

# One-Dimensional Inorganic Polymers: Synthesis and Structural Characterization of the Main-Group Metal Polymers $\text{K}_2\text{HgSnTe}_4$ , $(\text{Et}_4\text{N})_2\text{HgSnTe}_4$ , $(\text{Ph}_4\text{P})\text{GeInTe}_4$ , and $\text{RbInTe}_2$

Sandeep S. Dhingra<sup>†</sup> and Robert C. Haushalter\*

NEC Research Institute, 4 Independence Way, Princeton, New Jersey 08540

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Four new one-dimensional tellurides have been synthesized and structurally characterized by single-crystal X-ray diffraction. The reaction of  $\text{K}_4\text{SnTe}_4$  with  $\text{HgCl}_2$  in a 1:1 molar ratio in ethylenediamine (en) at 100 °C for 2 days, in a sealed evacuated quartz ampule, gives a nearly quantitative yield of the novel one-dimensional (1-D) telluride polymer  $\text{K}_2\text{HgSnTe}_4$  (**1**). Black cubic-shaped crystals of **1** crystallize in the tetragonal space group  $I4/mcm$  (No. 140) with  $a = 8.580(2)$  and  $c = 7.358(4)$  Å,  $V = 541.6(4)$  Å<sup>3</sup>,  $Z = 4$ , and  $R(R_w) = 0.046(0.047)$ . The en extraction of an alloy of the composition  $\text{K}_2\text{HgSnTe}_4$  followed by treatment with  $\text{Et}_4\text{NI}$  gives  $(\text{Et}_4\text{N})_2[\text{HgSnTe}_4]$  (**2**) in 30% yield. Telluride **2** crystallizes in the tetragonal space group  $P4_2/mnm$  (No. 136) with  $a = 14.614(2)$  and  $c = 7.585(1)$  Å,  $V = 1619.9(4)$  Å<sup>3</sup>,  $Z = 4$ , and  $R(R_w) = 0.040(0.053)$ . The reaction of  $\text{K}_4\text{Ge}_4\text{Te}_{10}$  with  $\text{InCl}_3$  in the presence of  $\text{Ph}_4\text{PBr}$  in ethylenediamine (en) at 100 °C for 3 days, in a sealed evacuated quartz ampule, affords a new (1-D) telluride polymer  $(\text{Ph}_4\text{P})[\text{GeInTe}_4]$  (**3**) in 68% yield. Black tetragonal plate crystals of **3** crystallize in the tetragonal space group  $P4_2/n$  (No. 86) with  $a = 14.2770(8)$  and  $c = 7.029(1)$  Å,  $V = 1432.8(2)$  Å<sup>3</sup>,  $Z = 2$  and  $R(R_w) = 0.071(0.086)$ . The high-temperature reaction of  $\text{Rb}_2\text{Te}_2$ , In, and Te at 400 °C, in a sealed evacuated quartz tube for 24 h followed by slow cooling gives the one-dimensional polymer  $\text{RbInTe}_2$  (**4**) in 64% yield. Red needle crystals of **4** crystallize in the tetragonal space group  $I4/mcm$  (No. 140) with  $a = 8.8168(6)$  and  $c = 7.376(1)$  Å,  $V = 573.3(1)$  Å<sup>3</sup>,  $Z = 4$ , and  $R(R_w) = 0.034(0.042)$ . Single crystal X-ray diffraction studies revealed that the four structures have similar anions and consist of 1-D chains of edge-sharing tetrahedra with metal atoms at the center of each tetrahedron. The chains in telluride **1** and **4** crystallize such that the Te atoms are close packed with the alkali-metal cations occupying interchain 1-D tunnels that run parallel to [001], whereas in **2** and **3** the chains are well separated by the organic cations. Diffuse scans along the  $c$  axis for **1** and **2** show no evidence of superstructures, indicating that the Hg and Sn form a solid solution in both structures. The 1-D chains of  $[\text{GeInTe}_4]^-$  in telluride **3** have the  $\text{Ge}^{4+}$  and  $\text{In}^{3+}$  atoms situated on two crystallographically independent sites. Powder X-ray diffraction measurements indicate that it is also possible to prepare  $\text{K}_2\text{HgSnTe}_4$  (**1**) from  $\text{K}_2\text{Te}$ , Sn, Hg, and Te at 500 °C.

## Introduction

There are a reasonably large number of examples of main group oxides that have structures with one dimensional (1-D) character, such as  $\text{SeO}_2$ ,  $\text{Sb}_2\text{O}_3$ , and  $\text{HgO}$ , and the chain silicate materials like those of the pyroxene group.<sup>1</sup> Corresponding examples of low dimensional materials among the heavier chalcogenides are much less common, but examples for sulfur are found in the  $\text{SiS}_2$ <sup>2</sup> and  $\text{KFeS}_2$ <sup>3</sup> structure types, both of which display infinite chains of tetrahedra sharing opposite edges. In the selenium system, compounds such as  $\text{TiSe}$ ,  $\text{NaInSe}_2$ , and  $\text{TiAlSe}_2$  are known,<sup>4</sup> while structures such as  $\text{A}_x\text{MTe}_2$  ( $\text{M} = \text{Al, Ga, In; } x = 1$  with  $\text{A} = \text{Na, K; } x = 0.5$  with  $\text{A} = \text{Sr, Ba}$ )<sup>5</sup> have been characterized in the tellurium system. We recently

