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Anomalies in the Properties of $Hf(S_{2-x}Te_x)_{1-y}$ and $Hf(Se_{2-x}Te_x)_{1-y}$ near the Metal–Insulator Transition*

DAVID T. HODUL

Varian Associates, Central Research, 611 Hansen Way,
Palo Alto, California 94303

AND ANGELICA M. STACY†

Department of Chemistry, University of California,
Berkeley, California 94720

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The solid solutions $Hf(S_{2-x}Te_x)_{1-y}$ and $Hf(Se_{2-x}Te_x)_{1-y}$ were prepared to examine changes in the electronic structure in a narrow composition range near the metal–insulator transition. Powder X-ray diffraction analysis and resistivity measurements are presented. The x^3 dependence of the hexagonal c parameter for the sulfur solutions is due to large packing mismatches in the layers. In the selenium solutions, anomalous behavior is observed in the composition dependence of the a and c hexagonal lattice parameters in the range $0.05 < x < 0.10$, $y \sim 0$. Between these concentration limits, both lattice parameters show positive deviations from smooth behavior and the diffraction linewidths broaden. The temperature dependence of the resistivity suggests that the $Hf(S_{2-x}Te_x)_{1-y}$ solutions have an energy of activation for conduction at room temperature for $0 < x < \frac{7}{8}$; the sample of composition $x = \frac{5}{8}$ has a metal–insulator transition as a function of temperature below room temperature. The band gap goes to zero with composition for $Hf(Se_{2-x}Te_x)_{1-y}$ in the range $x = 0.080$ to $x = 0.095$. Nonstoichiometry, phase separation, and changes from covalent to metallic bonding explain the structural and electronic changes observed in the seleno-telluride system near the metal–insulator transition.

Introduction

Among the many scientific contributions of Professor Michell J. Sienko were his studies of the metal–insulator transition (some of the more recent works include Refs. (*1–13*)). He investigated systems with a metal–insulator transition as a function of composition and determined changes in structure and the evolution of the electronic properties as the composition was varied. Professor Sienko's insights and experiments have expanded our understanding of the metal–insulator transition in metal–ammonia and metal–methylamine solutions, as well as in transition metal oxides. Most recently, his interests turned to studies of the layered transition metal dichalcogenides. In this paper, we present a study of the structural and electronic properties of solid solutions of the layered transition

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* Dedicated to Dr. M. J. Sienko.

† Author to whom correspondence should be addressed.

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metal chalcogenides $Hf(S_{2-x}Te_x)_{1-y}$ and $Hf(Se_{2-x}Te_x)_{1-y}$, work initiated in his laboratories. Our ideas and conclusions about the mechanism of the metal–insulator transition in these systems were influenced by many discussions with Professor Sienko; therefore, this paper is dedicated in memory of him.

The transition metal chalcogenides have been studied extensively in recent years, in large part because of the wide range of properties derived from their layered structure. The laminar form of these materials gives rise to anisotropic conductivity (*14*), intercalation chemistry (*15*), and lubrication properties (*16*). Interesting studies of their electronic properties include: superconductivity (*17*), charge density waves (*18*), photoelectrochemistry (*19*), and catalysis (*20*).

The IVB layered dichalcogenides have the hexagonal CdI_2 structure. The transition metal is coordinated to six chalcogen anions with D_{3d} point group symmetry. A hexagonal plane of metal is sandwiched between two hexagonally ordered layers of chalcogen anions. These sandwiches are held together by weak van der Waals forces.

HfS_2 and $HfSe_2$ are indirect gap semiconductors (*21*) with band gaps of 1.96 and 1.13 eV, respectively, and can be prepared very near the 1 : 2 metal to chalcogen stoichiometry. $HfTe_{2-y}$ is nonstoichiometric with a composition range of $0.05 < y < 0.40$ (*6, 22, 23*). The nonstoichiometry is properly written with tellurium vacancies (*24*) as the majority defect, but one must be aware of possible minority defects similar to those which occur in the $ZrTe_{2-x}$ system (*25*). $HfTe_{1.95}$ has a gold luster and the conductivity decreases with increasing temperature as is typical for a metal (*22*). It is believed that the metallic conductivity of $HfTe_{1.95}$ is governed by impurity bands due to defects and the overlap of the tellurium *sp* band with the hafnium *d* band (*6*).

