The fact that no depolymerization of the hexatantalate was observed even in the most alkaline solutions studied is not surprising, for the charge per tantalum would be too high for species like TaO_6^{-7} to be stable, and condensed species are formed. Since tantalum seems to occur only with a coordination number of six for oxygen, monomeric anions like TaO_4^{-3} appear quite unlikely.

Acknowledgment.—The authors wish to express their appreciation to Mr. Norman Sweeney of Central Research, The Minnesota Mining and Manufacturing Company, St. Paul, Minn., who provided the differential thermal and gravimetric analyses. We should also like to thank Professor Milton Kerker for transmitting results on his studies of the light scattering of aqueous solutions of tungstophosphoric and tungstosilicic acids prior to publication.

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E. I. du Pont de Nemours and Co., Wilmington, Delaware

X-Ray Study and Thermoelectric Properties of the $W_{x/2}Mo_{x/2}Ta_{1-x}Se_2$ System

By L. H. Brixner and G. Teufer

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The pseudo-binary system between the compounds $TaSe_2$ and $W_{0.5}Mo_{0.5}Se_2$ has been investigated structurally and with regard to such thermoelectric parameters as Seebeck coefficient, electrical resistivity, and thermal conductivity. Eighteen compositions with x varying from 0.2 to 0.99 have been prepared. With the exception of a narrow two-phase region near $x = 0.7$, all compositions crystallize as single phases, either of the $CdCl_2$ or the MoS_2 type. Compounds of interest for thermoelectric power generation in the intermediate temperature range (500–700°) were found for $x = 0.9$–0.99. As corollaries, the system $W_xMo_{1-x}Se_2$ and some compositions of the five-component system $W_{x/2}Mo_{x/2}Ta_{1-x}Se_yTe_{2-y}$ were also invesitgated.

Introduction

In an earlier paper,[1] we have described the system $W_xTa_{1-x}Se_2$, and we have demonstrated how useful thermoelectric properties can be achieved by finding the optimum for x. Compositions such as $W_{0.97}Ta_{0.03}Se_2$ exhibited respectable Seebeck coefficients and relatively low electrical resistivities, but the thermal conductivity of some 70 mwatts/cm.-deg. was somewhat high and could stand some improvement. This was our major goal during the present investigation, which led us to the more complex $W_{x/2}Mo_{x/2}Ta_{1-x}Se_2$ system. The principle followed was essentially that laid down by Airapetiants.[2] He showed that semiconducting compounds of the type we are dealing with can be regarded as consisting of a cation and anion sublattice, and that electron scattering will be more strongly affected by changes in the anion sublattice, while the converse will be true for holes. The uncharged phonons, on the other hand, show essentially no preference. Since all of the useful compositions in the $W_xTa_{1-x}Se_2$ system were p-type, these considerations suggest that one should introduce substituents in the cation sites in order to reduce the thermal conductivity without affecting the electrical conductivity to an equal degree. Therefore, we were led to the system $W_{0.5}Mo_{0.5}Se_2$–$TaSe_2$, where half the tungsten atoms are replaced by molybdenum. (The practical purpose of the minor amount of tantalum substituted in the cation sites, of course, is to adjust the carrier concentration to the optimum level.) Since tungsten and molybdenum have an atomic mass ratio of almost 2:1, we are introducing a considerable mass fluctuation, which should cause further phonon scattering and therefore lower the thermal conductivity. Although the lattice parameters of both $MoSe_2$ and WSe_2 were well established and complete solid solubility could be expected, we studied the $Mo_xW_{1-x}Se_2$ system in some more detail and these data are also reported. Finally, we also prepared some compositions of the even more complex five-component system $W_{x/2}Mo_{x/2}Ta_{1-x}Se_yTe_{2-y}$ and these data are also included.