reported the first example of a 1-D telluride chain structure with totally isolated chains such as those of the  $\text{SiS}_2$  structure, in the electrochemically synthesized indium telluride  $[(\text{C}_4\text{H}_9)_4\text{N}]\text{InTe}_2$ .<sup>6</sup> In this paper we report the solution-phase synthesis in ethylenediamine (en), high-temperature synthesis, and single-crystal X-ray structural characterization of four new 1-D metal tellurides  $\text{K}_2\text{HgSnTe}_4$  (**1**),  $(\text{Et}_4\text{N})_2[\text{HgSnTe}_4]$  (**2**),  $(\text{Ph}_4\text{P})[\text{GeInTe}_4]$  (**3**), and  $\text{RbInTe}_2$  (**4**). The basic structure type,  $[\text{M}^{\text{III}}\text{Te}_2]^-$  has several examples in the literature<sup>5,7</sup> but the mixing of two elements at the  $\text{M}^{3+}$  site, as in the metal telluride chains of  $[\text{HgSnTe}_4]^{2-}$ , is very rare. We are unaware of any previous examples with a 1:1

<sup>†</sup> Current address: Mobil Research and Development Corp. Central Research Division, PO Box 1025, Princeton, NJ 08540.

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ratio of  $M^{2+}:M^{4+}$  at the M site as seen in 1 and 2. The  $[\text{GeInTe}_4]^-$  chains in 3 are also isosteric to the  $[\text{M}^{\text{III}}\text{Te}_2]^-$  structure type; however, it is the first example with a  $M^{3+}:M^{4+}$  in 1:1 ratio at the M site, thus leading to a new anion with a lower overall charge.

### Experimental Section

**General Techniques.** All manipulations were performed under an atmosphere of oxygen free helium. The telluride  $\text{K}_2\text{SnTe}_4$  was prepared as previously described.<sup>8</sup>  $\text{K}_2\text{Te}$  was obtained by combining stoichiometric amounts of K metal and very fine Te powder in liquid ammonia under a nitrogen atmosphere.  $\text{K}_4\text{Ge}_4\text{Te}_{10}$  was prepared by the reaction of  $\text{K}_2\text{Te}$ , Ge metal, and finely divided Te powder, in appropriate mole ratios, under an inert atmosphere at 500 °C. The ethylenediamine (en) was dried by distillation over  $\text{CaH}_2$  and subsequently purified by a second distillation from a red solution of  $\text{K}_4\text{Sn}_9$ .

**Syntheses.  $\text{K}_2\text{HgSnTe}_4$  (1).** *Method A:* A mixture of 0.200 g of  $\text{K}_4\text{SnTe}_4$  (0.255 mmol) and 0.069 g of  $\text{HgCl}_2$  (0.254 mmol) was treated with 0.3 mL of ethylenediamine and sealed in a quartz tube under vacuum. After heating for 48 h at 100 °C, the solution was cooled, and the small, metallic gray, cubic-shaped crystals were filtered and washed with ethylenediamine, yield = 95%.

*Method B:* It was also possible to prepare  $\text{K}_2\text{HgSnTe}_4$  at high temperatures by the reaction of 0.200 g of  $\text{K}_2\text{Te}$  (0.972 mmol), 0.195 g of Hg (0.972 mmol), 0.115 g of Sn (0.969 mmol), and 0.372 g of Te (2.915 mmol) at 500 °C for 10 h in an evacuated quartz tube. The major product of this high temperature reaction was  $\text{K}_2\text{HgSnTe}_4$ , identified by comparing its X-ray powder diffraction pattern to a pattern calculated from the coordinates found in the single-crystal study. One of the minor products formed is 10% crystalline impurity of a binary phase,  $\text{SnTe}$ , determined by the powder pattern, which is likely due to the loss of Hg metal from the alloy at these temperatures. It was observed that the final product of the high temperature reaction upon grinding to a fine powder is partially soluble in en. This suggests that there may be some amorphous components in the alloy which are soluble, probably consisting of smaller anions exhibiting different structures than 1 which might act as a mineralizer, thus enhancing the solubility of the bulk material.

**$(\text{Et}_4\text{N})_2[\text{HgSnTe}_4]$  (2).** Telluride (2) was prepared by ethylenediamine extraction of an alloy of nominal composition  $\text{K}_2\text{HgSnTe}_4$ , prepared from the fusion of  $\text{K}_2\text{Te}$ , Sn, Hg, and elemental Te in the appropriate molar ratios in a quartz ampule under  $\text{N}_2$ . The alloy was crushed to a fine black powder and stored under He atmosphere. The red brown extract obtained by the addition of 10 mL of en to 1.00 g of  $\text{K}_2\text{HgSnTe}_4$  alloy was filtered and carefully layered with a solution of 0.566 g of  $\text{Et}_4\text{NI}$  in 10 mL of en which, after 4 days, gave large crystals of 2 in 30% yield (based on the starting alloy). The crystals are insoluble in en.

**$(\text{Ph}_4\text{P})[\text{GeInTe}_4]$  (3).** A mixture of 0.200 g of  $\text{K}_4\text{Ge}_4\text{Te}_{10}$  (0.116 mmol), 0.052 g of  $\text{InCl}_3$  (0.235 mmol) and 0.098 g of  $\text{Ph}_4\text{PBr}$  (0.234 mmol) was treated with 0.3 mL of ethylenediamine and sealed in a quartz tube under vacuum. After heating for 4 days at 100 °C, the tube was cooled. Large crystals of 3 were isolated, as a single-phase product, under an inert atmosphere by filtration and washed with ethylenediamine, yield 68% based on  $\text{InCl}_3$ .