Because the hafnium dichalcogenides have similar structures, mixed materials can be synthesized over the entire composition range. This provides not only materials with new properties but also allows the study of composition-dependent behavior such as metal–insulator transitions. One expects a metal–insulator transition as a function of composition in $Hf(S_{2-x}Te_x)_{1-y}$ and $Hf(Se_{2-x}Te_x)_{1-y}$, where y changes from 0 to 0.05, as x increases. Previous studies of the resistivity and magnetic susceptibility of $Hf(Se_{2-x}Te_x)_{1-y}$ indicate a metal–insulator transition near $x \simeq 0.1$ (*6*).

We have prepared samples of $Hf(Se_{2-x}Te_x)_{1-y}$ in a narrow range $0 < x < 0.2$ to examine changes in structure and electronic properties associated with the metal–insulator transition. An interesting anomaly is observed in the volume of the system in this concentration range. Furthermore, we have prepared solid solutions of $Hf(S_{2-x}Te_x)_{1-y}$ over a wide compositional range to compare the metal–insulator transition in the sulfo–tellurides with that in the seleno–tellurides. The $Hf(S_{2-x}Te_x)_{1-y}$ compounds are quite different from the selenium analogs and remain semiconductors for compositions at least as large as $x = \frac{7}{8}$. By studying the changes that occur in the properties of these solid solutions as a function of the composition, we hope to gain a better understanding of the role of nonstoichiometry and disorder on the bonding and electronic properties of the IVB dichalcogenides.

Experimental

Samples of $Hf(S_{2-x}Te_x)_{1-y}$ and $Hf(Se_{2-x}Te_x)_{1-y}$ were prepared from the elements by high-temperature reaction. The starting materials, from Ventron-Alfa Corporation, were 99.9% hafnium powder (zirconium ~1%), 99.9999% sulfur lumps, 99.999% selenium shot, and 99.9998% tellurium pieces. The elements were loaded into silica tubes that were cleaned by rinsing with dilute hydrofluoric acid and outgassing under vacuum. Samples of $Hf(S_{2-x}Te_x)_{1-y}$ were prepared with compositions in the range $0 < x < 2.0$ and with $y = 0$. Samples of $Hf(Se_{2-x}Te_x)_{1-y}$ were prepared in a much narrower composition range, $0 < x < 0.2$ and $y = 0$. Nominal compositions are reported throughout this paper even though the stoichiometry of the products may deviate by a small amount from the starting ratios.

The reaction tubes, loaded with the starting materials, were pumped for 15 min at $\sim 10^{-5}$ Torr, with a nitrogen trap. At this point, iodine was sublimed into the reaction tubes, in a concentration of 5 mg/cm^3 of reaction volume. The iodine was needed as a mineralizing agent and greatly improved the crystallinity of the product. For comparison, a few samples were reacted without a mineralizing agent, as indicated in Table I for $Hf(S_{2-x}Te_x)_{1-y}$. The sealed tubes were reacted in flat furnaces for one week at 600°C and 2 weeks at 800°C. Samples were cooled to room temperature in approximately 10 min. All samples were fine powders, approximately 325 mesh.

