactions, have resulted in mostly polycrystalline products. It is noteworthy that the synthetic conditions employed in this study are milder and more ambient than those reported[10,11] for $Cs_2Te_4O_{12}$ and $K_2Te_4O_{12}$. A powder XRD study of these products has revealed that both methods are successful only in the case of known $Cs_2Te_4O_{12}$. It is in conjunction with a single-crystal XRD investigation that $Rb_4Te_8O_{23}$ (**1**) is identified to be the product formed in both hydrothermal and solid-state reactions, whereas the corresponding potassium compound (**2**) is formed by the solid-state reaction only. Na_3-

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Table 1. Pertinent Crystallographic Data for $Rb_4Te_8O_{23}$ (**1**)

formula	$Rb_4Te_8O_{23}$
fw	1730.68
space group (No.)	*Pna2₁* (33)
Z	4
a (Å)	19.793(4)
b (Å)	14.664(4)
c (Å)	7.292(4)
α	90
β	90
γ	90
V (Å^3)	2116.5(1)
T (K)	293(2)
λ(Mo Kα) (Å)	0.710 69
ρ (g/cm^3)	5.431
μ(Mo Kα) (mm^{-1})	20.114
^aR	0.0390
^bR_w	0.0737

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(|F_o|^2)^2]^{1/2}$.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2 \times 10^3$) for $Rb_4Te_8O_{23}$ (**1**)

atom	x	y	z	$^*U_{(eq)}{}^a$
Te(1)	5(1)	0(2)	6295(3)	9(1)
Te(2)	4(1)	5001(2)	6295(3)	10(1)
Te(3)	3774(1)	1284(1)	3795(3)	10(1)
Te(4)	2564(1)	2606(1)	6285(1)	9(1)
Te(5)	2563(1)	2612(1)	1279(1)	11(1)
Te(6)	1363(1)	1211(1)	8766(3)	13(1)
Te(7)	3907(1)	3729(1)	3753(3)	11(1)
Te(8)	1295(1)	3822(1)	8794(3)	12(1)
Rb(1)	4376(1)	2543(1)	8784(6)	23(1)
Rb(2)	1871(1)	60(1)	3785(5)	25(1)
Rb(3)	3226(1)	48(1)	8784(5)	28(1)
Rb(4)	709(1)	2506(1)	3780(7)	28(1)
O(1)	4694(6)	3802(9)	1921(17)	12(3)
O(2)	4693(2)	4745(3)	8760(30)	14(1)
O(3)	858(7)	493(10)	6794(18)	13(3)
O(4)	4644(7)	3825(10)	5631(18)	17(3)
O(5)	892(7)	470(11)	840(20)	19(3)
O(6)	4449(6)	1058(9)	1944(16)	18(3)
O(7)	742(6)	4254(8)	1528(16)	7(2)
O(8)	4910(2)	432(3)	8810(30)	17(1)
O(9)	4380(5)	1021(8)	5714(15)	11(3)
O(10)	755(8)	4236(10)	6150(20)	29(4)
O(11)	3399(2)	84(3)	3830(20)	14(1)
O(12)	3093(5)	1546(8)	1947(15)	11(3)
O(13)	3166(6)	1553(8)	5715(16)	16(3)
O(14)	4171(2)	2487(3)	3860(20)	13(1)
O(15)	1811(6)	1896(7)	6321(18)	19(3)
O(16)	2372(3)	2949(4)	3730(30)	21(1)
O(17)	3315(5)	3405(7)	6141(16)	11(2)
O(18)	2778(2)	2256(3)	8800(30)	18(1)
O(19)	2060(6)	3692(8)	6998(17)	23(3)
O(20)	1837(5)	1768(7)	1285(18)	16(2)
O(21)	3350(6)	3323(8)	1265(18)	18(3)
O(22)	1994(5)	3624(7)	675(15)	10(2)
O(23)	792(3)	2164(4)	8730(30)	30(2)