Experimental

Preparation.—The routine procedure for the preparation of all solid solutions was to vacuum-seal the constituent elements W, Mo, Ta, and Se, weighed to the nearest 0.1 mg., into a quartz ampoule, 15 mm. in diameter and 20 cm. long. All tubes were carefully heat-treated under vacuum in order to eliminate moisture as much as possible. The constituent elements were of best commercially available purity, usually 99.9+%, and were not given any special purification treatment prior to the reaction. Charges of approximately 20–30 g. were fired at 600–700° for 10–15 hr., after which time usually a black, free-flowing reaction product of apparently high surface area was obtained that could be effectively remixed inside the quartz tube by shaking. A second firing step at 1000–1200° for another 10–15 hr. assured completion of the reaction, and a homogeneous polycrystalline product of gray metallic luster was obtained which could be removed quite easily from the quartz after breaking the ampoule.

Crystallographic Characterization.—All X-ray data are based on powder diffraction patterns obtained with a Phillips 114.6-mm. diameter camera at 25°. The samples, which were taken from the center of the final reaction product, were ground to −325 mesh and were sealed into 2-mm. diameter Lindemann

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[1] L. H. Brixner, *J. Electrochem. Soc.*, **110**, 289 (1963).

[2] S. V. Airapetiants, *et al.*, *Soviet Phys.*, **2**, 2009 (1957).

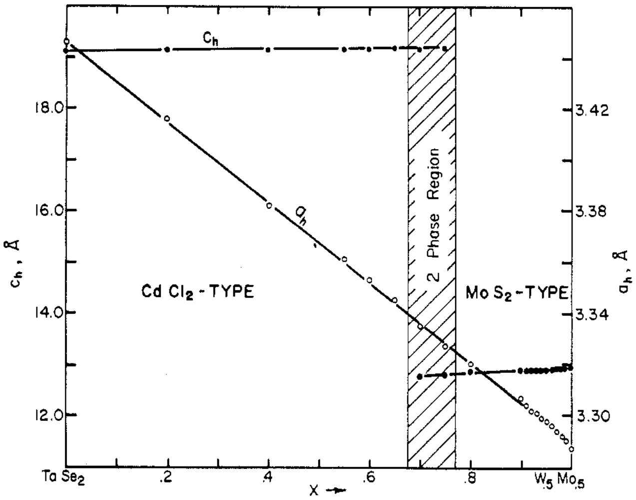

Fig. 1.—Lattice parameters as a function of composition for the $W_{x/2}Mo_{x/2}Ta_{1-x}Se_2$ system.

glass capillaries. Exposure times to the Kα radiation of copper (λ = 1.5418 Å.) varied between 2 and 6 hr. Accurate parameters were obtained by extrapolating both a_0 and c_0 according to the function $^1/_2(\cos^2 \theta/\sin \theta + \cos^2 \theta/\theta)$ given by Nelson and Riley.[3]

The lattice parameters are summarized in Fig. 1. Parameters can be considered accurate to ±0.001 Å. for the a-direction and to ±0.002 Å. for the c-direction. Figure 1 shows that the D^5_{3d} space group of the $CdCl_2$-type is retained up to x = 0.65; we then have a narrow two-phase region where both types coexist in roughly equal intensity, and from x = >0.8 all compositions crystallize in the D^4_{6h} space group of the MoS_2-type.

Densities of powdered specimen were determined by vacuum distilling CCl_4 onto the specimen contained in a 5-ml. pycnometer. This procedure gave experimental values which were generally 1–3% lower than the densities calculated from the X-ray data, which can be considered good agreement. Typical results are given for two compositions each of the $CdCl_2$ and the MoS_2 region

$W_{0.20}Mo_{0.20}Ta_{0.6}Se_2$ ρ(pycn.) 8.28 g. ml.$^{-1}$
ρ(X-ray) 8.464 g. ml.$^{-1}$
$W_{0.10}Mo_{0.10}Ta_{0.8}Se_2$ ρ(pycn.) 8.42 g. ml.$^{-1}$
ρ(X-ray) 8.519 g. ml.$^{-1}$
$W_{0.49}Mo_{0.49}Ta_{0.02}Se_2$ ρ(pycn.) 8.01 g. ml.$^{-1}$
ρ(X-ray) 8.159 g. ml.$^{-1}$
$W_{0.40}Mo_{0.40}Ta_{0.2}Se_2$ ρ(pycn.) 8.13 g. ml.$^{-1}$
ρ(X-ray) 8.285 g. ml.$^{-1}$

Since one of the constituents ($W_{0.5}Mo_{0.5}Se_2$) of the $W_{x/2}Mo_{x/2}Ta_{1-x}Se_2$ system already represents a solid solution of the two compounds $MoSe_2$ and WSe_2, we investigated the complete $W_xMo_{1-x}Se_2$ system structurally as a function of x and these data are summarized in Table I.