The hexagonal lattice constants were obtained by powder X-ray diffraction analysis using Debye–Scherrer cameras with a diameter of 114.6 mm. All samples were prepared for X-ray analysis in an argon-atmosphere dry box by sifting through a <325 mesh screen, loading into a 0.3 mm glass capillary and sealing. The lines on the diffraction patterns were read to 0.03 mm. Distances and angles were determined by

TABLE I

PREPARATION OF $Hf(S_{2-x}Te_x)_{1-y}$

X	a parameter (Å)	c parameter (Å)	Mineralizer	Color	Comments
0.00	3.6310(10)	5.8560(20)	None	Red–brown Brown	[a,b]
0.00	—	—	None	Red–brown	
0.123	—	—	$HfCl_4$		[c]
0.251	3.6616(8)	6.0984(10)	I_2	Black	[e]
0.374	—	—	$HfCl_4$		[c]
0.50	—	—	None	Black	[a]
0.50	3.70	6.30	None	Black	[e]
0.624	—	—	$HfCl_4$		[c]
0.746	3.741(4)	6.443(6)	I_2	Black–gold	[d]
0.871	—	—	$HfCl_4$		[c]
1.00	—	—	None	Black	[a]
1.00	3.776	6.54	None	Black–gold	[f]
1.248	3.824(4)	6.599(7)	I_2	Gold	[e]
1.50	—	—	None	Gold	[a]
1.50	3.6616(8)	6.0984(1)	None	Gold	
1.748	3.9103(12)	6.6583(11)	I_2	Gold	[e]
2.000	3.951(3)	6.658(8)			[b]

[a] Reaction only to 600°C, reported for color.
[b] Lattice parameters from Ref. (*33*).
[c] Used for conductivity measurement.
[d] Extra phase seen in X-ray pattern.
[e] Color for single crystal growth with $TeCl_4$.
[f] Color for single crystal growth with I_2.

the Straumanis method (*26*) which corrects for film shrinkage and systematic errors derived from the camera geometry. Lattice parameters were determined by the method of Cohen's least squares for hexagonal systems (*27*), using back reflection lines with $\theta > 60°$.

Additional samples were prepared under similar conditions to the powders but with $HfCl_4$ as a mineralizing agent. Chlorine was superior to iodine in mineralizing these samples and crystals of the approximate size 0.5 mm × 0.5 mm × 40 μm were obtained. Larger single crystals of these solid solutions were obtained by vapor-phase transport with $TeCl_4$ as the transporting agent in a concentration of 3 mg/cm^3 of reaction volume. A temperature gradient of 800 to 700°C over a 15 cm silica tube was used. The crystals were black hexagonal plates, as large as 5 mm × 5 mm × 40 μm.

The temperature dependence of the conductivity was measured between 77 K and room temperature on pressed pellets of various samples. The conductivity data reported is for powders mineralized with $HfCl_4$. These powders were chosen over the single crystals since measurements made on the crystals were not reproducible within a batch or with different mineralizing agents. This choice was a trade-off between the purity of the powders, and the superior conductivity measurement on single crystals but contaminated with halogens. A two-probe, low-frequency (37 Hz) method was used. Pieces of gold foil pressed into the faces of the pellet were used to make electrical contact. The ac constant currents were 0.1–1.0 mA and the voltage was detected by a lock-in amplifier in-phase with the current source. Since it is not possible to obtain absolute resistivities on powder samples, the ratio of the resistivity to the resistivity at 300 K is plotted to show the temperature dependence.

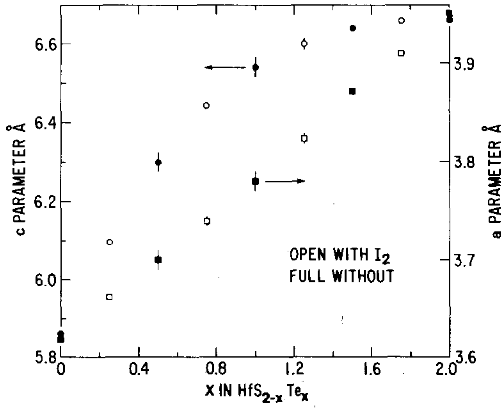

FIG. 1. Hexagonal *a* and *c* parameter versus the nominal composition for $Hf(S_{2-x}Te_x)_{1-y}$. The open squares and circles represent samples reacted with iodine and the filled ones were reacted without iodine.