[a] $^*U_{(eq)}$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

$Te_{10.5}O_{28}$ is the major phase formed in the solid-state reaction. Hydrothermal synthetic attempts for the potassium and sodium phases have yielded single crystals of $K_2[Te_3O_8(OH)_4]$[19] and unidentified polycrystalline products. Crystal growth of rubidium, potassium, and sodium phases, obtained by the solid-state reactions intended for $A_2Te_4O_{12}$ compounds, led to the isolation of single crystals of only two compounds, $Rb_4Te_8O_{23}$ (**1**) and $Na_3Te_{10.5}O_{28}$, enabling the determination of the compositions and structures by a single-crystal X-ray diffraction study. Compounds **1** and **2** could be prepared by the solid-state reactions from stoichiometric mixtures of the reactants, whereas the hydrothermal method is successful only in the case of compound **1**. The orthorhombic unit cell parameters of compound **2** are $a = 19.573(3)$, $b = 14.448(2)$, and $c = 7.273(8)$ Å. The monophasic nature of these compounds was established by comparing their powder XRD patterns (Figure 1) with those simulated, by the program LAZY PULVERIX,[20] from the single-crystal X-ray structure of compound **1**.

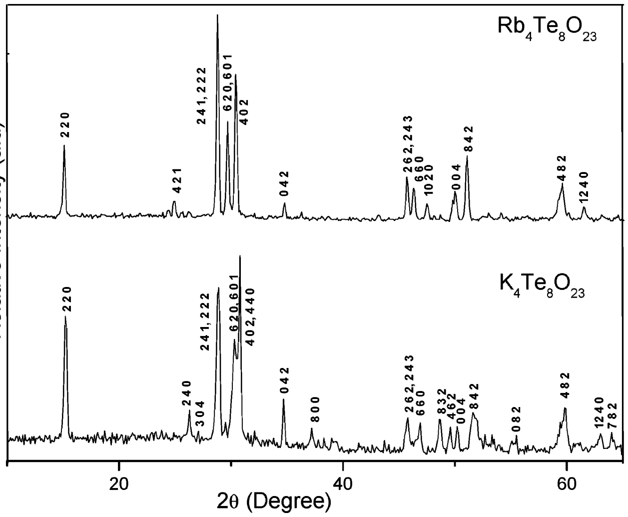

Figure 1. Powder XRD patterns of $A_4Te_8O_{23}$ (A = Rb and K) compounds.

Table 3. Selected Bond Lengths (Å) for $Rb_4Te_8O_{23}$(**1**)

Te(1)−O(3)	1.873(14)	Te(5)−O(21)	1.874(12)
Te(1)−O(1)	1.911(14)	Te(5)−O(16)	1.894(19)
Te(1)−O(4)	1.927(15)	Te(5)−O(20)	1.896(11)
Te(1)−O(5)	1.934(14)	Te(5)−O(22)	1.914(11)
Te(1)−O(2)	1.941(18)	Te(5)−O(18)	1.93(2)
Te(1)−O(2)	1.976(18)	Te(5)−O(12)	1.945(11)
Te(2)−O(7)	1.844(11)	Te(6)−O(23)	1.798(6)
Te(2)−O(10)	1.866(15)	Te(6)−O(3)	2.043(14)
Te(2)−O(8)	1.930(18)	Te(6)−O(5)	2.080(15)
Te(2)−O(8)	1.946(18)	Te(6)−O(20)	2.218(12)
Te(2)−O(6)	1.950(13)	Te(6)−O(15)	2.231(12)
Te(2)−O(9)	1.987(12)	Te(7)−O(14)	1.897(5)
Te(3)−O(9)	1.882(11)	Te(7)−O(4)	2.007(14)
Te(3)−O(13)	1.888(12)	Te(7)−O(1)	2.056(13)
Te(3)−O(11)	1.911(5)	Te(7)−O(17)	2.151(11)
Te(3)−O(6)	1.927(12)	Te(7)−O(21)	2.204(13)
Te(3)−O(14)	1.931(5)	Te(8)−O(11)	1.947(5)
Te(3)−O(12)	1.945(11)	Te(8)−O(22)	1.970(11)
Te(4)−O(15)	1.817(11)	Te(8)−O(19)	2.012(13)
Te(4)−O(17)	1.897(11)	Te(8)−O(10)	2.288(15)
Te(4)−O(19)	1.950(13)		
Te(4)−O(18)	1.95(2)		
Te(4)−O(16)	1.966(19)		
Te(4)−O(13)	1.995(12)		