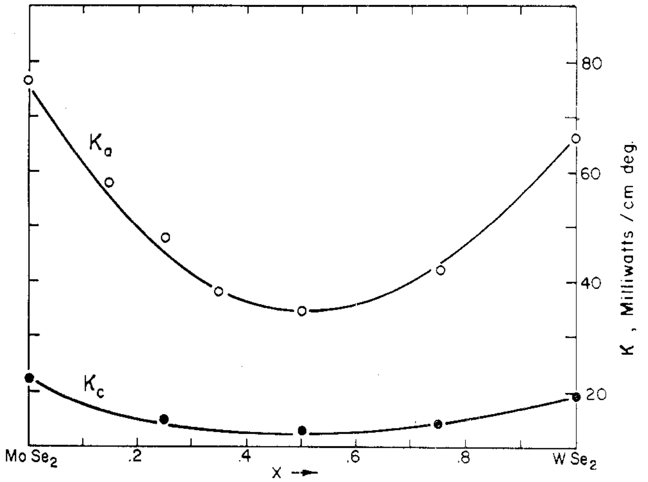

Fig. 2.—Thermal conductivity for the $W_xMo_{1-x}Se_2$ system as a function of x.

TABLE I

LATTICE PARAMETERS OF THE $W_xMo_{1-x}Se_2$ SYSTEM

Composition	a_0, Å.	c_0, Å.	c/a	ρ (X-ray), g. ml.$^{-1}$	Unit cell volume, Å.^{3}
$MoSe_2$	3.289	12.930	3.931	6.959	121.128
$Mo_{0.85}W_{0.15}Se_2$	3.289	12.935	3.933	7.318	121.175
$Mo_{0.75}W_{0.25}Se_2$	3.288	12.941	3.936	7.560	121.157
$Mo_{0.65}W_{0.35}Se_2$	3.288	12.945	3.937	7.799	121.195
$Mo_{0.25}W_{0.75}Se_2$	3.287	12.965	3.944	8.754	121.308
WSe_2	3.286	12.976	3.949	9.353	121.337

All these compositions crystallize in the MoS_2-type, and if one plots a_0, c_0, c/a, ρ, or the unit cell volume as a function of x, straight lines are obtained in each case. It is interesting to note that with successive replacement of Mo by W, a_0 decreased, c_0 increased, and the unit cell volume also slightly expanded.

Table II, finally, summarizes some structural parameters of compositions of the system $W_{x/2}Mo_{x/2}Ta_{1-x}Se_yTe_{2-y}$ which will be discussed briefly in the part concerned with electrical and thermal properties. Compositions with tellurium concentrations in excess of 1.5 moles were all of lower symmetry and could not be identified structurally lacking single crystals.

Electrical Properties and Thermal Conductivity.—The electrical resistivity and the Seebeck coefficient were measured by standard techniques. Thermal conductivity at high temperature was measured by the comparative procedure described by Francl[4] and the absolute room temperature values were obtained by the technique described by Weiss.[5] Some of the data obtained are summarized in Table III.