Results

Visual inspection of the reaction tubes showed a color change from the black $HfSe_2$ to a black–brown material of nominal composition $Hf(Se_{1.8}Te_{0.2})$. This color change did not depend on the presence of mineralizing agents. In contrast, the color changes in the sulfo–telluride system depended on whether a mineralizing agent was present or not. The samples prepared with iodine changed from the reddish-brown color of HfS_2 to black as x increased and finally to gold near $x \simeq 0.75$. For samples prepared without a mineralizing agent, the black-to-gold transition occurred near $x \simeq 1.00$ (see Table I). The X-ray powder patterns for samples reacted with iodine or chlorine were sharp and free of extra phases. Those samples reacted without iodine gave patterns with broad diffraction lines.

The lattice parameters for $Hf(S_{2-x}Te_x)_{1-y}$ obtained from the least-squares fit of the data are shown in Fig. 1. No obvious lattice anomalies associated with the metal–insulator transition are observed. Figure 2 is a plot of the difference of the measured *c* parameter and that predicted by Vegard's law, which is a linear extrapolation be-

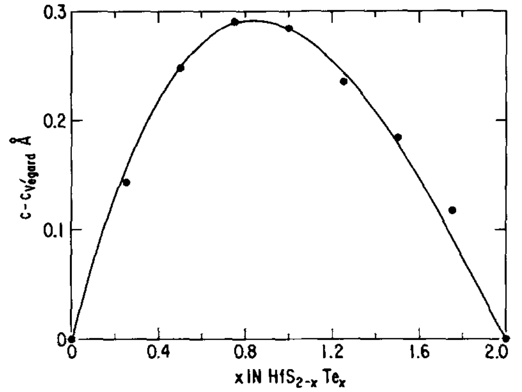

FIG. 2. Deviation of the hexagonal c parameter from Vegard's law for $Hf(S_{2-x}Te_x)_{1-y}$. The curve is for a cubic power law fit to the data. Vegard's law predicts that the c parameter will change linearly with composition. The deviation from this prediction suggests that there are severe packing mismatches in the layers.

tween the c parameters of HfS_2 and the phase of nominal composition $HfTe_2$. This difference has a c parameter dependence of x^3, implying very severe packing mismatches in these solutions (*28*).

The lattice parameters for $Hf(Se_{2-x}Te_x)_{1-y}$ are shown in Fig. 3. For both the hexagonal a and c parameters anomalies are observed in the range $0.05 < x < 0.10$. Between these composition limits, both lattice parameters show deviations from smooth behavior, the c parameter having a larger percentage deviation than the a parameter. Furthermore, in this concentration range the diffraction linewidths are measurably broad as compared with the sharp lines observed below $x = 0.05$ and above $x = 0.12$. The maximum linewidths occur near $x = 0.08$. The lattice parameters over the larger concentration range $0 < x < 2.0$ have been reported previously (*28*) and are consistent with these results. The relation of the lattice anomaly with the metal–insulator transition is discussed below.

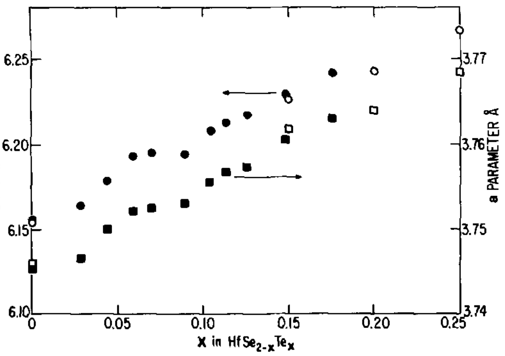

FIG. 3. Hexagonal a and c parameter versus the nominal composition for $Hf(Se_{2-x}Te_x)_{1-y}$. The open squares and circles are from Ref. (*22*). An anomaly in the lattice parameters occurs for $0.05 < x < 0.10$.