$Rb_4Te_8O_{23}$ crystallizes in the $Pna2_1$ space group with one molecule per asymmetric unit. It is a three-dimensional compound having five hexavalent telluriums, represented by Te(1)−Te(5) with octahedral coordination, and three tetravalent telluriums, Te(6)−Te(8) with square-pyramidal and

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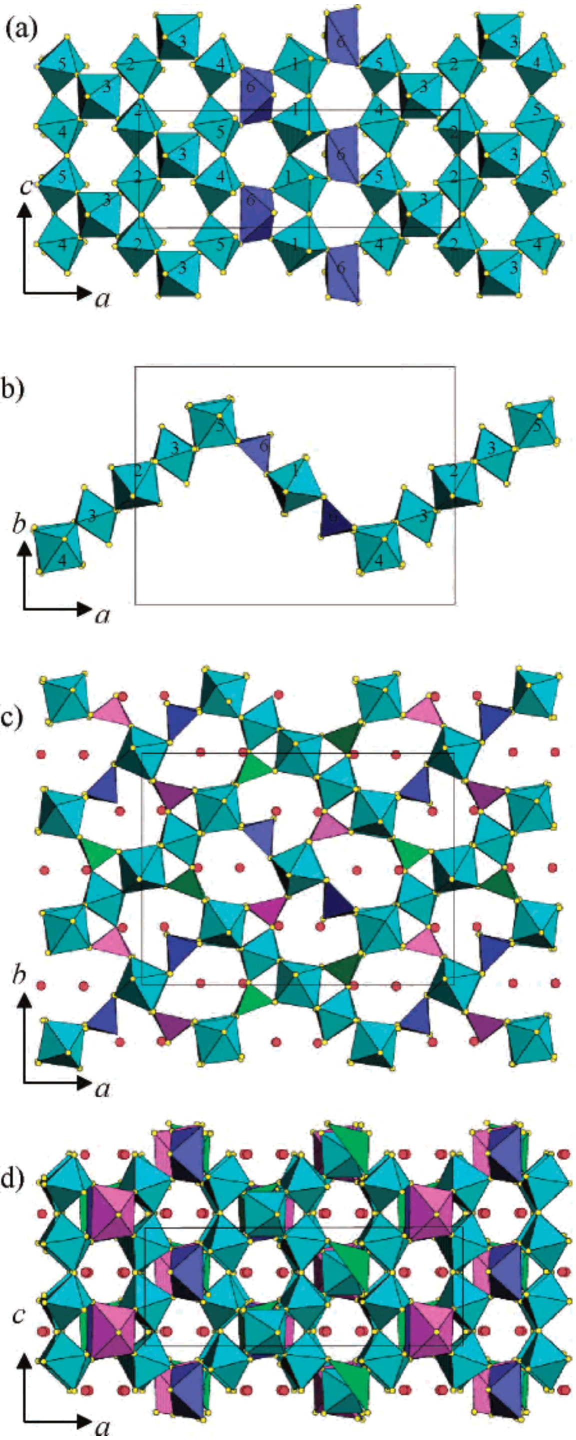

Figure 2. Polyhedral representations of (i) [Te_6O_{23}] layer viewed along the (a) *b* axis and (b) *c* axis and (ii) unit cell of $Rb_4Te_8O_{23}$ viewed along the (c) *c* axis and (d) *b* axis. [TeO_6 octahedra of Te(1)−Te(5), light blue; Te(6)O_5, blue; Te(7)O_5, pink; Te(8)O_4, green; rubidium, red circles; oxygen, yellow circles. Numbers shown in a and b are those of crystallographically distinct telluriums.]

