ADVANCES IN INORGANIC CHEMISTRY AND RADIOCHEMISTRY, VOL. 23

SOLID-STATE CHEMISTRY OF THIO-, SELENO-, AND TELLUROHALIDES OF REPRESENTATIVE AND TRANSITION ELEMENTS

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I. Introduction

The aim of this review is to discuss the modern, solid-state chemistry of members of a well-defined class of compounds with respect to their preparative methods, structural features, and physical properties. The thio-, seleno-, and tellurohalides of the metallic elements seem to be well suited for this purpose. In contrast to such binary compounds as oxides and halides, they fit into the frame of the restricted space available, and, with the exception of alkaline and alkaline-earth elements, examples are found in all groups of the periodic system. The large group of oxyhalides, as well as the chalcogenide fluorides, have been excluded. Oxyhalides have been extensively reviewed (*182, 405*), and the properties of the fluorides are closely related to this group; in addition, the behavior differs in some respects from that of the chalcogenide halides treated here. A typical feature of the compounds under consideration is that of nonstoichiometry (*54, 296*). Besides, they may have a complicated, overall composition, due, for instance, to metal–metal bonds, and they may exhibit a broad range of existence over many mole percent, and, within such a phase width, the chemical potential of an elementary component can vary over powers of ten (*54, 298*). On the other hand, the numerous addition compounds and adducts, such as K_2TeBr_6, $TeCl_4{\cdot}AlCl_3$, $SnCl_4{\cdot}SCl_4$, and most molecular structures will not be treated.

As regards organization, the indicated compounds of the elements are discussed separately, or in groups as subdivisions of sections devoted to the different groups of the Periodic Table. Usually, after introductory remarks covering, if necessary, the historical background, the preparative methods are described, including the growth of single crystals. This topic becomes more and more important because of the need not only for small crystals for structure determinations but also for large crystals of high purity for the evaluation of physical properties. A number of preparative methods typical for solid-state chemistry and crystal-growth techniques are mentioned in the text, such as vapor growth, including chemical transport reactions (Section VI,5), hydrothermal syntheses (Section II,D,2), and melt growth techniques such as Bridgman–Stockbarger, flux, and others.

In the succeeding discussion, the chemical behavior of the respective compounds is given. An important role is played by the phase relationships in the respective systems, as they are a prerequisite not only for efficient crystal growth but also for the discussion of the thermodynamic properties. Among the crystallographic data, the occurrence of metal–metal bonds within the transition-element compounds, especially those of groups VB and VIB, should be mentioned, as these lead to the formation of metal clusters as building units of the structures. Almost the whole spectrum of physical properties, not only playing a role in modern, solid-state physics, but also of technical importance, is found among chalcogenide halides. Ionic conductors, which can be used as solid electrolytes in primary and secondary batteries (Section II,D,1), exist among the copper compounds. Semiconductors, among which are the group VA compounds of the SbSI type, play an important part, as these photoconductors exhibit ferroelectric, piezoelectric, nonlinear optical, electromechanical, and other properties. In this group, especially among the arsenide halides, are also found the vitreous semiconductors. Among the metallic conducting phases, such cluster compounds as $Mo_6S_6Br_2$ (Chevrel phases) are superconductors having extremely high, critical fields (Section VII,B,5).

Although chalcogenide halides are mentioned in the literature as early as the end of the last century, this class of compounds has excited growing interest in the scientific world during the past three decades only, as documented by the fact that, during the preparation of this article, two reviews of thio-, seleno-, and tellurohalides appeared (*8, 320*) that were, however, restricted to transition-metal compounds and to somewhat different aspects. The current literature will be cited as comprehensively as possible, with some exceptions, however, as, for instance, of the group VA compounds, where a discussion of the growing literature on the physical properties would exceed the scope of this article; the same applies to compounds of mercury. The older literature will be only partially mentioned, as the existence of many compounds is not well established at this time, and their inclusion would lead to some confusion. In such cases, we have referred to the respective volumes of Gmelin's famous "Handbook of Inorganic Chemistry." The reader interested in more-detailed information may readily find his way via the many references to the topic of interest.

The authors trust that one or more readers may even be stimulated, and start personal research-work in the many unexplored fields of this interesting class of compounds.

II. Group IB

A. COPPER

Despite the tremendous amount of work on the binary compounds, copper chalcogenide halides were first reported in 1969 (*304*). Nine compounds of selenium and tellurium have been found, and they are listed in Table I. Copper sulfide halides are still unknown.

1. *Preparative Methods*

In polycrystalline form, the compounds are obtained by annealing stoichiometric amounts of the respective copper(I) halides with Se (T = 300°C) and Te (T = 350°C) in closed ampoules for some days. After grinding, the reaction product has to be treated once more in the same way (*307*), in order to complete the reaction. In some cases, small single crystals for X-ray measurements may also be isolated (*125*). Small single crystals of all chalcogenide halides may be obtained by hydrothermal synthesis in the respective halogen hydracids (*300*) (see Section II,D,2). The synthesis of copper chalcogenide halides by chemical-transport reactions (*336*) has been reported (*63, 65*). Large crystals of CuTeBr (*5*) and $CuSe_3I$ (*122*) have been obtained by the Bridgman–Stockbarger technique (*55*) (see Fig. 34).

2. *Chemical Properties*

Crystals of all of these compounds are stable in air and in alkaline solutions, and dissolve quickly in hot, conc. HNO_3 and H_2SO_4, the selenium compounds also dissolving in hot, alkaline solutions (*307*).

3. *Phase Diagrams and Thermodynamics*

The system CuCl–Cu_2S is of the simple, eutectic type (*394, 400*), whereas the systems CuX–Se and CuX–Te (X = Cl, Br, or I) are pseudobinary cuts in the ternary diagram Cu–X–Se (Te) and show one (Se) and two (Te) intermediate compounds (*308*) (see Fig. 1). Both congruent and incongruent ternary phases are found, as shown in Fig. 2 for the system CuBr–Te (*299*). CuTeBr exhibits a first-order, displacive phase-transition with ΔH_u and ΔS_u of only 76.8 cal/g-mol and 0.222 cal/g-mol·K, respectively (*5*). Single crystals therefore retain their crystallinity during transition. This phenomenon is of interest, in that it allows the investigation of physical properties during the transition in a single-crystal specimen (*70*). The vapor above the copper se-

TABLE I

COPPER CHALCOGENIDE HALIDES

Compound	Symmetry	*a* (Å)	*b* (Å)	*c* (Å)	β (degrees)	*Z*	Structure ref.	Decomposition or melting point (°C)
CuSe$_2$Cl	Monoclinic	7.724	4.655	14.573	134.96	4	*433*	319
CuSe$_3$Br	Orthorhombic	14.363	4.488	7.696		4	424	338
CuSe$_3$I	Rhombohedral	14.083[a]		14.187[a]		18		394
CuTeCl	Tetragonal	15.63		4.78		16	*123*	400
CuTeBr	Tetragonal	16.417		4.711		16	*63,64*	430
	Orthorhombic[b]	23.22	23.22	14.13		96		
CuTeI	Tetragonal	17.170		4.876		16	*125*	442
	Orthorhombic[b]	24.258	24.292	14.611		96	*123,126*	
CuTe$_2$Cl	Monoclinic	8.207	4.935	15.279	134.92	4	*120*	~420
CuTe$_2$Br	Monoclinic	8.358	4.951	15.704	135.1	4		416
CuTe$_2$I	Monoclinic	8.672	4.881	16.493	135.0	4		400

[a] For the hexagonal cell. [b] For the superstructure.