**$\text{RbInTe}_2$  (4).** The high-temperature reaction of 0.100 g of  $\text{Rb}_2\text{Te}_2$  (0.235 mmol), 0.027 g of In (0.235 mmol), and 0.090 g of Te (0.705 mmol) in an evacuated quartz tube at 400 °C for 24 h followed by slow cooling to 200 °C at 2 °C/h and subsequently cooling to 50 °C in 10 h. Red needle crystals of 4 were isolated under an inert atmosphere and washed with ethylenediamine, yield 64% based on In metal.

**Crystallography.** The single crystals of all the compounds were flame sealed in thin walled glass capillaries under He

**Table 1. Comparison of the Refinement of the Structure and Atomic Coordinates of  $\text{K}_2\text{HgSnTe}_4$  (1) in  $I4/mcm$  and  $I\bar{4}c2$**

formula	K <sub>2</sub> HgSnTe <sub>4</sub>	K <sub>2</sub> HgSnTe <sub>4</sub>		
space group	<i>I4/mcm</i> (No. 140)	<i>I</i> $\bar{4}$ <i>c</i> 2 (No. 120)		
FW	907.88	907.88		
crystal color, habit	black, cube	black, cube		
<i>a</i> (Å)	8.580 (2)	8.580 (2)		
<i>c</i> (Å)	7.358 (4)	7.358 (4)		
<i>V</i> (Å <sup>3</sup> )	541.6(4)	541.6(4)		
<i>Z</i>	2	2		
2θ <sub>max</sub> (deg)	55	55		
no. of data collected	209	209		
data <i>I</i> ≥ 3σ( <i>I</i> )	160	160		
no. of variables	11	13		
final <i>R</i> / <i>R</i> <sub>w</sub>	0.046/0.047	0.022/0.014		
Positional Parameters of K <sub>2</sub> HgSnTe <sub>4</sub> in <i>I4/mcm</i>				
atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (eq)
Hg(1)	0.0000	0.5000	0.2500	3.2(5)
Te(1)	0.1762(2)	0.6762	0.0000	2.00(4)
Sn(1)	0.0000	0.5000	0.2500	1.2(6)
K(1)	0.0000	0.0000	0.2500	2.4(2)
Positional Parameters of K <sub>2</sub> HgSnTe <sub>4</sub> in <i>I</i> $\bar{4}$ <i>c</i> 2				
atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (eq)
Hg(1)	0.0000	0.0000	0.5000	1.41(3)
Te(1)	0.17631(7)	0.1763	0.2500	1.99(1)
Sn(1)	0.0000	0.0000	0.5000	5.7(1)
K(1)	0.0000	−0.5000	0.5000	2.58(8)

for data acquisition. The crystallographic data were collected on a Rigaku AFC7R four-circle diffractometer at 22 °C equipped with a RU300 18 kW rotating anode using  $\omega$ – $2\theta$  scans. Accurate unit cell dimensions were determined from 20–25 reflections in the range of  $20^\circ < 2\theta < 45^\circ$ . The intensities of three check reflections were monitored every 150 reflections during the course of data collection to check the crystal integrity. A decay in intensities of 0.5% in 1, 2.1% in 2, 0.6% in 3, and 0.7% in 4 were observed and a linear correction for 1 and a polynomial decay correction for the rest were applied to the data. The structures were solved by direct methods and refined using the teXsan crystallographic software package from Molecular Structure Corp. All the atoms in the structures were refined anisotropically, except two carbon atoms in 3. The  $\text{Et}_4\text{N}^+$  cations in 2 are disordered such that the inner carbon atoms of each of the ethyl groups are situated over two sites of equal occupancy. The  $\text{Ph}_4\text{P}^+$  cations in 3 are disordered such that two phenyl rings lie perpendicular to each other, sharing two carbon atoms, which have full occupancy of 1 and the other four carbon atoms on each phenyl ring have only half occupancy. The disorder of the cation is crystallographically imposed because the phosphorus atom is situated on a  $4_2$  screw axis at ( $1/4, 3/4, 0.2180$ ). The complete data collection parameters and details of structure solution and refinement are summarized in Tables 1–5.

### Discussion

Single crystals of  $\text{K}_2\text{HgSnTe}_4$  (1) were prepared by the treatment of  $\text{K}_4\text{SnTe}_4$ , which was prepared from the reaction of  $\text{KSn}$  and Te, with 1 equivalent  $\text{HgCl}_2$  in ethylenediamine at 100 °C. This reaction produced an essentially quantitative yield of small (maximum diameter ca. 50  $\mu\text{m}$ ) black-gray crystals of the title compound. Energy-dispersive X-ray analysis in the SEM indicated the presence of K, Hg, Sn, and Te. Despite the rather small size of the crystals, the high quality of the crystals, the abundance of heavy atoms in the structure, and the intensity of the rotating anode X-ray source allowed a total of 77% of the reflections to be observed and even 67% were observed between 50 and 55° in  $2\theta$ . The systematic absences indicated the space group to be