TABLE II

LATTICE PARAMETERS OF SOME COMPOSITIONS OF THE $W_{x/2}Mo_{x/2}Ta_{1-x}Se_yTe_{2-y}$ SYSTEM

Composition	a_0, Å.	c_0, Å.	c/a	Type	ρ (X-ray), g. ml.$^{-1}$	Unit cell volume, Å.^{3}
$Mo_{0.47}W_{0.47}Ta_{0.06}Se_{0.5}Te_{1.5}$[a]	3.400	13.770	4.050	MoS_2	8.991	137.851
$Mo_{0.47}W_{0.47}Ta_{0.06}SeTe$	3.390	13.560	4.000	MoS_2	8.586	134.951
$Mo_{0.47}W_{0.47}Ta_{0.06}Se_{1.5}Te_{0.5}$	3.345	13.273	3.968	MoS_2	8.381	128.611
$Mo_{0.47}W_{0.47}Ta_{0.06}Se_{1.7}Te_{0.3}$	3.328	13.218	3.972	MoS_2	8.247	126.780

[a] As prepared, this composition showed lower symmetry, different from $CdCl_2$ and MoS_2; only upon grinding were the above given parameters obtained.

Compared to the electrical properties of the $W_xTa_{1-x}Se_2$ compositions reported earlier,[1] we can notice that the resistivities generally run higher, especially in the region of x > 0.9 where thermoelectrically interesting compositions are found. If one

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(3) J. B. Nelson and D. P. Riley, *Proc. Phys. Soc.* (London), **57**, 160 (1945).

(4) J. Francl and W. D. Kingery, *J. Am. Ceram. Soc.*, **37**, 80 (1954).

(5) H. Weiss, *Ann. Phys.* (Leipzig), **4**, 121 (1959).

Table III

Electrical Properties of the $W_{x/2}Mo_{x/2}Ta_{1-x}Se_2$ System

x	ρ, mohm-cm., 25°	ρ, mohm-cm., −196°	S, μv./deg., 25°	S^2/ρ	Type	ΔS,[a] μv./deg.
0	0.4	0.3	10	2.5×10^{-7}	n	Constant
0.2	1.0	.7	9	8.1×10^{-8}	n	Constant
.4	1.1	.7	5	2.3×10^{-8}	n	−0.02
.55	1.3	1.1	1	7.7×10^{-10}	p	+ .02
.60	1.1	0.9	5	2.3×10^{-8}	p	+ .03
.65	1.2	1.0	8	5.3×10^{-8}	p	+ .04
.70	1.1	0.8	11	1.1×10^{-7}	p	+ .05
.75	1.1	.9	15		p	+ .06
.80	1.2	.9	18	2.7×10^{-7}	p	+ .05
.90	1.2	.8	40	1.3×10^{-6}	p	+ .05
.91	1.3	.9	45	1.5×10^{-6}	p	+ .06
.92	1.3	1.0	47	1.7×10^{-6}	p	+ .07
.93	1.4	1.2	52	1.9×10^{-6}	p	+ .11
.94	1.6	1.3	55	1.9×10^{-6}	p	+ .15
.95	2.2	1.7	60	1.6×10^{-6}	p	+ .18
.96	3.0	2.6	64	1.4×10^{-6}	p	+ .22
.97	3.8	3.7	67	1.2×10^{-6}	p	+ .42
.98	9.2	6.6	92	9.2×10^{-7}	p	+ .33
.99	40.1	219	300	2.2×10^{-6}	p	− .39
1.00	94×10^3	83×10^6	880	8.2×10^{-8}	p	− .36

[a] This column gives the changeof Seebeck coefficient per degree over a temperature range from 25 to 200°.

looks at the electrical properties of the $W_xMo_{1-x}Se_2$ system, as summarized in Table IV, this can easily be understood.

Table IV

Electrical Properties of Some Compositions of the $W_xMo_{1-x}Se_2$ System

Composition	ρ, ohm-cm., 25°	S, μv./deg.	Type
WSe_2	0.72	+700	p
$W_{0.75}Mo_{0.25}Se_2$	117	+274	p
$W_{0.5}Mo_{0.5}Se_2$	94	−880	n
$W_{0.35}Mo_{0.65}Se_2$	22	−790	n
$W_{0.25}Mo_{0.75}Se_2$	17	−800	n
$W_{0.15}Mo_{0.85}Se_2$	9.5	−800	n
$MoSe_2$	3.5	−1000	n

Since the conduction mechanism in $MoSe_2$ (electrons) and WSe_2 (holes) is of different type, the solid solution of these constituents exhibits higher resistivities due to compensation of the two opposing conductivity mechanisms. Particularly since $W_{0.5}Mo_{0.5}Se_2$ is still of n-type, larger quantities of the p-type doping agent, tantalum, have to be added to achieve resistivities comparable to the molybdenum-free system.