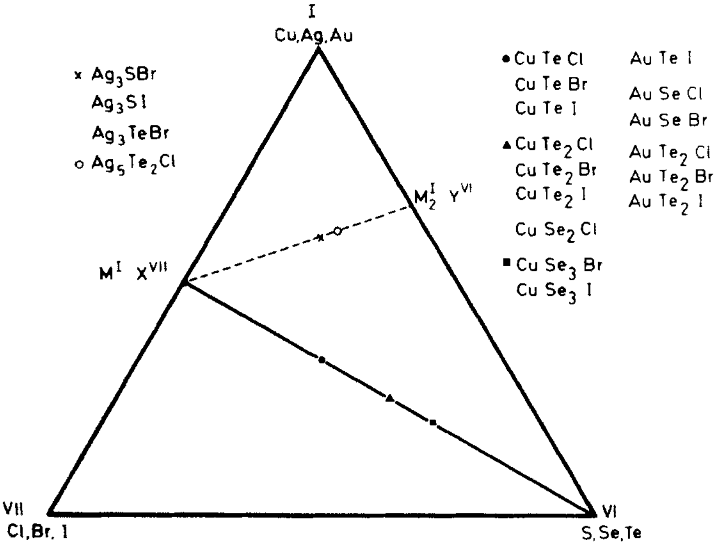

FIG. 1. Chalcogenide halides in ternary systems having the components: the Group IB elements Cu, Ag, and Au, the chalcogens S, Se, and Te, and the halogens Cl, Br, and I. They are indicated as M^{I}, Y^{VI}, and X^{VII}, respectively. (Redrawn from A. Rabenau, H. Rau, and G. Rosenstein, *J. Less-Common Metals* **21**, 395 (1970), Fig. 4, p. 401.)

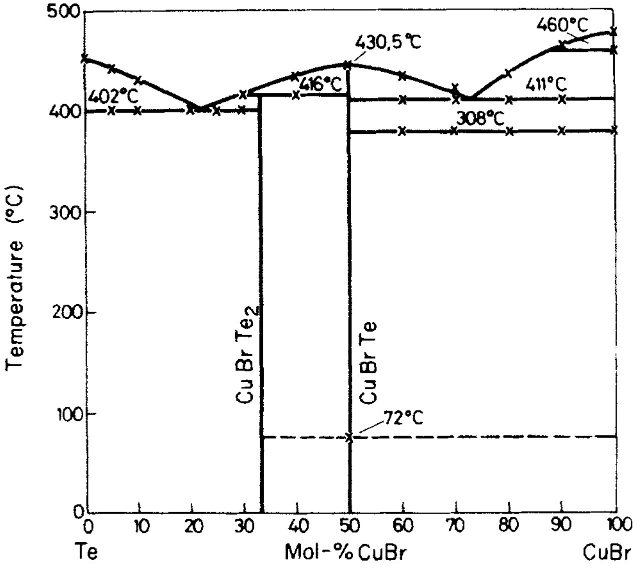

FIG. 2. Phase diagram for CuBr–Te.

lenium halides consists exclusively of selenium and p_{Se_t} can be measured by using the effusion method. From these data, the free energy of reaction can be calculated (*307*).

$$\text{CuCl,c} + 2\ \text{Se,c} = \text{CuClSe}_2\text{,c};\ \Delta G^\circ = -1800 + 2.3\ T\ \text{cal/mol} \qquad (1)$$

$$\text{CuBr,c} + 3\ \text{Se,c} = \text{CuBrSe}_3\text{,c};\ \Delta G^\circ = -3100 + 4.0\ T\ \text{cal/mol} \qquad (2)$$

$$\text{CuI,c} + 3\ \text{Se,c} = \text{CuISe}_3\text{,c};\ \Delta G^\circ = +1900 - 3.9\ T\ \text{cal/mol} \qquad (3)$$

Due to the high heats of formation of the binary components, these small values seem to be representative for most of the chalcogenide halides discussed in this article.

4. Crystallographic Data

For crystallographic data, see Table I. The compounds of the type CuTeX and $CuTe_2X$ (X = Cl, Br, or I), respectively, are isotypic, and their crystal structures have been determined. Copper has the oxida-

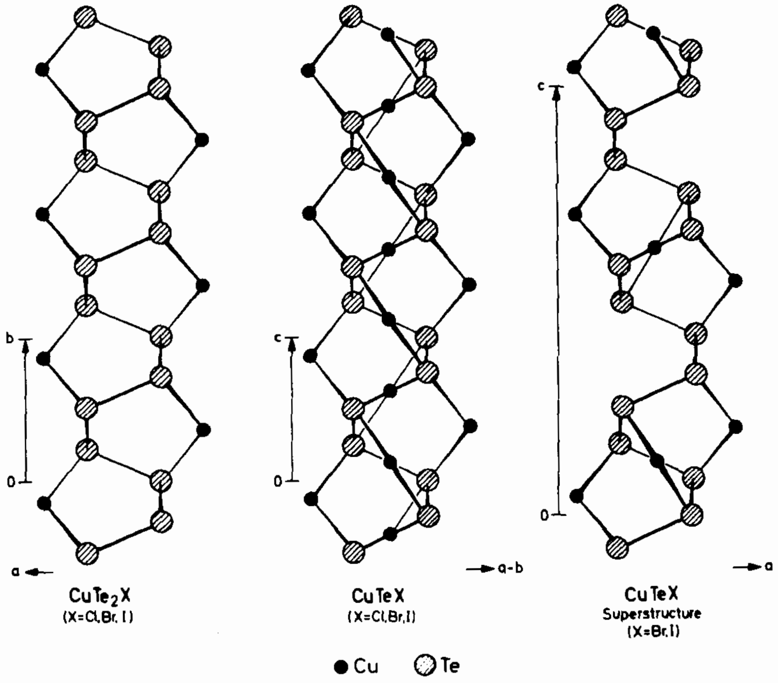

FIG. 3. Tellurium helices in copper telluride halides. (*Redrawn from* J. Fenner and H. Schulz, *Acta Cryst.* **B35**, 307 (1979), Fig. 2, p. 311.)

TABLE II

OCCUPATION PROBABILITIES OF THE COPPER ATOMIC SITES IN CuTeX COMPOUNDS

Atomic site	Number of equivalent positions	Occupation probabilities			
		CuTeI	CuTeBr (20 °C)	CuTeBr (100 °C)	CuTeCl
Cu(1)	8	0.34(1)	0.26(1)	0.35(2)	0.42(1)
Cu(2)	8	0.23(1)	0.19(1)	0.14(2)	0.07(2)
Cu(3)	16	0.52(1)	0.51(1)	0.60(1)	0.66(1)
Cu(4)	16	0.20(1)	0.26(1)	0.15(1)	0.08(1)

tion state +1, and is tetrahedrally surrounded by either four halogens, or two halogens and two telluriums. The main feature of these structures is infinite, pseudofourfold, tellurium helices, symmetry-related by crystallographic screw axes (see Fig. 3). These infinite, Te–Te bonds have only been found in cases where the formal oxidation state of tellurium lies between zero and unity, as in elemental tellurium (*72*) and the tellurium subhalides (*188*). In the CuTeX compounds, the copper atoms are distributed statistically over several crystallographic positions. This is the reason for the observed high copper ionic conductivity (*4*). The occupation probability of the copper sites is similar in CuTeBr and CuTe I (see Table II). These two compounds show a superstructure having a partial ordering of the occupation probabilities of the copper atomic sites (*126*). In the case of CuTeBr, this superstructure disappears with the phase transition at 72°C, and the occupation probabilities become similar to those of CuTeCl (*123*), as shown in Table II.