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**Table 2. Crystallographic Data for (Et<sub>4</sub>N)<sub>2</sub>[HgSnTe<sub>4</sub>] (2), (Ph<sub>4</sub>P)[GeInTe<sub>4</sub>] (3), and RbInTe<sub>2</sub> (4)**

compound	(Et <sub>4</sub> N) <sub>2</sub> [HgSnTe <sub>4</sub> ]	(Ph <sub>4</sub> P)[GeInTe <sub>4</sub> ]	RbInTe <sub>2</sub>
formula	H <sub>20</sub> C <sub>8</sub> N <sub>1</sub> HgSnTe <sub>4</sub>	H <sub>20</sub> C <sub>24</sub> P <sub>1</sub> GeInTe <sub>4</sub>	RbInTe <sub>2</sub>
FW	1090.19	1037.21	455.49
crystal color, habit	black, plate	black, plate	red, needles
<i>a</i> (Å)	14.614(2)	14.2770(8)	8.8168(6)
<i>c</i> (Å)	7.585(1)	7.029(1)	7.376(1)
<i>V</i> (Å <sup>3</sup> )	1619.9(4)	1432.8(2)	573.3(1)
<i>Z</i>	2	2	4
space group	<i>P</i> 4 <sub>2</sub> / <i>mnm</i> (No. 136)	<i>P</i> 4 <sub>2</sub> / <i>n</i> (No. 86)	<i>I</i> 4/ <i>mcm</i> (No. 140)
<i>D</i> <sub>cal</sub> (g cm <sup>-3</sup> )	2.235	2.404	5.276
<i>μ</i> (cm <sup>-1</sup> )	90.50	59.10	223.41
crystal size (mm)	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.30	0.15 × 0.05 × 0.05
2θ <sub>max</sub> (deg)	60	60	60
no. of data collected	1415	2402	274
data <i>I</i> ≥ 3σ( <i>I</i> )	580	1180	224
no. of variables	45	99	10
final <i>R</i> / <i>R</i> <sub>w</sub>	0.040/0.053	0.071/0.086	0.034/0.042

**Table 3. Fractional Atomic Coordinates and *B*(eq) Values for (Et<sub>4</sub>N)<sub>2</sub>[HgSnTe<sub>4</sub>] with Their Standard Deviations in Parentheses**

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (eq) <sup>a</sup>
Hg(1)	0.5000	0.0000	0.2500	3.14(6)
Te(1)	0.5392(1)	0.1358(1)	0.5000	3.18(4)
Sn(1)	0.5000	0.0000	0.2500	3.0(1)
N(1)	0.211(1)	0.211	0.500	3.4(4)
C(1)	0.226(3)	0.114(2)	0.408(5)	6(2)
C(2)	0.208(2)	0.034(2)	0.500	8(2)
C(3)	0.285(3)	0.213(3)	0.365(5)	8(3)
C(4)	0.301(1)	0.301	0.270(4)	8(1)

<sup>a</sup> Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as  $B(\text{eq}) = \frac{1}{3}[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos \gamma)B_{12} + ac(\cos \beta)B_{13} + bc(\cos \alpha)B_{23}]$ .

**Table 4. Fractional Atomic Coordinates and *B*(eq) Values for (Ph<sub>4</sub>P)[GeInTe<sub>4</sub>] with Their Standard Deviations in Parentheses**

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (eq) <sup>a</sup>
Te(1)	0.13502(8)	0.3336(1)	0.5002(3)	3.80(5)
In(1)	0.2500	0.2500	0.2500	2.10(4)
Ge(1)	0.2500	0.2500	0.7500	3.5(1)
P(1)	0.2500	-0.2500	0.2180(6)	0.6(3)
C(1)	0.182(2)	-0.165(3)	0.402(5)	3(1)
C(2)	0.125(1)	-0.214(1)	0.493(5)	6(1)
C(3)	0.070(3)	-0.157(3)	0.660(6)	3.2(7)
C(4)	0.080(4)	-0.063(4)	0.67(1)	6(1)
C(5)	0.141(1)	-0.018(1)	0.502(4)	4.3(8)
C(6)	0.196(3)	-0.072(3)	0.390(5)	3(2)
C(7)	0.185(3)	-0.180(2)	0.604(5)	3(1)
C(8)	0.192(3)	-0.076(3)	0.613(7)	4(2)
C(9)	0.081(2)	-0.054(2)	0.370(5)	3(1)
C(10)	0.075(3)	-0.153(4)	0.346(6)	4(2)

<sup>a</sup> Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as  $B(\text{eq}) = \frac{1}{3}[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos \gamma)B_{12} + ac(\cos \beta)B_{13} + bc(\cos \alpha)B_{23}]$ .

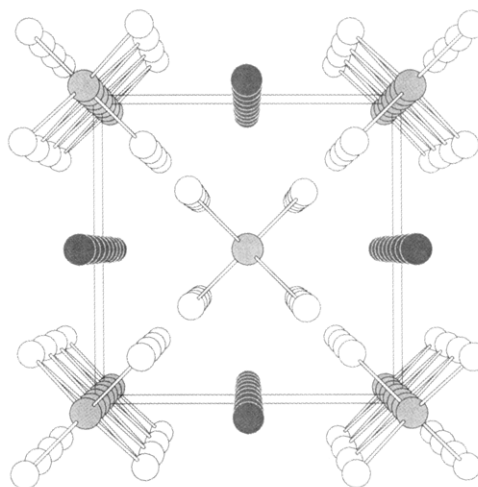
*I*4*cm*, *I*4̄*c*2, or *I*4/*mcm*, and the Laue symmetry was determined to be 4/*mmm*. Initial attempts to solve the structure in the highest symmetry point group of *I*4/*mcm* were unsuccessful but a solution was immediately found in *I*4̄*c*2 (Table 1) and refined to *R*(*R*<sub>w</sub>) = 0.022(0.014).