The measurements of the resistivity of the $Hf(S_{2-x}Te_x)_{1-y}$ samples are shown in Fig. 4. All these materials have resistivities between 1 and 100 ohm-cm. Since the tem-

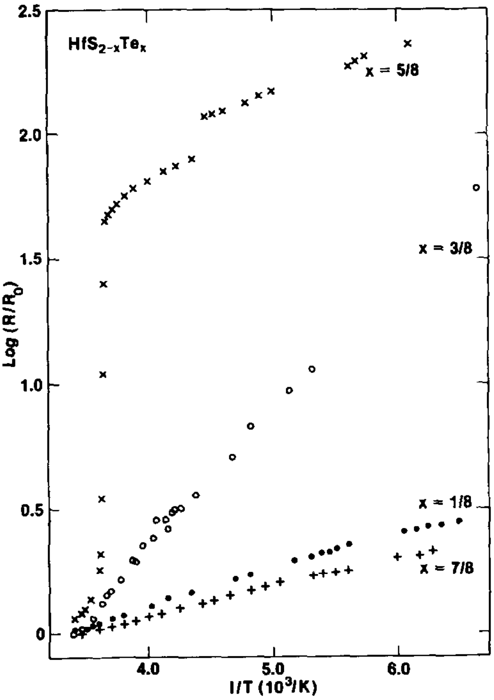

FIG. 4. Log of the ratio of resistance to room-temperature resistance versus reciprocal temperature for four compositions of $Hf(S_{2-x}Te_x)_{1-y}$. The temperature dependence suggests that all four samples have a small energy of activation for conduction at room temperature. A metal–insulator transition as a function of temperature is observed for the material of composition $x = \frac{5}{8}$.

perature dependence of the resistivity $d\rho/dT$ is positive, these samples have a small energy of activation for conduction (~0.01 to 0.10 eV). The transition to the metallic state as a function of composition, (i.e., no energy of activation for conduction) is not observed for values of x as large as $\frac{7}{8}$. The sharp break in the resistivity as a function of temperature for the sample of composition $x = \frac{5}{8}$ suggests that this sample has a metal–insulator transition induced by temperature. Additional X-ray data and Hall mobility measurements as a function of temperature are needed to verify and interpret this feature.

Resistivity measurements for two samples of $Hf(Se_{2-x}Te_x)_{1-y}$ with $x = 0.080$ and $x = 0.095$ are shown in Fig. 5. Both samples have resistivities of ~1 ohm-cm. The sample with $x = 0.080$ has a small energy of activation for conduction (~0.01 eV) with the resistivity at 100 K approximately 1.5 times larger than the value at 300 K. The sample with $x = 0.095$ has a resistivity which is nearly constant over the temperature range studied. These results indicate that the band gap becomes zero in the range $0.080 < x < 0.095$. Resistivity data for samples with $x > 0.10$ have been reported previously (*6*).