5. *Physical Properties*

All of these compounds exhibit a temperature-independent diamagnetism, as is to be expected for compounds of monovalent copper; this is of the same order of magnitude as for copper(I) halides (*307*). Spectral-reflectance measurements are presented in Fig. 4, a–c. Here, the logarithm of the reciprocal relative reflectance is plotted against photon energy (*306*). The steep increase above the level of the residual absorption is correlated with the band gap. In the case of the isotypic compounds CuTeX and $CuTe_2X$, the substitution of the halogen seems to have no significant influence on the band gap, as may be seen from Fig. 4, a and b, respectively. This result confirms a concept developed by Goodman (*149*) that, in the case of substitutional derivation (within a given structure), the energy gap should be determined by the weakest bond in the lattice, largely in terms of bond-electronegativity difference. This decreases in the sequence Cu–Cl, Cu–Br, Cu–I, and Cu–Te, the weakest bond being the Cu–Te. This principle no longer holds if the stoichiometry and the structure change (see Fig. 4c). The compounds of the type CuTeX show a high partial, Cu^+-ionic conductivity at rather low temperatures, with a negligible electronic contribution

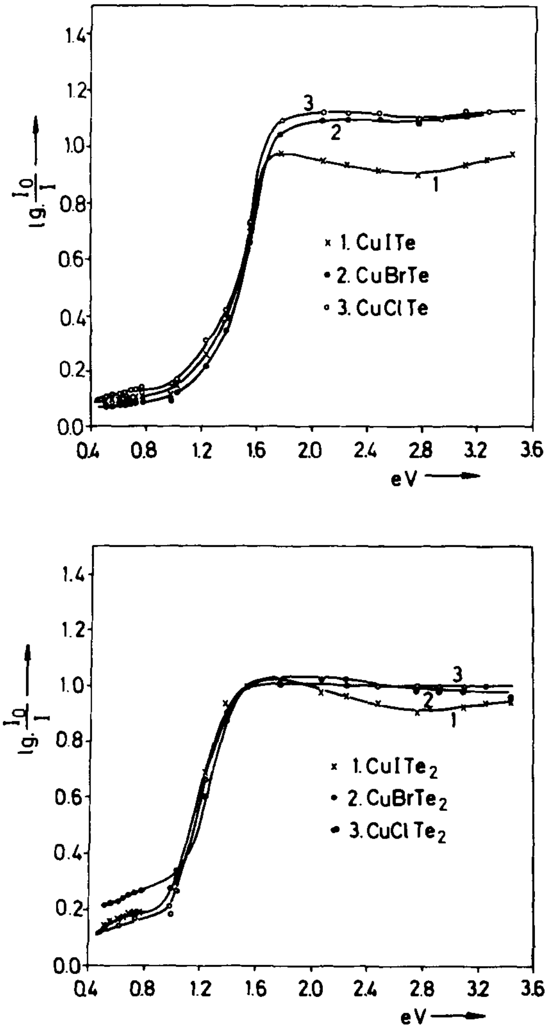

FIG. 4. Spectral reflectance measurements in copper telluride halides. (Redrawn from A. Rabenau, H. Rau, and G. Rosenstein, *Solid State Commun.* **7**, 1281 (1969), Fig. 1, p. 1281.)

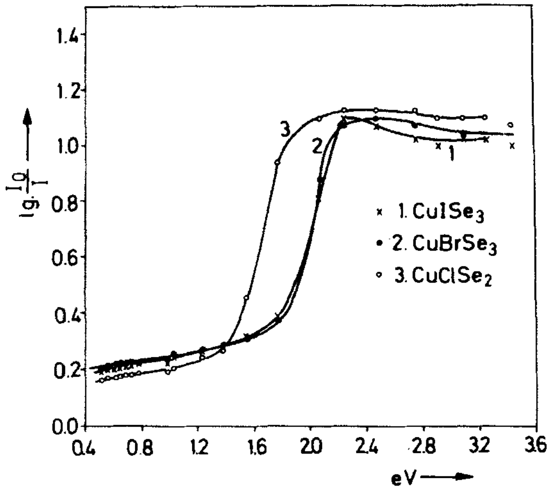

FIG. 4. (*continued*)

(*4, 299, 430*). The ionic conductivity is much higher than in the corresponding copper halides (see Fig. 5). At temperatures above 250°C, they enter the region of optimized ionic conductors (*150*).

B. SILVER

The possible existence of a silver sulfide bromide was suggested from the results of conductivity measurements of aqueous Ag_2S–AgBr mixtures, in 1955 (*360*). The compounds Ag_3SBr and Ag_3SI were first prepared by Reuter and Hardel in 1960 (*315*). The interest in these materials was stimulated by the discovery of their high ionic conductivity (*316, 317, 319, 370*). Little is known about the three other silver chalcogenide halides Ag_3TeBr (*46, 49, 180*), Ag_6TeBr_4 (*180*), and Ag_5Te_2Cl (*46, 49, 53*), which need further investigation. It is remarkable, however, that all of the silver chalcogenide halides lie on a cut formed by the respective silver(I) halide and silver(I) chalcogenide (see Fig. 1).

1. *Preparative Methods*

The sulfide bromide Ag_3SBr may be obtained by annealing of stoichiometric amounts of Ag_2S and AgBr in closed, glass ampoules at 280°C. The reaction product is ground, and repeatedly treated in the same way (*317*); the end of the reaction is determined by powder patterns. In a similar way, the low-temperature modification of Ag_3SI, β-

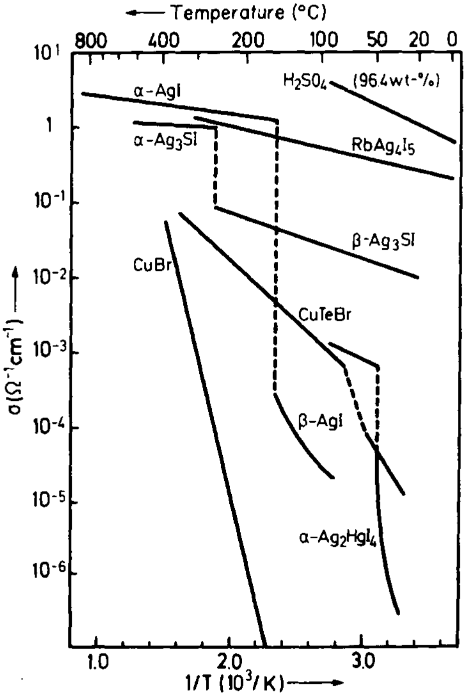

FIG. 5. Ionic conductivity of Group IB compounds.

Ag_3SI, is prepared at 210–215°C. In both cases, it takes several weeks to complete the reaction. The high-temperature modification α-Ag_3SI, which is stable above 235°C, can be obtained either by a treatment at 280°C instead of 210–215°C, as for β-Ag_3SI, or by annealing of the latter for some hundreds of hours at 280°C and quenching to room temperature (*317*). α-Ag_3SI forms in only 17 hours if the reaction takes place at 550°C under various sulfur pressures (*370*).

Ag_3TeBr and Ag_6TeBr_4 were obtained by heating the respective stoichiometric mixtures of Ag_2Te and AgBr for 250 hours at 560°C, cooling, and annealing for 1400 hours at 350°C. They were identified by X-ray powder patterns (*180*). Their existence needs further confirmation. A compound having the probable composition Ag_5Te_2Cl was obtained during the investigation of the Ag_2Te–AgCl system from Ag_2Te and AgCl (*53*). The samples were tempered for 480 hours at 330°C in closed ampoules. Ag_3TeBr and Ag_5Te_2Cl have been prepared in a similar way, just by annealing at 350°C for 480 hours (*49*). All of these compounds were reported to be of the peritectic type, which may explain the uncertainty of the data acquired.

2. *Chemical Properties*

The black Ag_3SBr decomposes above 430°C into Ag_2S and AgBr. β-Ag_3SI has the same color, and transforms to α-Ag_3SI at 235°C (*317*). The latter shows no signs of decomposition in DTA measurements up to 800°C (*370*); if, however, a temperature gradient is applied, decomposition starts below this temperature, by sublimation of AgI. Both compounds decompose slowly in light. In such complex-forming solvents as thiosulfate, thiocyanate, or cyanide, the respective silver halide is dissolved (*317*).

3. *Crystallographic Data*

The structures of Ag_3SBr, β-Ag_3SI, and α-Ag_3SI have been determined on the basis of powder pattern, by trial and error (*318*). Ag_3SBr and β-Ag_3SI are isotypic, and crystallize in a structure that can be derived from the ideal, antiperovskite structure by displacement of silver ions from the face centers in the direction of the edges of the unit cell (see Fig. 6). α-Ag_3SI crystallizes bcc, and is homotypic with α-AgI and α-Ag_2S. These structures differ in two points. (*i*) The corners and the center of the body-centered, cubic cell are occupied by 2 I in α-AgI (see Fig. 7), 2 S in α-Ag_2S, and statistically by 1 S and 1 I in α-Ag_3SI, respectively. (*ii*) Within the 12 tetrahedral voids of the packing of ions,

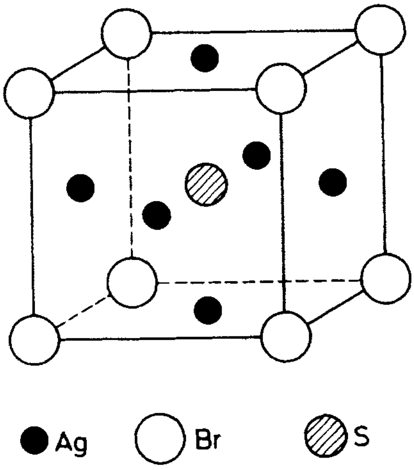

Fig. 6. Ideal antiperovskite structure of Ag_3SBr. (Redrawn from B. Reuter and K. Hardel, *Z. Anorg. Allg. Chem.* **340**, 168 (1965), Fig. 1, p. 171.)