The structure consists of metal-centered tellurium tetrahedra sharing opposite edges to form 1-D chains that run parallel to [001] as shown in Figure 1. In *I*4̄*c*2, the Te atoms reside at the Wyckoff *e* site with *x* = 0.17631(7) with 2-site symmetry and the K atoms at the *d* site with 222 symmetry. The centers of all of the Te tetrahedra are located at the *b* site (4 point symmetry), and since diffuse scans along the *c* axis show

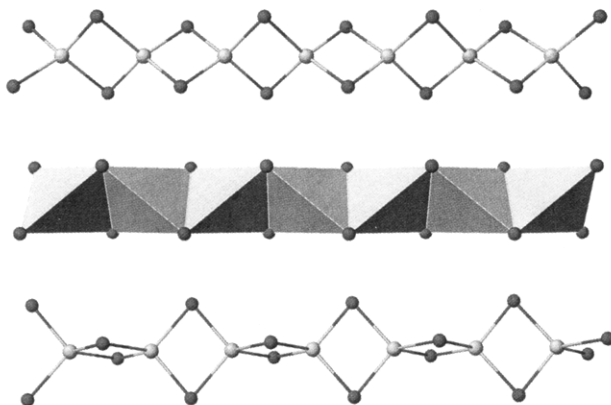
**Table 5. Fractional Atomic Coordinates and *B*(eq) Values for RbInTe<sub>2</sub> with Their Standard Deviations in Parentheses**

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (eq) <sup>a</sup>
Te(1)	0.32953(10)	0.1705	0.5000	1.14(1)
In(1)	0.5000	0.0000	0.2500	1.20(2)
Rb(1)	0.0000	0.0000	0.2500	1.58(3)

<sup>a</sup> Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as  $B(\text{eq}) = \frac{1}{3}[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos \gamma)B_{12} + ac(\cos \beta)B_{13} + bc(\cos \alpha)B_{23}]$ .

**Figure 1.** View of the unit cell of K<sub>2</sub>HgSnTe<sub>4</sub> down the crystallographic *c* axis showing the one-dimensional chains running along the [001] direction. The dark circles represents the K, the lighter shaded circles are the Hg and Sn, and the empty circles are the Te atoms.

no evidence of a superstructure, the Hg and Sn are forced to form a solid solution at the Wyckoff *b* site. Since the Te are 2- and the K are 1+, a 1:1 ratio of Hg<sup>2+</sup>:Sn<sup>4+</sup> is consistent with the overall average charge requirement of 3+ per metal site, the energy-dispersive X-ray analysis in the SEM, as well as the reasonable derived thermal parameters (Table 1). Each chain is surrounded by four other chains that are offset by one-half unit-cell translation along *c* as required by the *I* centering (Figure 1). The Te atoms are essentially close packed with Te-Te contacts along the chain direction of 4.279 and 4.763, and 4.091 Å between the chains which are similar to the van der Waals distance of Te<sup>2-</sup> (Figure 2). The K<sup>+</sup> cations reside between the chains with a K-Te distance of 3.6584(3) Å. The metal Hg/Sn site is at the tetrahedral void in the chain and displays

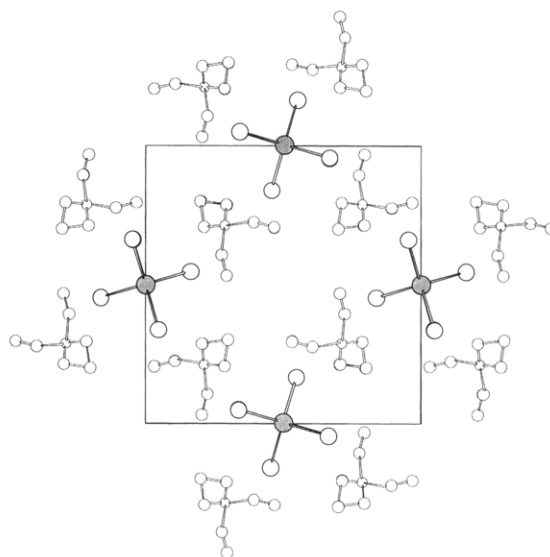


**Figure 2.** Three different views of the one-dimensional chains, all perpendicular to [001] showing the bonding motif of tetrahedra-sharing opposite edges characteristic of this structure type.

bonds of 2.8213(6) Å to the four Te neighbors which can be compared with 2.737 Å for the Hg–Te bonds in  $\text{Hg}_4\text{Te}_{12}^{4-9}$  or 2.799 Å for the bridging Sn–Te bonds in  $\text{Sn}_2\text{Te}_6^{4-10}$ .

Although this structural model was very well behaved in  $I\bar{4}c2$ , and gave reasonable expected values for the structural parameters, examination of the structure revealed an apparently centric arrangement of the atoms. After some initial difficulties requiring the use of several cycles of constrained refinements, the same structural model was successfully transformed and refined unconstrained in  $I4/mcm$  with essentially the same derived bond lengths but with somewhat different thermal parameters. The data and calculated parameters for the refinements in both  $I4/mcm$  and  $I\bar{4}c2$  can be compared in Table 1. Despite the fact that the structure appears centric and the relative positional parameters are essentially identical, a lower  $R$  value was obtained in the acentric space group (Table 1). One may speculate that the anisotropic thermal parameters refined in  $I\bar{4}c2$  provide a better description of the data than the corresponding parameters in the centric space group. All of the other compounds reported in the literature that are isotypic with  $\text{K}_2\text{HgSnTe}_4$  are reported to be centric and in space group  $I4/mcm$ .<sup>7</sup> We report the structure in the centric group  $I4/mcm$  because of its relationship to other related structures in the literature and because of the apparently centric arrangement of the atoms but it is entirely possible that it could actually crystallize in  $I\bar{4}c2$ . Additional physical property measurements would be required to distinguish the centric and acentric cases.