Strong emphasis was therefore placed on the thermal conductivity measurements, which were to determine whether a sufficient lowering of k could be achieved to improve the over-all picture with regard to the figure of merit. Figure 2 represents the thermal conductivity data for the $W_xMo_{1-x}Se_2$ system. It can be seen that by replacing half of the tungsten by molydenum and thereby creating a considerable mass fluctuation in the cation sites, a substantial reduction of the thermal conductivity was achieved. Table V gives a comparison of the room temperature figure of merit of some molybdenum-substituted compositions with $W_{0.97}Ta_{0.03}Se_2$. We notice that the substitution of tantalum did not affect the thermal conductivities of these compositions, which are about the same as for $Mo_{0.5}W_{0.5}Se_2$.

Table V

Comparison of Room Temperature Data for $W_{0.97}Ta_{0.03}Se_2$ and Some Compositions of the $W_{x/2}Mo_{x/2}Ta_{1-x}Se_2$ System

Composition	ρ, mohm-cm.	S, μv./deg.	k, watts/cm.-deg.	Z, deg.$^{-1}$ $\times 10^3$
$W_{0.97}Ta_{0.03}Se_2$	2.1	+79	0.07	0.042
$W_{0.485}Mo_{0.485}Ta_{0.03}Se_2$	3.8	+51	.036	.019
$W_{0.49}Mo_{0.49}Ta_{0.02}Se_2$	9.2	+99	.034	.031
$W_{0.495}Mo_{0.496}Ta_{0.01}Se_2$	40.1	+300	.039	.057

It appears from these data that the advantage gained by effectively lowering the thermal conductivity is largely offset by worsened electrical properties, indicating that essentially no over-all improvement was gained. However, since properties of the molybdenum-free compositions improved considerably with increasing temperature, we determined all parameters as a function of temperature, to be presented and discussed following the section on anisotropy.

Anisotropy.—All electrical and thermal properties quoted are characteristic only of the particular density (usually around 90% of theoretical) in which the specimens were obtained, since no extrapolation to 100% dense materials was attempted. A further complicating factor, arising from the layer-like structure of the compositions with large crystallographic c/a ratios and a flake-like exterior habitus, is the anisotropy of physical data. If these materials are pressed they tend to orient to a very significant degree in such a way that the crystallographic c-direction coincides with the direction of applied pressure. All electrical data given so far are, therefore, characteristic of the crystallographic a-direction only, or the plane normal to the direction of pressing. In order to get an idea of the degree of difference of these properties due to the anisotropy effect, we give the data obtained in the different directions on a 0.5-in. cube of $W_{0.485}Mo_{0.485}Ta_{0.03}Se_2$: In the crystallographic a-direction ρ = 3.98 mohm-cm., S = +66 μv./deg., k = 32.0 mwatts/cm.-deg., and $Z = 3.4 \times 10^{-5}$ deg.$^{-1}$; in the crystallographic c-direction ρ = 7.28 mohm-cm., S = +67 μv./deg., k = 15.6 mwatts/cm.-deg., and $Z = 3.9 \times 10^{-5}$ deg.$^{-1}$.

It appears that the Seebeck coefficient is essentially independent of direction, and the figures of merit are practically identical. This is different from the simple $W_xTa_{1-x}Se_2$ system where a distinct advantage could be demonstrated in the a-direction.

Since the figure of merit of $W_{0.97}Ta_{0.03}Se_2$ improved substantially with increasing temperature, we also determined the thermoelectric properties of $W_{0.485}Mo_{0.485}Ta_{0.03}Se_2$ and $W_{0.49}Mo_{0.49}Ta_{0.02}Se_2$ as a function of temperature. Figure 3 gives a typical result and Table VI summarizes the 600° data in comparison with $W_{0.97}Ta_{0.03}Se_2$.