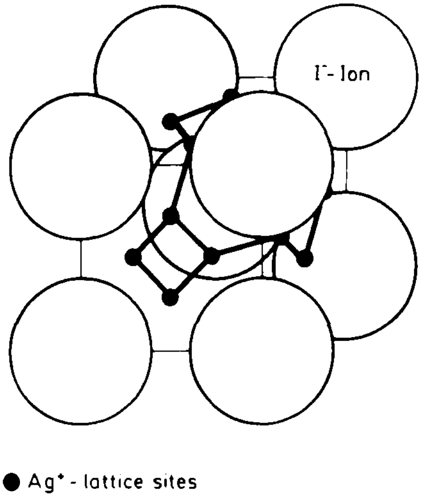

FIG. 7. *α-AgI structure, tetrahedral sites, and diffusion path of Ag^+.*

2 Ag in α-AgI (see Fig. 7), 3 Ag in α-Ag_3SI, and 4 Ag in α-Ag_2S are distributed statistically.[1] No crystallographic data are available for silver telluride halides.

4. *Phase Diagrams*

Stimulated by the search for optimized ionic conductors, phase-diagram investigations of silver(I) halide–silver(I) chalcogenide systems are numerous (see Table III). The phase diagrams for AgX–Ag_2Y (X = Cl, Br, and Y = S, Se Te) are summarized in Fig. 8. They are quasibinary cuts of the eutectic and peritectic type, respectively (*46, 47, 49*). As indicated by the dashed lines, not everything is yet clarified. The compound Ag_3SBr dissolves up to 20 mol-% of Ag_2S (*317*). According to Karbanov *et al.* (*180*), the system AgBr–Ag_2Te is not a quasibinary one, and the occurrence of a second ternary compound having the composition Ag_6TeBr_4 was claimed. These authors also found a high solubility of AgBr in Ag_2Te at ~500°C. The discrepancies have to be clarified (*46*). Whereas, in the system AgI–Ag_2S near room temperature, β-Ag_3SI is the only stable compound, which forms solid solutions containing up to 20 mol-% of Ag_2S, similar to Ag_3SBr, a very complicated phase-diagram was reported for temperatures above

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[1] In contrast to the established concept, it has been found that, in α-AgI, silver is exclusively distributed on the tetrahedral voids (*135, 69*); it may be assumed that the same holds for α-Ag_3SI and α-Ag_2S.

TABLE III

INVESTIGATIONS OF THE TERNARY DIAGRAMS OF $Ag-X^{VII}-Y^{VI}$ (X = Cl, Br, OR I; Y = S, Se, OR Te)

System	Ref.	System	Ref.	System	Ref.
$AgCl-Ag_2S$	*46,47*	$AgBr-Ag_2S$	*46,47,317*	$AgI-Ag_2S$	*46,47,317,372,373*
$AgCl-Ag_2Se$	*46,49,52*	$AgBr-Ag_2Se$	*49,52*	$AgI-Ag_2Se$	*369*
$AgCl-Ag_2Te$	*46,49,53*	$AgBr-Ag_2Te$	*46,49,180*	$AgI-Ag_2Te$	*46,369*

100°C (*373*), with additional ternary phases at 25 and 75 mol-% of Ag_2S, respectively, which decompose at room temperature to $AgI + Ag_3SI + Ag_2S$, respectively. The situation around the composition Ag_3SI is given in ref. (*372*). In the pseudobinary $AgI-Ag_2Se$ system, no compound was found at any temperature or composition (*369*). The diagram shows a peritectic, reaction isotherm at 635°C, the peritectic composition being 45 mol-% of Ag_2Se. The same situation was proposed for the system $AgI-Ag_2Te$ (*369*), with values of 560°C and 30 mol-% of Ag_2Te, respectively. Complete solubility was found between Ag_3SBr and β-Ag_3SI by X-ray measurements (*317*).

5. *Physical Properties*

Ag_3SBr, β-Ag_3SI, and α-Ag_3SI are cationic conductors due to the structural disorder of the cation sublattices. Ag_3SI (see Fig. 5) has been discussed for use in solid-electrolyte cells (*209, 371, 374, 414–416*) because of its high silver ionic conductivity at rather low temperatures (see Section II,D,1). The practical use seems to be limited, however, by an electronic part of the conductivity that is not negligible (*370*), and by the instability of the material with respect to loss of iodine (*415*).

C. GOLD

Gold telluride iodide, $AuTe_2I$, was the first example of a gold chalcogenide halide, and was found in 1969 (*305*). Systematic investigations confirmed the existence of at least six compounds: four telluride halides and two selenide halides (see Table IV). No sulfide halides have been reported.

1. *Preparative Methods*

The four tellurium compounds are obtained as polycrystalline samples by annealing stoichiometric amounts of the elements in sealed silica or Pyrex tubes at temperatures between 280 (AuTeI) and 350°C

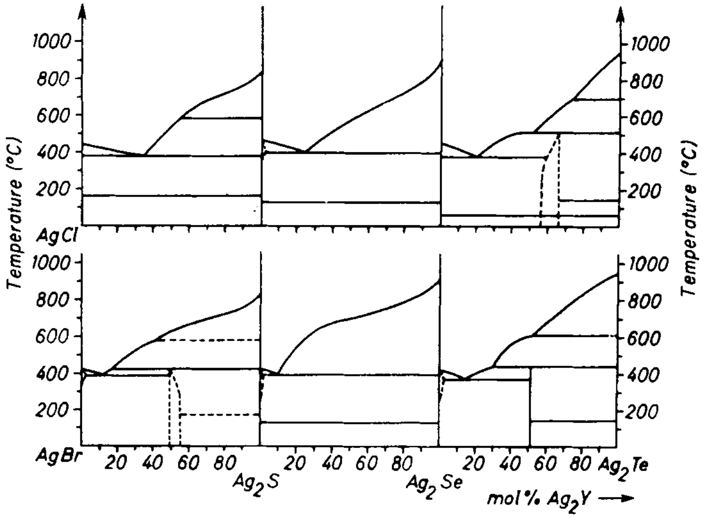

FIG. 8. Some phase diagrams for AgX–Ag_2Y (X = Cl or Br, and Y = S, Se, or Te). (Redrawn from R. Blachnik and G. Kudermann, *Z. Naturforsch.* **28B**, 1 (1973), Fig. 1, p. 2.)

($AuTe_2I$) (*308*). In the case of the selenium compounds, the reaction of the elements remains incomplete, because of partial recrystallization of the highly active gold used for the syntheses (*309*). The best way of preparation proved to be hydrothermal synthesis in halogen hydracids in the arrangement given in Section II,D,2 (*308, 309*). Some compounds, for example, $AuTe_2Cl$, AuSeCl, and AuSeBr, are not formed in the presence of water.[2] For them, an anhydrous hydrogen halide, HCl or HBr, was used as the solvent, introduced into the ampoule via a vacuum system. The telluride halides are silvery white spears (see Fig. 9), or square crystals. Crystals grown in anhydrous media are of pronouncedly poorer quality, pointing out the role that water plays as a mineralizer.

2. *Chemical Properties*

The tellurium compounds are insoluble in dilute acids and alkali, and decompose in dilute nitric acid or conc. sulfuric acid. For melting or decomposition temperatures, see Table IV. No data are given for the selenium compounds, of which only a few, small crystals have as yet been obtained.