Once the stoichiometry of the title compound was established by the structural study, an attempt was made to prepare it by direct high temperature synthesis. It was found that it is also possible to prepare  $\text{K}_2\text{HgSnTe}_4$  via high temperature reactions in evacuated quartz ampules by the reaction of  $\text{K}_2\text{Te}$ , Sn, Hg and Te at 500 °C in the appropriate mole ratios. The major product was identified as  $\text{K}_2\text{HgSnTe}_4$  by the comparison of its X-ray powder diffraction pattern to the pattern simulated from the  $\text{K}_2\text{HgSnTe}_4$  coordinates obtained from the



**Figure 3.** View of the unit cell of  $(\text{Et}_4\text{N})_2[\text{HgSnTe}_4]$  down the crystallographic  $c$  axis showing the one-dimensional chains running along the [001] direction. The dark circles represent the Hg and Sn, the empty dark circles are the Te atoms, and the light shaded circles are the tetraethylammonium cations.

**Table 6. Selected Bond Lengths (Å) and Bond Angles (deg) in  $[\text{HgSnTe}_4]^{2-}$  Chains in  $\text{K}_2\text{HgSnTe}_4$  (1) and  $(\text{Et}_4\text{N})_2[\text{HgSnTe}_4]$  (2)**

	$\text{K}_2\text{HgSnTe}_4$	$(\text{Et}_4\text{N})_2[\text{HgSnTe}_4]$
bond distances		
M(1)–Te(1)	2.821(2)	2.804(1)
bond angles		
Te(1)–M(1)–Te(1)	115.17(2)	117.22(2)
Te(1)–M(1)–Te(1)	98.60(8)	94.88(4)
M(1)–Te(1)–M(1)	81.40(8)	85.12(4)

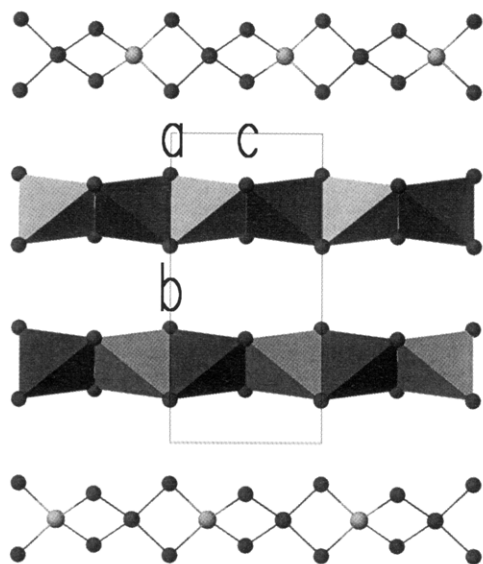
single-crystal study; however it was not a single-phase product and has about 10–15% impurities.

Surprisingly, the extraction of the alloy of the nominal composition  $\text{K}_2\text{HgSnTe}_4$ , synthesized by the high-temperature reaction, with ethylenediamine and further treatment with tetraethylammonium iodide gave single crystals of  $(\text{Et}_4\text{N})_2[\text{HgSnTe}_4]$  (2). Telluride 2 contains the same anionic structure, consisting of metal-centered tellurium tetrahedra sharing opposite edges to form 1-D chains that run parallel to [001] as shown in Figure 3. The Te atoms reside at the Wyckoff  $j$  site with  $m$  site symmetry and the metal centers are located at the  $d$  site ( $\bar{4}$  point symmetry). Diffuse scans along the  $c$  axis again show no evidence of a superstructure; thus the Hg and Sn atoms are again forced to form a solid solution. The chains are well separated by the tetraethylammonium cations. The comparison of the bond distances and bond angles of the two compounds are presented in Table 6.

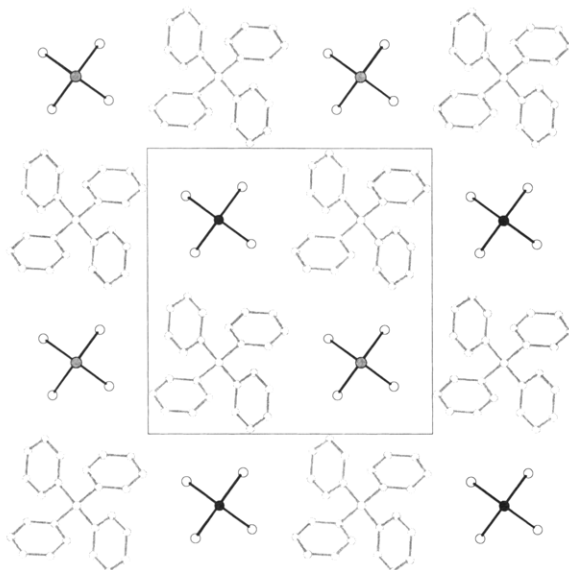
Single crystals of  $(\text{Ph}_4\text{P})[\text{GeInTe}_4]$  (3) were prepared by the treatment of  $\text{K}_4\text{Ge}_4\text{Te}_{10}$  with 2 equiv of  $\text{InCl}_3$  in the presence of tetraphenylphosphonium bromide in ethylenediamine at 100 °C. The reaction afforded large black single crystals of 3 as a single-phase product. The  $[\text{GeInTe}_4]^-$  anion is isosteric to the first two compounds, consisting of metal-centered tellurium tetrahedra sharing opposite edges to form 1-D chains that run parallel to [001] as shown in Figure 4. The Ge and In atoms are arranged in strict alternation in these chains and are situated on two crystallographically independent  $\bar{4}$  sites in space  $P4_2/n$  group with the In atoms at Wyckoff