It is quite obvious that the more complex quaternary compositions at best only approach the quality of the better $W_xTa_{1-x}Se$-compounds and the advantage gained by lowering the thermal

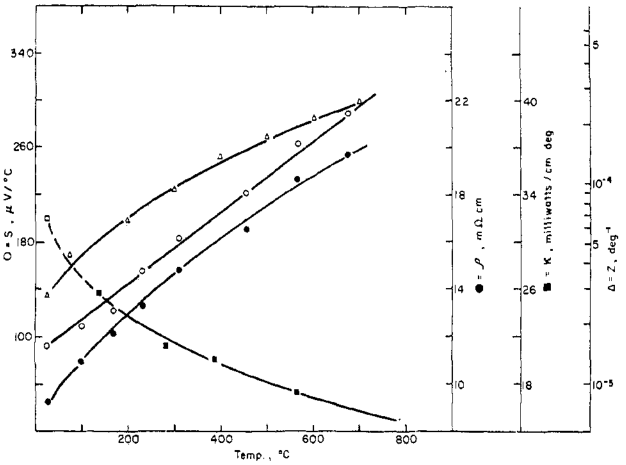

Fig. 3.—Thermoelectric properties of $W_{0.49}Mo_{0.49}Ta_{0.02}Se_2$ as a function of temperature.

TABLE VI

COMPARISON OF THERMOELECTRIC PROPERTIES IN THE CRYSTALLOGRAPHIC a-DIRECTION FOR SOME COMPOSITIONS AT 600°

Composition	S, μv./deg.	ρ, mohm-cm.	k, mwatts/cm.-deg.	Z, deg.$^{-1}$ × 10^{-3}
$W_{0.99}Ta_{0.01}Se_2$	370	7.02	0.02	0.98
$W_{0.97}Ta_{0.03}Se_2$	184	3.27	.02	.52
$W_{0.49}Mo_{0.49}Ta_{0.02}Se_2$	265	18.80	.019	.22
$W_{0.485}Mo_{0.485}Ta_{0.03}Se_2$	240	7.90	.018	.40

conductivity is not reflected in an improved figure of merit due to poorer electrical properties and a smaller decrease of thermal conductivity with increasing temperature.

Despite the considerations given in the Introduction, we finally made a last attempt at improving the over-all properties by also alloying in the anion sites and thereby getting into the yet more complex five-component $W_{x/2}Mo_{x/2}Ta_{1-x}Se_yTe_{2-y}$ system.

Table VII summarizes some room temperature data and Fig. 4 gives some high temperature data for $W_{0.47}Mo_{0.47}Ta_{0.06}SeTe$. Despite the further lowering of the thermal conductivity, the figure of merit of these complex compositions was not improved.

TABLE VII

ELECTRICAL PROPERTIES OF SOME COMPOSITIONS OF THE $W_{x/2}Mo_{x/2}Ta_{1-x}Se_yTe_{2-y}$ SYSTEM

x	y	ρ, mohm-cm.	S, μv./deg.	k, watts/cm.-deg.	Z, deg.$^{-1}$ × 10^3
0.94	0.5	1.3	30	19.2	1.0 × 10^{-5}
.94	.6	1.8	34	. . .	. . .
.94	.7	2.4	37	. . .	. . .
.94	.8	2.9	44	. . .	. . .
.94	1.0	2.3	50	18.1	6.0 × 10^{-5}
.94	1.3	3.2	55	. . .	. . .
.94	1.5	3.8	62	18.8	5.5 × 10^{-5}
.94	1.7	9.6	68	. . .	. . .

The anisotropy problem although less pronounced was also experienced with these complex compositions. For $W_{0.47}Mo_{0.47}Ta_{0.06}SeTe$, we obtained in the crystallographic a-direction ρ = 2.3 mohm-cm., S = +50 μv./deg., k = 18.1 mwatts/cm.-deg., Z = 6.0 × 10^{-5} deg.$^{-1}$; in the crystallographic c-direction ρ = 5.7 mohm-cm., S = +54 μv./deg., k = 10.2 mwatts-cm.-deg., Z = 5.0 × 10^{-5} deg.$^{-1}$. It appears that for this composition, the figure of merit is again essentially the same for the two crystallographic directions. In some cases, thermal conductivities as low as 6.2 mwatts/cm.-deg. were measured, which is an exceptionally low value for materials of this type, lower even than that of $AgSbTe_2$.