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[2] In the case of selenium compounds in the presence of water, only gold selenide, AuSe, is formed (*309*).

TABLE IV

GOLD CHALCOGENIDE HALIDES

Compound	Symmetry	a (Å)	b (Å)	c (Å)	β (degrees)	Z	Space group	Ref.	Melting or decomposition point (°C)
AuITe	Monoclinic	7.313	7.624	7.255	106.26	4	$P2_1/c$	*124,308*	360
$AuITe_2$	Orthorhombic	4.056	12.579	4.741		2	Pmmb	*155,308*	440
$AuBrTe_2$	Orthorhombic	4.033	12.375	8.942		4	Cmcm	*155,308*	457
$AuClTe_2$	Orthorhombic	4.020	11.867	8.773		4	Cmcm	*155,308*	447
AuBrSe	Orthorhombic	6.77	12.22	7.38		8	Pnma	*229*	—
AuClSe	Orthorhombic	6.69	11.85	7.24		8	Pnma	*229,309*	—

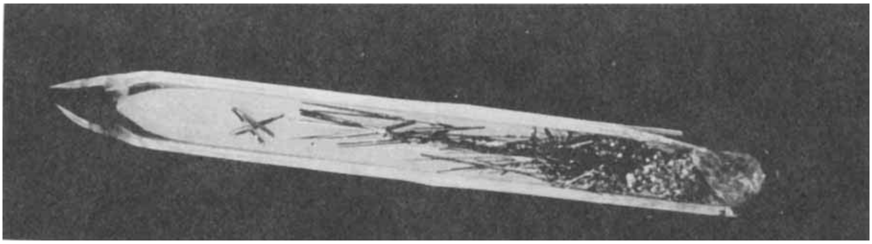

FIG. 9. Quartz glass ampoule with $AuTe_2I$ and Au. [From A. Rabenau, *In* "Crystal Growth: an Introduction" (P. Hartmann, ed.), Fig. 7.1., p. 201. North-Holland Publ. Co., Amsterdam, 1973.]

3. *Crystallographic Data*

Crystallographic data are summarized in Table IV. All structures have been solved. $AuTe_2I$ and $AuTe_2Cl$, the latter being isotypic to $AuTe_2Br$, have similar arrangements. They consist essentially of corrugated, two-dimensional nets of gold and tellurium atoms, with interleafing halogen atoms. The tellurium atoms form pairs, joined to successive gold atoms in a -Au-Te-Te-Au- sequence. Each gold atom is coordinated to four tellurium atoms, and each tellurium pair is likewise coordinated to four gold atoms (see Fig. 10). These considerations, and an unusually long gold-halogen distance, suggest that, structurally, the $AuTe_2X$ compounds might conceivably be represented as $[Au^{III}(Te_2)_{4/4}]^+X^-$ (*155*).

Interesting relationships to other structures exist in AuTeI (*124*). The four bonds between Au and the nonmetal atoms (one terminal I atom and three bridging Te atoms) generate a two-dimensional net parallel to the *b*/*c*-plane (see Fig. 11). Adjacent nets are stacked on each other by lattice translations along the *a* axis. Geometrically, this net can be derived from the CdI_2 structure, with the metal atoms enclosed in octahedral voids (see Fig. 36, Section XII,C,4). This geometrical relationship may be of crystal-chemical meaning, inasmuch as BiTeI, a telluride iodide of analogous composition, has been reported, once, as a *true* isotype of CdI_2 (*108*), with disorder of Te and I atoms; and, once, with a hexagonal structure *similar* to that of CdI_2 (*390*), with an ordered distribution of all atoms, (see Section XII,C,4).

In AuSeBr and the isotypic AuSeCl, two gold atoms on mirror planes of the space group, and one nonmetal atom of each kind in general positions, form infinite ribbons parallel to the *a* axis. In these ribbons one Au atom is bonded to two Br atoms and two Se atoms, while the other Au makes four bonds to Se atoms only (see Fig. 12). In both cases, the

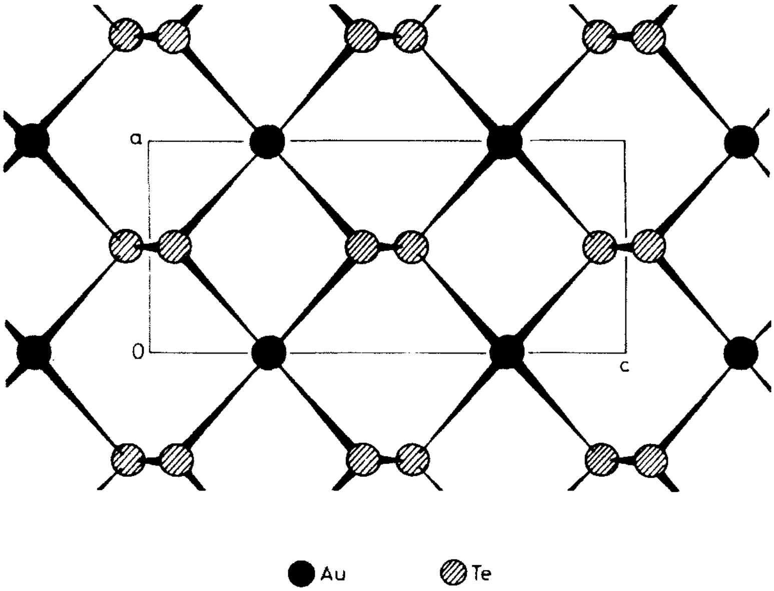

FIG. 10. $AuTe_2Cl$: Au–Te_2 net, shown perpendicular to the *b* axis. (Redrawn from H. M. Haendler, D. Mootz, A. Rabenau, and G. Rosenstein, *J. Solid State Chem.* **10,** 175 (1974), Fig. 1, p. 180.)

coordination is of a planar, distorted-square type. The ribbons are interlocked into sheets perpendicular to the *b* axis (*229*). The (sometimes distorted) square-planar coordination of gold in all gold chalcogenide halides shows that Au(III) is involved. In this oxidation state, gold forms four coplanar, covalent bonds (*407*). The gold compounds bear no relation to the copper(I) compounds of the same stoichiometry (see Fig. 1). The significant differences between these two systems may be summarized as follows (*308*). (*i*) The structure of corresponding compounds is different. (*ii*) In addition to (*i*), no detectable, mutual solubility has been observed. (*iii*) Whereas the cuts $M^{I}X^{VII}–Y^{VI}$ (see Fig. 1) in the copper systems are pseudobinary ones, this is not the case with the gold systems. (*iv*) The compounds of the type $AuTe_2X$ (X = Cl, Br, I) exhibit a metallic type of conductivity, and the corresponding copper compounds are semiconductors.

4. *Physical Properties*

Resistivity measurements on single crystals of $AuTe_2I$ and $AuTe_2Br$ established the metallic character of the conductivity. Single crystals

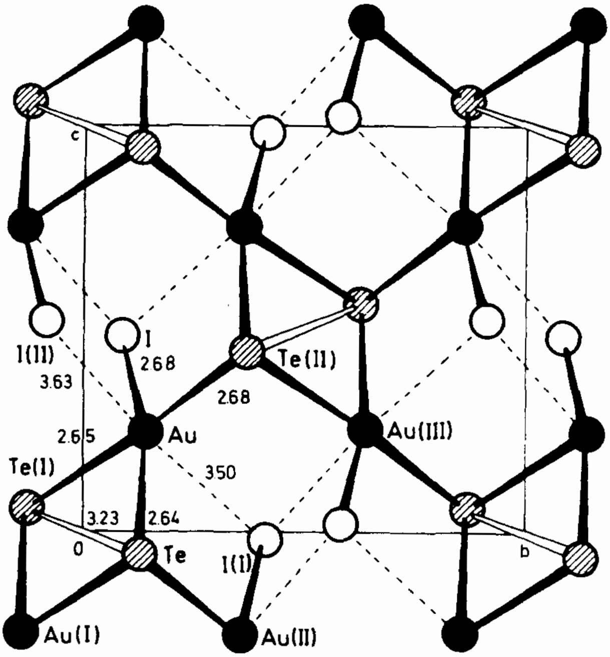

FIG. 11. Corrugated net of the AuTeI structure. (Redrawn from J. Fenner and D. Mootz, *J. Solid State Chem.* **24**, 367 (1978), Fig. 1, p. 368.)