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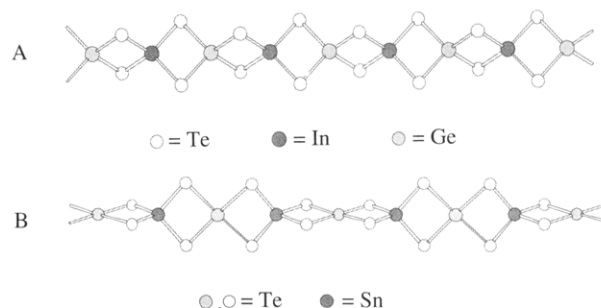
**Figure 4.** View down the crystallographic  $a$  axis of the unit cell of  $(\text{Ph}_4\text{P})[\text{GeInTe}_4]$  showing the one-dimensional chains consisting of alternating Ge- and In-centered edge-sharing tetrahedra; the organic cations have been omitted for clarity.



**Figure 5.** View of the unit cell of  $(\text{Ph}_4\text{P})[\text{GeInTe}_4]$  down the crystallographic  $c$  axis showing the one-dimensional chains running along the  $[001]$  direction. The dark circles represent the Ge, the light shaded circles are the In, and the empty dark circles are the Te atoms.

$a$  site and the Ge at Wyckoff  $b$  site. The chains are well separated by the tetraphenylphosphonium cations as shown in Figure 5. Our ability to isolate a new anion of  $[\text{MM}'\text{Te}_4]^-$  is primarily due to the mixture of  $\text{M}^{\text{III}}$  and  $\text{M}'^{\text{IV}}$  metals in the telluride chains, thus increasing the number of atoms in the repeat unit over which each anionic charge is associated, which necessarily requires an organic cation of a higher volume to charge ratio.

Comparison of **3** with other structurally characterized indium and germanium tellurides shows numerous structural similarities (based on the  $\text{MTe}_4$  tetrahedral unit). The Ge–Te bond distance of 2.684(2) Å in the chains is significantly longer compared to the other known germanium tellurides with bridging Te atoms, the bond distances range from 2.507 to 2.651 Å.<sup>11</sup> However, the In–Te bond distance of 2.686(2) Å in the 1-D chains is rather short in comparison to the other



**Figure 6.** Comparison of the structures of the 1-D chains in (A)  $(\text{Ph}_4\text{P})[\text{GeInTe}_4]$  and (B)  $\text{K}_2\text{SnTe}_5$  (shaded Te atoms are in a square-planar environment).

**Table 7. Selected Bond Lengths (Å) and Bond Angles (deg) in 1-D Chains in  $(\text{Ph}_4\text{P})[\text{GeInTe}_4]$  (**3**) and  $\text{RbInTe}_2$  (**4**)**

	$(\text{Ph}_4\text{P})[\text{GeInTe}_4]$	$\text{RbInTe}_2$
bond distances		
In(1)–Te(1)	2.686(2)	2.8139(9)
Ge(1)–Te(1)	2.684(2)	
bond angles		
Te(1)–In(1)–Te(1)	115.39(4)	115.43(2)
Te(1)–In(1)–Te(1)	98.18(7)	98.12(3)
In(1)–Te(1)–In(1)		81.88(3)
Te(1)–Ge(1)–Te(1)	115.34(4)	
Te(1)–Ge(1)–Te(1)	98.28(7)	
In(1)–Te(1)–Ge(1)	81.77(3)	

indium tellurides which usually fall in the range of 2.786–2.883 Å.<sup>12</sup> These unusual bond distances are possibly the result of similar sized holes or voids formed by the close packed Te atoms along the chain. This would lead to the In atoms to be held rather tightly and the Ge atom to rattle slightly in the voids, and this is observed as higher temperature factor for Ge atoms as compared to In in the final structure refinement. The bond distances and angles for the anion in **3** are listed in Table 7.

The 1-D chains in **1–3** are related to the chains in  $\text{K}_2\text{SnTe}_5$ <sup>13</sup> and isotypic  $\text{Rb}_2\text{SnTe}_5$ ,<sup>14</sup> which can be seen by simply replacing either a tetrahedral Ge or In site in the 1-D chains of **3** with a square-planar Te (Figure 4). Closer examination of the structure of  $\text{K}_2\text{SnTe}_5$  suggests that it could have been reported in an incorrect space group and, in fact, may crystallize in the same space group  $I4/mcm$  as  $\text{K}_2\text{HgSnTe}_4$  and  $\text{RbInTe}_2$ . Visual examination of the structure of  $\text{K}_2\text{SnTe}_5$  in the reported acentric space group  $I4cm$  fails to reveal an acentric arrangement of the atoms but apparently does show a mirror plane perpendicular to the  $c$  axis. Although one cannot be absolutely sure the structure is centric without refining the structure from the observed struc-

(11) (a)  $\text{K}_2\text{GeTe}_4$ : Eisenmann, B.; Schrod, H.; Schäfer, H. *Mater. Res. Bull.* **1984**, *19*, 293–298. (b)  $\text{LiGeTe}_2$ : Eisenmann, B.; Schwerer, H.; Schäfer, H. *Mater. Res. Bull.* **1983**, *18*, 1189–1194. (c)  $\text{Na}_8\text{Ge}_4\text{Te}_{10}$ : Eisenmann, B.; Schäfer, H.; Schwerer, H. *Z. Naturforsch.* **1983**, *B38*, 924–929. (d)  $\text{Na}_8\text{Ge}_4\text{Te}_{10}$ : Eisenmann, B.; Schwerer, H.; Schäfer, H. *Rev. Chim. Miner.* **1983**, *20*, 78–87. (e)  $(\text{Et}_4\text{N})_4\text{Ge}_4\text{Te}_{10}$ : Dhingra S. S.; Haushalter, R. C. *Polyhedron*, in press.