disphenoid coordinations. The anionic $[Te_8O_{23}]^{4-}$ framework could be conceived to be built from corrugated [Te_6O_{23}] layers, connected to one another by Te(7) and Te(8). In these [Te_6O_{23}] layers (Figure 2a), consisting of TeO_6 octahedra of Te(1)−Te(5) and square-pyramidal Te(6)O_5, each polyhedron is corner-connected to four polyhedra, giving rise to hexagonal and triangular windows, similar to those in HTO layers[1] of [Mo_3O_{12}] in $Cs_2Mo_3TeO_{12}$. Thus, square-pyramidal Te(6)O_5 has one unshared oxygen corner, whereas the five TeO_6 octahedra each have two unshared oxygen corners. The unshared corners are trans in the octahedra of Te(1)−Te(3) and cis in Te(4)O_6 and Te(5)O_6. It is only at these two octahedra that the layers are corrugated (Figure 2b). These layers are stacked along the crystallographic *b* axis and are connected by interlayer bonding of the unshared oxygen atoms of the octahedra, to Te(7) and Te(8), which have square-pyramidal and disphenoid geometries, respectively (Figure 2c). The resulting three-dimensional $[Te_8O_{23}]^{4-}$ framework has, for charge compensation, four crystallographically distinct Rb^+ ions in the channels, parallel to the *b* axis, of the hexagonal windows (Figure 2d).

The polyhedral corner connection (Figure 2a) can be summarized as follows. Te(1)O_6 units are corner-connected to one another and also to Te(6)O_5. Similarly, Te(2)O_6 units, also connected to one another, share corners with Te(3)O_6. The Te(4)O_6 and Te(5)O_6 units are corner-connected to one another and also to Te(3)O_6 and Te(6)O_5 polyhedra. The atom labeling scheme followed for the tellurium and oxygen atoms is represented in Figure 3. O(23) is exclusively bonded to Te(6). The octahedra are regular and do not differ significantly from one another in the values of bond angles and bond lengths. The values of the Te−O bond lengths (Table 3) vary from 1.817(14) to 1.995(12) Å. The values of the Te−O bond lengths in Te(6)O_5, Te(7)O_5, and Te(8)O_4 (Table 3) compare well with those reported for square-pyramidal and disphenoid coordinations of tellurium.[10,21] The variation in bond lengths is greater in Te(6)O_5 than in Te(7)O_5. The bond valence sums[22,23] are found to be in the ranges of 5.86−6.15 and 3.44−4.24 for hexavalent and tetravalent telluriums, respectively. Rb(1) and Rb(2) are 11-coordinated, whereas Rb(3) and Rb(4) are 10- and 9-coordinated, respectively.

The choice of *Pna*2_1 over *Pnma* merits some discussion. For *Pna*2_1, the corresponding centric space group without cell transformation is *Pnam*, for which the origin is chosen along the 2_1 screw axis, which is parallel to the *c* axis. In the structure solved in *Pna*2_1, the screw axis present at (0.5, 0.5) contains Te(1) atoms (Figure 2c). Projection of the structure along the *b* axis (Figure 2d) clearly shows the absence of any such true inversion center along this screw axis. However, a pseudo inversion center seems to be present at the midpoint of the hexagonal window. An examination of the projections of the structure in other directions reveals that many oxygen atoms violate this apparent inversion. These pseudo centers of inversion might be responsible for an approximate structure solution in the centric *Pnma* space group.

The reported[10,11] $A_2Te_4O_{12}$ (A = K, Cs) compounds differ from $A_4Te_8O_{23}$ (A = Rb, K) phases in the fractional content of Te^{4+} to Te^{6+}. A higher Te^{6+} content could be achieved by solid-state reaction in open air in the case of $Cs_2Te_4O_{12}$,