of $AuTe_2Cl$ were too small to be measured in the same way, but, qualitatively, they show the same behavior. For the (semiconducting) AuTeI, a band gap of ~0.9 eV results from measurements of the spectral reflectance (*308*). For the metallic conducting compounds $AuTe_2I$ and $AuTe_2Br$, a small, temperature-independent diamagnetism was found: the feeble paramagnetism due to the charge carriers does not compensate for the diamagnetism of the compounds. AuTeI also shows a temperature-independent diamagnetism with $\chi_M = -0.14 \times 10^{-3}$, in good agreement with the value $\chi_M = -0.15 \times 10^{-3}$, calculated for the diamagnetic susceptibilities per gram-ion for $Au^{3+}I^{-}Te^{2-}$ (*308*). $AuTe_2I$ shows pronounced oscillations in the magnetoresistance at liquid-helium temperature (Shubnikov–de Haas effect). Measurements, on well developed, single crystals, of the angular dependence of the oscillations have been used to determine the Fermi surface. The layer structure of $AuTe_2I$ is reflected by the high anisotropy, of at least 10:1, of one of the ellipsoidal, Fermi surfaces (*341, 342*).

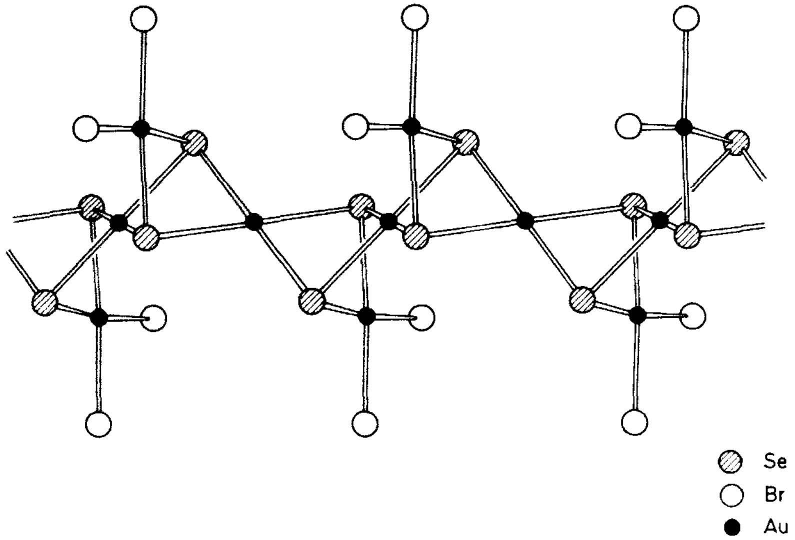

FIG. 12. Perspective view of an atomic ribbon of AuSeBr. (Redrawn from D. Mootz, A. Rabenau, M. Wunderlich, and G. Rosenstein, *J. Solid State Chem.* **6**, 583 (1973), Fig. 1, p. 584.)

D. MISCELLANEOUS

1. Solid State Electrolytes

The most important physical property exhibited by members of the Group IB chalcogenide halides (also, with respect to practical applications) is the enhanced, ionic conductivity found for Ag_3SI and the copper compounds of the type CuTeX. Solid-state electrolytes, where the electric current is due exclusively to the movement of ions, have been known for a long time. In such extreme cases as α-AgI, this conductivity is of the order of magnitude of that of concentrated, liquid electrolytes (see Fig. 5). Unfortunately, AgI loses this property because of a phase transition at 147°C. With the discovery of Ag_3SI by Reuter and Hardel (*316*), the first, optimized, ionic conductor at moderate temperatures was found (*150*). As may be seen from Fig. 5, this and other examples can be formally derived from the binary compound by a substitution in the respective, cation lattice (Ag_3SI, CuTeBr), or anion lattice ($RbAg_4I_5$).

Figure 13 shows the principle of a galvanic cell having solid-state electrolytes. By closing the outer circuit, e.g., by a load, silver from the

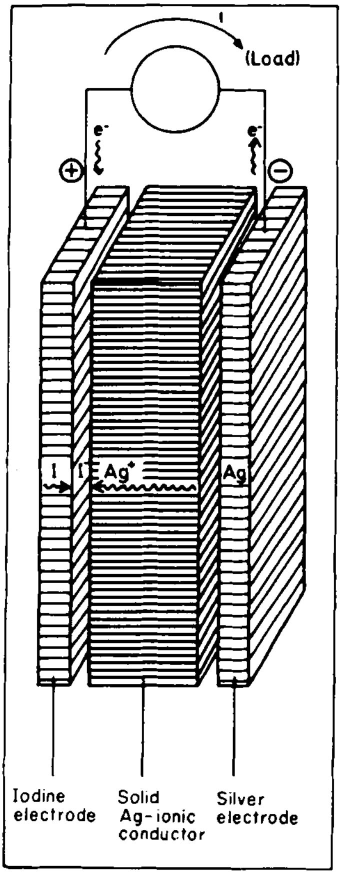

FIG. 13. Galvanic cell having a solid-state silver electrolyte.

cathode dissolves: $Ag \rightarrow Ag^+ + e^-$. The Ag^+ ions move through the solid electrolyte, e.g., Ag_3SI, causing an ionic current in the inner circuit. On the anode, an equivalent amount of I^- is formed by the reaction of iodine with the electrons from the outer circuit. On the interface anode–solid electrolyte, I^- combines with Ag^+. It is the chemical energy of the reaction $Ag + I \rightarrow AgI$ that is transformed directly into electrical energy. Besides many technical applications, such as solid-state batteries (*209*), the scientific significance of solid, ionic conductors for thermodynamic and kinetic investigations plays an increasing role. A number of review articles on this topic have been published (*133, 135, 150, 167, 168, 408*).

2. Hydrothermal Synthesis in Acid Solutions

Most of the chalcogenide halides can, in principle, be prepared by high-temperature reactions, e.g., by heating the respective elements or binary compounds (or both) together in sealed, quartz-glass ampoules. A certain amount of knowledge as to the thermal stabilities of the respective compounds is needed. Separation from other phases, however, often causes difficulties. The true composition has, therefore, to be known, making the method unsuitable for exploring new systems. Here, hydrothermal synthesis in acid solutions (*297, 300, 301*) has proved to be the most important tool, as it leads directly to isolated, single crystals of the ternary compounds, suitable for their identification by chemical analysis and X-ray investigation.

Many of the chalcogenide halides mentioned in the different Sections have been obtained in this way. As this method is not yet com-

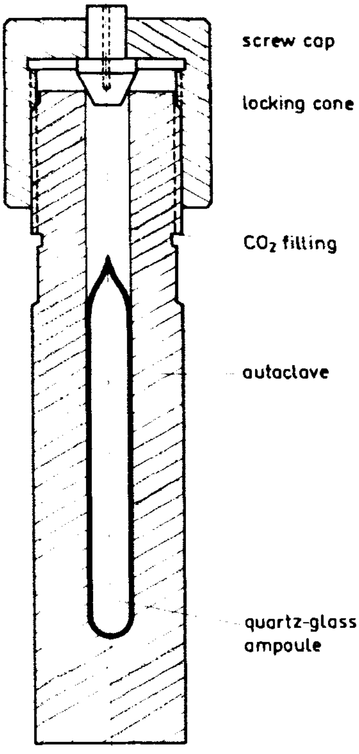

FIG. 14. Equipment for the hydrothermal method, with hydrohalic acids as solvents.

mon practice, the principle will be given. A quartz-glass ampoule having a diameter of ~15 mm is filled to between 50 and 70% of capacity with the respective hydrohalic acid. The acid is frozen with the aid of liquid nitrogen, and the components (elements or binary compounds, or both, not necessarily in stoichiometric proportions) are introduced into the ampoule. Then, the ampoule is evacuated, sealed, and placed in an autoclave (see Fig. 14). To prevent damage to the ampoule by the internal pressure developed during heating, the free volume of the autoclave is filled with solid carbon dioxide. The amount is calculated for an external pressure of ~2500 bar at the working temperature, a pressure that the ampoule can easily support. After about ten days, there have been formed crystals of sufficient size and quality that can be readily separated (see Fig. 9).