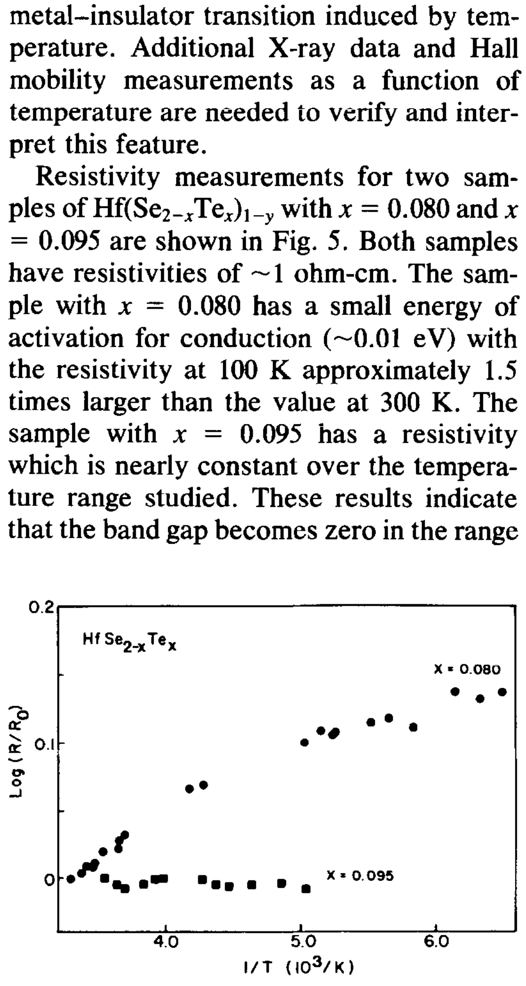

FIG. 5. Log of the ratio of resistance to room-temperature resistance versus reciprocal temperature for two compositions of $Hf(Se_{2-x}Te_x)_{1-y}$. The temperature dependence suggests that the sample with $x = 0.080$ has a small energy of activation for conduction and the sample with $x = 0.095$ has an energy of activation near zero.

Discussion

The solid solutions of hafnium disulfide and hafnium diselenide with hafnium ditelluride have two types of metal–insulator transitions: (1) changes in the electronic properties due to changes in composition, and (2) changes in the electronic properties due to changes in temperature. $Hf(S_{2-x}Te_x)_{1-y}$ has a metal–insulator transition as a function of temperature for the sample of composition $x = \frac{5}{8}$. Further structural and electrical measurements as a function of temperature are needed to verify this assertion. Below, we discuss the metal–insulator transition induced by composition and argue that for the sulfo–tellurides the electronic properties seem to be controlled by disorder, whereas for the seleno–tellurides the effects due to stoichiometry seem dominant.

For the IVB layered dichalcogenides it has been suggested (*21*) that the hexagonal c parameter correlates well to the band gap energy. If one extrapolates the band gaps of HfS_2 and $HfSe_2$ as a function of c parameter to the c parameter of $HfTe_{1.95}$, one expects $HfTe_{1.95}$ to be a −0.4 eV band gap semimetal. The band gap is expected to go to zero for $c \simeq 6.5$ Å. Using the lattice parameter data from Ref. (*6*), the metal–insulator transition is predicted near the composition $x \simeq 0.9$ for both the sulfo–tellurides and the seleno–tellurides. For $Hf(Se_{2-x}Te_x)_{1-y}$, the energy of activation for conduction goes to zero near $x \simeq 0.1$ indicating that the overlap of the hafnium d band with the chalcogen sp band is not the sole cause of the transition. The properties of these solutions are complicated by nonstoichiometry as discussed below. For $Hf(S_{2-x}Te_x)_{1-y}$, the energy of activation remains small but greater than zero for x as large as $\frac{7}{8}$. It is interesting to note that for $0.9 < x < 2.0$, both systems have the same c parameter for similar compositions, suggesting that when the intrinsic bands overlap the structure is determined by the electronic energies rather than by packing energies.

The conductivity measurements on samples of $Hf(Se_{2-x}Te_x)_{1-y}$ show that the band gap goes to zero in the range $0.080 < x < 0.095$. In this composition range, an interesting anomaly in the volume is observed (see Fig. 3). This anomaly occurs in addition to the parabolic dependence of the c parameter that has been reported previously (*28*). Two possible interrelated mechanisms for this anomaly in the volume are postulated and discussed below: (1) a nonstoichiometric to stoichiometric transition, and/or (2) the onset of phase separation at the metal–insulator transition.

One explanation for the observed lattice anomaly involves the nonstoichiometry of the $HfSe_2$–$HfTe_2$ solid solution. It is known that the highest tellurium to hafnium ratio for Hf–Te binary layered compounds is 1.95. This implies that while the nominal reaction composition was always a 2:1 chalcogen:metal ratio, somewhere in the full composition range this ratio must be reduced, i.e., y changes from 0 to 0.05. This reduction in chalcogen fraction is expected to reduce the packing mismatch in the layers and hence, reduce the cell volume; this effect should be larger for the c parameter. We feel this reduction in chalcogen-to-metal ratio occurs at the observed lattice anomaly and is associated with the metal–insulator transition. This implies that while in Fig. 3 the nominal reaction composition is given, the actual composition is best understood as follows: (1) for nominal $0 < x < 0.05$, the solution is in fact the stoichiometric $HfSe_{2-x}Te_x$ ($y = 0$), (2) for nominal $0.05 < x < 0.10$, the solution is $Hf Se_{2-x}Te_{0.05}$ (y increases from 0 to 0.05), and (3) for the $x > 0.10$, the actual composition is $HfSe_{2-x}Te_{x-0.05}$ ($y = 0.05$). This model implies that tellurium vacancies are formed linearly with composition in the range $0.05 < x < 0.10$ and that Te^{2-} vacancy donor states are responsible for the metal–insulator transition. The expected number of conduction electrons at $x = 0.10$ is therefore approximately 0.10 e^- per hafnium.