(12) (a)  $\text{Na}_5\text{InTe}_4$ ,  $\text{Na}_5\text{In}_2\text{Te}_6$ : Eisenmann, B.; Hofmann, A.; Zagler, R. *Z. Naturforsch.* **1990**, *B45*, 8. (b)  $\text{LiInTe}_2$ : Hönle, W.; Kühn, G.; Neumann, H. *Z. Anorg. Allg. Chem.* **1986**, *532*, 150. (c)  $\text{KInTe}_2$ : Hung, Y.-C.; Hwu, S.-J. *Acta Crystallogr.* **1993**, *C49*, 1588–1589. (d)  $\text{CaIn}_2\text{Te}_4$ : Klee, W.; Schäfer, H. *Z. Anorg. Allg. Chem.* **1981**, *479*, 125–133. (d)  $\text{InTe}_3\text{Cl}$ : Roos, V. G.; Eulenberger, G.; Hahn, H. *Z. Anorg. Allg. Chem.* **1973**, *396*, 284.

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**Table 8. Comparison of the Atomic Coordinates of  $K_2SnTe_5$  in  $I4cm$  and  $I4/mcm$** 

$I4cm$ (No. 108)			$I4/mcm$ (No. 140)		
atom	Wyckoff Site	$x, y, z$	atom	Wyckoff Site	$x, y, z$
Te(1)	8c	$x = 0.3146$	Te(1)	16l	$x = 0.3146$
		$y = 0.8146$			$y = 0.8146$
		$z = 0.1325$			$z = 0.1325$
Te(2)	8c	$x = 0.3224$	Te(2)	4d	$x = 0.0000$
		$y = 0.8224$			$y = 0.5000$
		$z = 0.8578$			$z = 0.0000$
Te(3)	4b	$x = 0.0000$	Te(3)	4b	$x = 0.0000$
		$y = 0.5000$			$y = 0.5000$
		$z = 0.0000$			$z = 0.0000$
Sn(1)	4b	$x = 0.0000$	Sn(1)	4a	$x = 0.0000$
		$y = 0.5000$			$y = 0.5000$
		$z = 0.2457$			$z = 0.2500$
K(1)	4b	$x = 0.0000$	K(1)	4c	$x = 0.0000$
		$y = 0.0000$			$y = 0.0000$
		$z = 0.2417$			$z = 0.2500$
K(2)	4a	$x = 0.0000$	K(2)	4c	$x = 0.0000$
		$y = 0.0000$			$y = 0.0000$
		$z = -0.0008$			$z = 0.0000$

ture factors, the conversion of the atomic coordinates from  $I4cm$  to  $I4/mcm$  gives the same structure with essentially identical derived metrical parameters. Table 8 shows that the conversion of the parameters from  $I4cm$  to  $I4/mcm$  is straightforward.

The high-temperature reaction of  $Rb_2Te_2$ , In, and Te at 400 °C, in a sealed evacuated quartz tube for 24 h, followed by slow cooling to room temperature, gave the one-dimensional polymer  $RbInTe_2$  (4). The structure is built of  $InTe_4$  tetrahedra sharing opposite edges to form 1-D chains and  $RbTe_8$  square antiprisms. It should be

noted that telluride 4 is isostructural with  $K_2HgSnTe_4$  as well as  $KInTe_2$ <sup>5</sup> and  $TlInTe_2$ .<sup>15</sup> The In–Te bond distance of 2.8139(2) Å in these chains is in general agreement with other structurally characterized indium tellurides.<sup>12</sup> Similar one-dimensional indium telluride chains were reported in the electrochemically synthesized  $[(C_4H_9)_4N]InTe_2$ ,<sup>6</sup> and the In–Te bond distances in this structure fall within the range 2.786(2)–2.814(2) Å. The bond distances and angles of the  $InTe_4$  tetrahedra in 4 are listed in Table 7.

The new 1-D telluride chain compounds  $K_2HgSnTe_4$  (1),  $(Et_4N)_2[HgSnTe_4]$  (2),  $(Ph_4P)[GeInTe_4]$  (3), and  $RbInTe_2$  (4) have been prepared by high-temperature or solution-phase reactions. The miscibility of two elements at the tetrahedral site within the Te chain suggests that many other types of substitutions may also be possible. The charge transport as well as other physical properties of these materials are currently under study. All these complexes are very air sensitive and decompose to give black amorphous solids.

**Supplementary Material Available:** Tables of crystal data, data collection, solution and refinement parameters, atomic coordinates, bond lengths and angles, anisotropic displacement coefficients, and nonbonded contacts for  $K_2HgSnTe_4$  (1),  $(Et_4N)_2[HgSnTe_4]$  (2),  $(Ph_4P)[GeInTe_4]$  (3), and  $RbInTe_2$  (4) (68 pages); listings of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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