III. Group IIB

A. ZINC AND CADMIUM

No chalcogenide halides of zinc and cadmium are known. The phase diagrams of $CdS-CdCl_2$ (*7, 198, 210*), $CdSe-CdCl_2$ (*210, 314*), $CdTe-CdCl_2$ (*368*), $CdTe-CdBr_2$ (*368*), and $CdTe-CdI_2$ (*323*) are of a simple, eutectic type. The system $CdS-CdCl_2$ shows a range of solubility of CdS in solid $CdCl_2$ that extends to 5% of CdS at room temperature, and increases to a maximum of 12.5% of CdS at 500°C (*7, 210*).

B. MERCURY

The most important mercury chalcogenide halides are of the type $Hg_3Y_2X_2$ (Y = S, Se, Te; X = Cl, Br, I). The corresponding sulfide halides have been known for over 150 years (*326*). Quite a lot of work has been performed concerning the preparation, structures, electronic and optical properties, and phototropic behavior of these compounds. Mercury chalcogenide halides of other compositions have been mentioned in the literature (*141*). As most of these compounds are not well established, they will not be treated in detail, with the exception of the latest contributions (see Table V).

1. Preparative Methods

The compounds $Hg_3Y_2X_2$ are formed as main products or by-products of many reactions. The most important, and most widely applicable, preparative routes are the following.

TABLE V

MERCURY CHALCOGENIDE HALIDES: BIBLIOGRAPHY[a]

Compound	Preparation, properties	Single crystals	Structure	Optical properties	Phototropy	Electric conductivity	Magnetism
$Hg_3S_2Cl_2$	*15,20,290*	*66,189,312* *381*	*10,66,110,132* *291*	*20*	*377*	*378*	*377*
$Hg_3S_2Br_2$	*15,20,290*	*381*	*289*	*20,204*	*204,377*	*378*	*377*
$Hg_3S_2I_2$	*15,20,290*	*381*	*288*	*20,204,375,376*	*204,205,233,375–377,380*	*378*	*375*
$Hg_3Se_2Cl_2$	*15,20,290*	*189*	*290,292*	*20*	*310*	—	—
$Hg_3Se_2Br_2$	*15,20,290*	—	*290*	*20,204*	*204*	—	—
$Hg_3Se_2I_2$	*15,20,290*	—	—	*20,204*	*204,207*	—	—
$Hg_3Te_2Cl_2$	*15,20,290*	*189,242*	*290,292*	*20,242*	—	—	—
$Hg_3Te_2Br_2$	*20,290*	*189*	*290,292*	*20*	—	—	—
$Hg_3Te_2I_2$	*15,20,290*	—	*290*	*20*	—	—	—
Hg_2YX	*14*	—	—	—	—	—	—
(Y = S,Se; X = Cl,Br,I)	*14*	—	—	—	—	—	—
$Hg_5Te_2X_6$ (X = Cl,Br)	*290*	—	—	—	—	—	—
Hg_2SCl_4	*62*	—	—	—	—	—	—
$Hg_3Te_2Br_3$	*15*	—	—	—	—	—	—
$Hg_3Te_2Br_8$	*179*	—	—	—	—	—	—
$Hg_3S_5Cl_2$	*51*	—	—	—	—	—	—
$Hg_2S_2I_2$	*313*	—	—	—	—	—	—

[a] For a more detailed review of the literature up to 1965, see ref. *141*.

(*i*) Sintering of Hg_2X_2 and the chalcogen in a sealed tube. S, Se, and Te react at 250, 350, and 500°C, respectively. The initial chalcogen–HgX_2 ratios vary between 5:1 for S and Se, and 4:3 for Te. The reaction is complete after 10–15 h. The excess of chalcogen is removed by dissolution (S) in CS_2, or sublimation (Se, Te) (*15, 20*).

(*ii*) Annealing of a stoichiometric mixture of HgX_2 and HgY at 150°C in evacuated tubes for 12 h. A microcrystalline product is formed (*290*).

(*iii*) Reaction of HgX_2 with H_2Y by passing the gaseous H_2Y through an aqueous or organic solution of HgX_2. An excess of HgX_2 must be present throughout. The reaction between $HgCl_2$ and H_2Te has to be conducted in an atmosphere of an inert gas. $Hg_3Te_2Br_2$ and $Hg_3Te_2I_2$ cannot be prepared by this method (*14, 59, 326*).

Other methods of preparation, especially for $Hg_3S_2Cl_2$, have been mentioned. For instance, $HgCl_2$ reacts with S-donors as different as $Na_2S_2O_3$, CS_2, or CuS to afford $Hg_3S_2Cl_2$. $Hg_3Te_2Cl_2$ can also be prepared by the reduction of Te(IV) in the presence of Hg(II), with the aid of SO_2 in an aqueous HCl solution (*50*). A complete survey up to 1964 is to be found in ref. (*141*). Baroni (*14*) observed the intermediate formation of compounds of the composition Hg_2YX_2 (Y = S, Se; X = Cl, Br, I) when gaseous H_2Y, which was diluted by N_2, was passed over the surface of a 1% solution of HgX_2. According to Puff and Kohlschmidt, compounds of the composition $Hg_5Te_2X_6$ (X = Cl, Br) are formed when a mixture of HgTe and an excess of HgX_2 is tempered in evacuated tubes at 150°C for 12 h (*290*). On the other hand, the authors could not confirm the existence of the compounds $Hg_4S_3Cl_2$, $Hg_5S_4Cl_2$, and $Hg_6S_5Cl_2$, which had been described by Poleck and Goercki (*276*). Similarly, the existence of the compounds Hg_2SCl_4, $Hg_4S_3I_2$, $HgBr_2{\cdot}x$Se, $Hg_3Te_2Br_3$, and $Hg_3Te_2Br_4$ does not seem to have been well established. For a résumé of the preparation and properties of these compounds, see (*141*). Leonova and Sviridov (*206*) have since reported the compounds $HgBr_2{\cdot}n$HgSe ($n = 0.1–2.1$), but their homogeneity was not definitely proved.

Growth of single crystals. Crystals of γ-$Hg_3S_2Cl_2$ (see *Crystallographic Data*) measuring 4 × 4 × 4 mm^3 can be grown over a period of 11 days by hydrothermal synthesis in the temperature range between 450 and 400°C, starting with HgS, and using 12 *M* HCl as the solvent (*312*). Single crystals of $Hg_3Y_2Cl_2$ (Y = S, Se, Te) and $Hg_3Te_2Br_2$ were obtained from polycrystallinic samples by hydrothermal synthesis in 25% aqueous HCl or HBr at 300–320°C (*189*). Crystals of α- and γ-$Hg_3S_2Cl_2$ (sizes: 1.4 × 1.4 × 1.4 and 4.4 × 1.9 × 0.6 mm^3, respectively) were prepared in a chemical-transport reaction (see Section VI,5) by the action of HCl gas on HgS in a sealed ampoule exposed to a temperature gradient ranging from 450 to 345°C (*66*). The γ-modification was mainly formed. Its preponderance was further increased by the presence of an excess of HCl. Takei and Hagiwara (*381*) obtained single crystals of $Hg_3S_2Cl_2$ and $Hg_3S_2Br_2$ by a gas-phase reaction between HgS and $HgCl_2$–$HgBr_2$. The reaction mixture was heated in an evacuated tube to a temperature of 450°C, and, within 30 h, single crystals of a maximum length of 1 mm were deposited at the remote, colder part of the tube, whose temperature was kept between 160 and 200°C for the bromide, and at ~290°C for the chloride. In a similar way, crystals of $Hg_3S_2I_2$ can be grown. In an evacuated, T-shaped tube, HgS and HgI_2 are placed in opposite side-arms, and heated to 500 and 300°C, respectively. After 2 h, the temperature is uniformly lowered at a rate of 30–40°/h. Crystals of $Hg_3S_2I_2$ (size: $4 \times 2 \times 0.4$ mm^3) appear on the walls of the central tube, kept at a temperature of 150–175°C (*381*). Also, if H_2S gas, diluted with N_2, is passed over HgI_2 at 330°C, crystals of $Hg_3S_2I_2$ (size: $1.2 \times 0.5 \times 0.1$ mm^3) are deposited at the cool end (~150°C) of the reaction tube (*381*).