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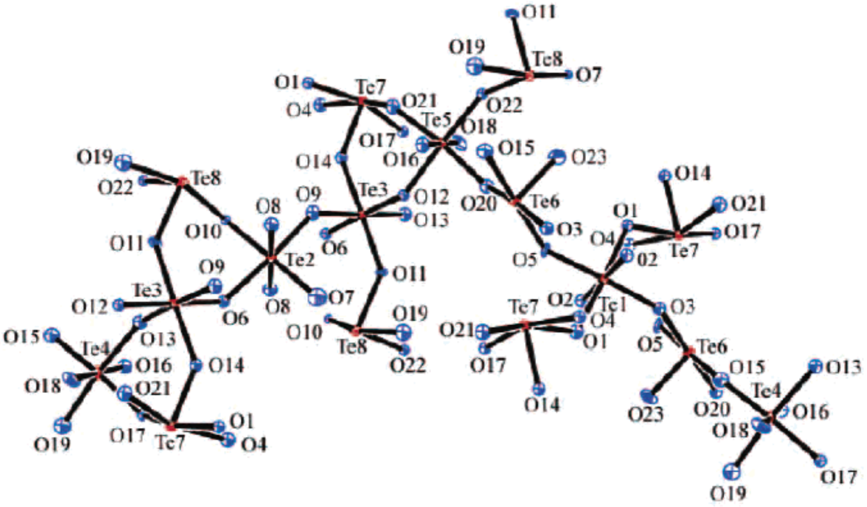

Figure 3. ORTEP diagram of coordination polyhedra of telluriums in $Rb_4Te_8O_{23}$, showing the atom labeling scheme. Thermal ellipsoids are drawn at the 50% probability level.

whereas a higher oxygen partial pressure or lower temperature seems to be required for the potassium and rubidium phases. Had the Te(6), in compounds **1** and **2**, also been hexavalent and octahedrally coordinated with an additional oxygen atom, then the resulting $A_4Te_8O_{24}$ phases, with corrugated $[Te_6O_{24}]$ layers, would have constituted a new structural modification of the $A_2Te_4O_{12}$ compounds. There are a few structurally characterized, mixed-valent tellurium oxides known[24−26] in other ternary and quaternary systems, and they contain different proportions of Te^{6+} with octahedral coordination and Te^{4+} with trigonal-pyramidal or disphenoidal coordination. $BaCuTe_2O_7$ and α and β modifications of $Hg_2Te_2O_7$ are two-dimensional compounds,[24,25] in which TeO_6 octahedra and TeO_4 disphenoids constitute $[Te^{6+}Te^{4+}O_7]^{4-}$ layers that are interleaved with divalent cations. These anionic layers are corrugated in β-$Hg_2Te_2O_7$ and are planar in α-$Hg_2Te_2O_7$ and $BaCuTe_2O_7$. The cadmium compounds,[26] $Cd_2Te_2O_7$ and $Cd_2Te_3O_9$, contain isolated TeO_3 trigonal pyramids, as well as Te−O anionic framework chains that are built from TeO_6 octahedra and TeO_3 trigonal pyramids.

The infrared and Raman spectra of the two compounds have some common features that could be reasonably accounted for. The peaks at 660 cm^{-1} and in the 790−725 cm^{-1} range are due to Te^{IV}−O stretching vibrations, and those in the 420−410 cm^{-1} range are due to Te^{IV}−O−Te^{IV} bending vibrations.[27] Symmetric and asymmetric stretching and bending vibrations of Te^{VI}−O bonds are observed,[28,29] respectively, in the ranges 690−620, 590−513, and 468−450 cm^{-1}. A TGA of these compounds (**1** and **2**), over the temperature range of 50−800 °C, showed that they are thermally stable up to 700 and 660 °C respectively, after which they decompose. DSC analysis, in the temperature range of −120 to 550 °C, showed an absence of any transition of these compounds.

Concluding Remarks

In conclusion, two isostructural, three-dimensional compounds, $A_4Te_8O_{23}$ (A = Rb and K), have been synthesized and characterized, by X-ray diffraction and infrared spectroscopy. They represent rare examples of mixed-valent tellurium oxides and contain tetravalent telluriums, having square-pyramidal and disphenoid geometries. These results reveal that there is a scope for synthetic and structural solid-state chemistry of new mixed-valent tellurium oxides.

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Supporting Information Available: The crystallographic file, in CIF format, for $Rb_4Te_8O_{23}$. This material is available free of charge via the Internet at http//:pubs.acs.org.

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