A second possible mechanism for the anomaly at $x \cong 0.1$ in $Hf(Se_{2-x}Te_x)_{1-y}$ is the onset of a phase separation associated with the metal–insulator transition. This separation need not be independent of the nonstoichiometry mechanism discussed above. Various authors have discussed the potential for phase separation near the metal–insulator transition (*29–31*). One expects fluctuations in composition to occur in systems where electron correlations play an important role in the metal–insulator transition, provided the system is at a temperature below the miscibility gap and the kinetic barrier for phase separations is not large. In the $Hf(Se_{2-x}Te_x)_{1-y}$ solid solution, since the kinetics of phase separation is slow compared to the quenching time from the 800°C reaction temperature to room temperature, a high-temperature phase has been locked in at the lower temperature where the lattice parameters have been determined. We believe that the synthesis temperature is above a miscibility gap in the temperature–composition phase diagram, but that composition fluctuations are present. The effect of these fluctuations can be seen in the diffraction line broadening in the region of the transition. It is possible these fluctuations are changes in the homogeneity of the samples due to the tellurium vacancies referred to in the above paragraph on nonstoichiometry.

The resistivity measurements for $Hf(S_{2-x}Te_x)_{1-y}$ show that the changes in the electronic properties with composition are quite different than for the seleno–telluride solutions. The sulfo–tellurides have an energy of activation for conduction for compositions with x as large as $\frac{7}{8}$, the largest tellurium concentration for which the resistivity was measured. The low resistivity of 1-ohm-cm for these samples implies that there are a large number of carriers, possibly due to anion vacancies. It is evident from the differences in color change between the halogen-mineralized samples and the powders prepared without halogens that disorder and/or impurities could play a significant role in determining the electronic properties. In $Hf(S_{2-x}Te_x)_{1-y}$, the metal–insulator transition occurs for lower values of x in the crystalline samples than in the pure powdered samples since the gold metallic color is observed for compositions nearer to HfS_2 for mineralized materials. Furthermore, the difference in the actual c parameter and that of a linear extrapolation between the c parameters of HfS_2 and $HfTe_{1.95}$ has a x^3 dependence as shown in Fig. 2. This implies very severe packing mismatches in the layers (*28*). We propose that the origin of the differences in the behavior of the sulfo–telluride systems as compared with the seleno–telluride system is due to disorder in the former system resulting from the large size differences of sulfur and tellurium.

We conclude that for the solid solutions $Hf(Se_{2-x}Te_x)_{1-y}$ the band gap goes to zero in the range $0.080 < x < 0.095$ due to the formation of an impurity band which overlaps with the hafnium *d* band. This impurity band is a donor band produced by tellurium vacancies. The anomalous changes in the lattice parameters with composition near the metal–insulator transition can be attributed to a stoichiometric–nonstoichiometric transition, composition fluctuations, and changes in bonding. The solid solutions $Hf(S_{2-x}Te_x)_{1-y}$ remain semiconductors up to the composition with $x = \frac{7}{8}$ due to disorder resulting from the large size differences of sulfur and tellurium. The disorder is evident in the x^3 dependence of the c parameter. We conclude that the electronic structure of the $Hf(Se_{2-x}Te_x)_{1-y}$ and $Hf(S_{2-x}Te_x)_{1-y}$ solutions are quite different, the former being influenced by tellurium vacancies which inject carriers into the hafnium *d* band and the latter, by disorder.

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