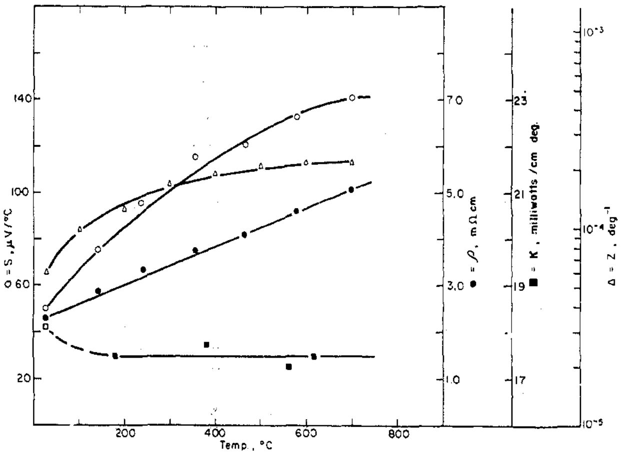

Fig. 4.—Thermoelectric properties of $Mo_{0.47}W_{0.47}Ta_{0.06}SeTe$ as a function of temperature.

Discussion

The $W_{x/2}Mo_{x/2}Ta_{1-x}Se_2$ system described in this paper is composed of the n-type semiconductor $W_{0.5}Mo_{0.5}Se_2$ and the essentially metallic conductor $TaSe_2$. At least a good part of the tantalum in the latter compound is ionic in the tetravalent state with one free electron. This is qualitatively confirmed by the fact that $TaSe_2$ is paramagnetic. If introduced into $W_{0.5}Mo_{0.5}Se_2$, Ta^{+5} acts as a p-type doping agent and increases the carrier concentration and the electrical conductivity. The Seebeck coefficient, varying logarithmically with the reciprocal of the charge carrier concentration, decreases at the same time. With these considerations in mind, we have already found the optimum Ta concentration in WSe_2 previously, and in this investigation we were particularly interested in finding the effect of alloying substantially in the cation-sites with the lower atomic weight molybdenum. Figure 2 showed that this can be done, effectively reducing the thermal conductivity at the 50% substitution level by about one-half. This behavior is very similar to the PbTe–PbSe system described by Ioffe.[6] Unfortunately, the decrease of thermal conductivity, which varied nearly with $1/T$ for $W_{0.97}Ta_{0.03}Se_2$, is considerably smaller for the alloyed compositions. This is an effect which Ioffe[6] describes in the same way for the PbTe–PbSe compositions. He points out that for heavily alloyed compositions the negligible drop of the phonon contribution to the thermal conductivity with temperature rise indicates the predominance of phonon scattering by impurities which are independent of temperature over scattering by thermal vibrations. Calculation according to the Wiedeman–Franz law shows that for most of the described compositions the electronic contribution to the thermal conductivity is smaller than 10%.

In summary, we can state that the original objective of lowering the thermal conductivity was achieved but

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(6) A. F. Ioffe, "Semiconductor Elements and Thermoelectric Cooling" Infosearch Ltd., London, 1957, pp. 65–66.

only by scarificing other properties such that no overall gain in the figure of merit can be claimed.

The $W_{x/2}Mo_{x/2}Ta_{1-x}Se_2$ system represents a rather interesting system both structurally and electrically and the preliminary data reported in this paper may well serve for the basis of more refined studies.

Acknowledgment.—The assistance of Mr. A. T. Weinmann in determining the lattice parameters was greatly appreciated.

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Strong Hydrogen Bonds. I. The Halide–Hydrogen Halide Systems[1]

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Hydrogen bond energies have been determined for $ClHCl^-$, $BrHBr^-$, and IHI^- in systems designed to minimize lattice energy effects and specific cation–anion interaction. Hydrogen bond energies were found to be 14.2, 12.8, and 12.4 kcal./mole, respectively, for these species. A mixed species $BrHCl^-$ has been found to have a hydrogen bond energy of 9.1 kcal./mole. Pressure–composition phase diagrams have been determined for a number of systems containing $X(HX)_n^-$ species.

Ketelaar[2] estimated the energy of the hydrogen bond in KHF_2 using the cycle

$$\begin{tikzcd} M^+(g) + F^-(g) + HF(g) \arrow[r, shift left, "1"] \arrow[d, shift left, "4"] & M^+(g) + HF_2^-(g) \arrow[l, shift left] \arrow[d, shift left, "2"] \\ MF(s) + HF(g) \arrow[u, shift left] \arrow[r, shift left, "3"] & MHF_2(s) \arrow[l, shift left] \arrow[u, shift left] \end{tikzcd} \qquad (1)$$

and obtained an energy of 30 to 50 kcal. for the hydrogen bond. Waddington,[3] using the same cycle but with better data and more refined calculations, obtained a hydrogen bond energy of 58 ± 5 kcal. A primary assumption in treating the cycle is that steps 2 and 4 involve no specific interactions requiring the use of low energy empty orbitals of the cation. Further, the lattice energy calculations are not unambiguous due to the assumptions necessary to handle the nonspherical FHF^- ion.

In order to eliminate, as far as possible, cation–anion interaction and to permit some experimental evaluation of the lattice energy effect, a study was undertaken of the heats of the reactions of the hydrogen halides with halide salts containing large cations. Among the cations used were the tris-(acetylacetonato)-silicon(IV) ion, the tetraphenylarsonium ion, and tetraalkylammonium ions. Of these the tetraalkylammonium salts appeared best suited for detailed studies since solid solution formation was least troublesome with these salts. Previous studies made in this area[4–6] indicated that the ammonium salts absorb the corresponding hydrogen halide to form stoichiometric compounds. Evidence for the existence of a $ClHCl^-$ species has been provided from spectral studies.[7] From the similarities in the spectra of compounds containing IHI^- and $BrHBr^-$ with those containing FHF^- and $ClHCl^-$ it may be concluded that a hydrogen bond is also present in the species involving bromides and iodides.

Experimental

Procedure.—Enthalpy changes for reactions of the type

$$R_4NX(s) + HX(g) \rightarrow R_4NXHX(s)$$

were obtained by two methods, *i.e.*, variations of the equilibrium constant as a function of temperature and/or by use of an ice calorimeter.[8]

Data for the pressure–composition isotherms (Fig. 1–6) were obtained by treating *ca.* 0.01 mole of dried tetraalkylammonium halide with anhydrous hydrogen halide gas. Phase equilibria required from 30 min. to several weeks depending on the sample, temperature, and hydrogen halide pressure. Systems exhibiting solid solution behavior in general required a longer time to attain equilibrium than those not showing such behavior. The primary criterion for the attainment of equilibrium was that the pressure be the same whether arrived at by absorption or desorption of the hydrogen halide. A secondary criterion was that the pressure should be time independent. Pressures were read on a mercury manometer. In the system used for the hydrogen bromide and hydrogen iodide studies a sickle gage was used to isolate the mercury manometer from the system. The pressures were read by a null point method to ±0.02 cm. Kel-F grease was used to lubricate the vacuum stopcocks in the sickle gage system.

Temperature control for the equilibrium studies was obtained by using solid–liquid or liquid–vapor phase equilibria. The slush baths used were: acetone, Dry Ice–acetone, chloroform, chlorobenzene, carbon tetrachloride, water, benzene, acetophenone, and *t*-butyl alcohol. Liquid reflux thermostats used were: acetone, benzene, and water. An automated slush bath[9] was developed near the end of the experimental work.

Temperatures were measured with mercury thermometers with an accuracy of ±0.1° or with copper constantan thermocouples (fabricated from Leeds and Northrup standardized thermocouple wire) with an accuracy of ±0.15°.

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