Nitsche (*242*) grew single crystals of $Hg_3Te_2I_2$ up to $4 \times 4 \times 4$ mm^3 in size by sublimation of the microcrystalline product, containing an excess of Te, in a sealed ampoule at 550°C. Within 10 days, crystals were formed at the colder (530°C) part of the ampoule.

2. *Chemical Properties*

The compounds $Hg_3Y_2X_2$ (Y = S, Se, Te; X = Cl, Br, I) are insoluble in water, dilute acids, and conc. HCl, and they are not attacked by these solvents. Conc. HNO_3 converts the sulfide chloride into the sulfide nitrate $Hg_3S_2(NO_3)_2$ (*20, 290*). With bases, rapid decomposition occurs, leading to the formation of oxide chacogenides (*20*), or a mixture of oxide and chalcogenide (*111*), a matter on which agreement has not yet been reached.

Solutions of HgSe and HgTe in $HgBr_2$ have been investigated by Jander and Brodersen (*178, 179*). From conductivity and cryoscopic measurements, they concluded that, at concentrations below 0.08 *M*, the chalcogenide is present in molecular form. With increasing concentrations, dissociation according to the equation $HgY + 2\ HgBr_2 = Hg_2YBr^+ + HgBr_3^-$ is followed by associative processes. The associates again dissociate into ionic species. HgTe, whose maximum solubility is 0.4 *M*, dissociates more strongly than HgSe. By extraction, from the solidified melts, of the excess of $HgBr_2$ with acetone, the compounds $Hg_3Se_2Br_2$ and $Hg_6Te_2Br_8$ were obtained.

3. *Crystallographic Data*

The cubic modifications of the mercury chalcogenide chlorides and $Hg_3Te_2Br_2$ are isotypic, and crystallize in the space-group $I2_13$ (*290, 292*). The structure contains distorted $HgY_{2/3}X_{4/6}$ octahedra (*10, 132, 291, 292*) (see Fig. 15). However, from the observed bond lengths, it can more realistically be considered as being built up of a covalent, $(Hg_3S_2)^{2+}$ network containing isolated, ionic, interstitial chlorides. The net can be derived from pyramidal (SHg_3) groups. Each mercury atom is partitioned by two pyramids. The Hg–S distances of 2.42 Å and the S–Hg–S angles of 165.1° are close to the corresponding parameters for the spiral chains of cinnabar (*9*). $Hg_3Se_2Br_2$ and $Hg_3S_2I_2$ both have orthorhombic symmetry, whereas $Hg_3Te_2I_2$ crystallizes in a monoclinic lattice (*288, 290*). The $(Hg_3S_2)^{2+}$ polycation is the fundamental, structural element of these compounds, also (*288*).

$Hg_3S_2Cl_2$ and $Hg_3S_2Br_2$ are polymorphic, affording a low-temperature α, a high-temperature β, and a metastable γ modification (*66, 289*). β-$Hg_3S_2Cl_2$, like the α form, has a cubic symmetry, with an almost doubled lattice-constant. γ-$Hg_3S_2Br_2$ crystallizes in a tetragonal lattice. The other modifications are rhombic. The α and β modifications of $Hg_3S_2Cl_2$ undergo a reversible, mutual transformation at ~300°C.

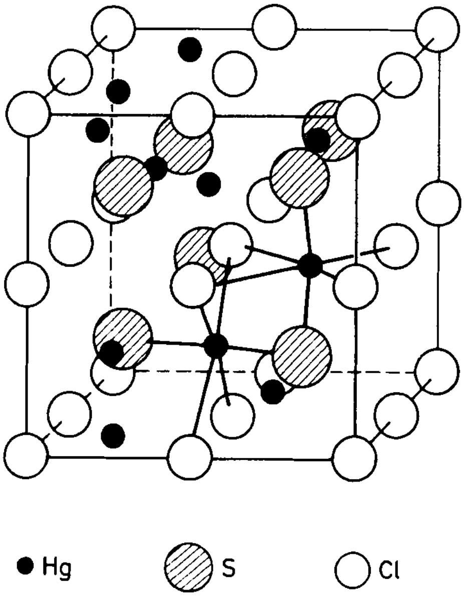

FIG. 15. The crystal structure of α-$Hg_3S_2Cl_2$. (Redrawn from A. J. Frueh and N. Gray, *Acta Cryst.* **B24**, 156 (1968), Fig. 1, p. 157.)

γ-$Hg_3S_2Cl_2$ has an OD-structure consisting of irregularly staggered layers (*110*). As in the α modification, a $(Hg_3S_2)^{2+}$ network, built up of (Hg_3S) pyramids that share Hg atoms, is formed. Four Cl^- again complete the coordination sphere of Hg to a distorted octahedron, but now, the (Hg_3S) net extends in only two dimensions. The layers are held together by weak Hg–Cl bonds.

Table VI summarizes the structural data on mercury chalcogenide halides.

4. *Physical Properties*

The phototropic behavior of the mercury chalcogenide halides has received particular attention. This interest was stimulated by the hope that these materials might allow the preparation of photolayers capable of repeated use for the production of images.

When exposed to daylight, the sulfide and selenide halides $Hg_3Y_2X_2$ are blackened within a few minutes. This black color reversibly disappears when the sample is heated to 90 to 120°C, or stored in the dark for several days (*204, 375–377*). The nature of this phototropic behavior has now been widely investigated by analytical, spectroscopic, structural, magnetic, EPR, and radiotracer investigations (*205, 233, 375–377, 379, 380, 382*). During irradiation of the compounds, electrons belonging to S^{2-} or I^- ions are excited to upper states. The result-

TABLE VI

CRYSTALLOGRAPHIC DATA FOR MERCURY CHALCOGENIDE HALIDES

Compound	Symmetry	*a* (Å)	*b* (Å)	*c* (Å)	β (deg.)	*Z*	Ref.
α-$Hg_3S_2Cl_2$	Cubic	8.94(1)				4	*10,290–292*
		8.949(2)				4	*66,132*
		8.937				4	*289*
β-$Hg_3S_2Cl_2$	Cubic	17.993				32	*289*
γ-$Hg_3S_2Cl_2$	Orthorhombic	9.094	16.843	9.349		8	*289*
		9.081(6)	16.82(1)	9.328(5)		8	*110*
α-$Hg_3S_2Br_2$	Orthorhombic	36.89	18.00	9.28		32	*289*
β-$Hg_3S_2Br_2$	Orthorhombic	18.22	9.19	9.24		8	*289*
γ-$Hg_3S_2Br_2$	Tetragonal	13.14		8.89		8	*289*
$Hg_3S_2I_2$	Orthorhombic	9.78	18.68	9.43		8	*288*
$Hg_3Se_2Cl_2$	Cubic	9.06				4	*290,292*
$Hg_3Se_2Br_2$	Orthorhombic	9.42	9.74	8.87		4	*290*
$Hg_3Te_2Cl_2$	Cubic	9.33				4	*290,292*
$Hg_3Te_2Br_2$	Cubic	9.54				4	*290,292*
$Hg_3Te_2I_2$	Monoclinic	9.78	14.09	14.14	96	8	*290*

ing, neutral S or I atoms diffuse toward the crystal surface, and leave as gaseous I_2 or SO_2. Some of the excited electrons neutralize Hg^{2+} ions. The Hg atoms thus formed also diffuse toward the crystal surface, and aggregate there as colloidal droplets that are responsible for the black color. Other excited electrons are captured by the positive holes, which were created by the leaving anions, to form F-centers. Formation of F-centers is irreversible, as is shown by the persisting, paramagnetic moment of the crystals (*375, 382*), but the printed-out mercury evaporates in the dark, and the crystals regain their original color. According to the results of the radiotracer experiments, considerably more sulfide than iodide is oxidized during irradiation (*233, 380*). The blackening during the irradiation of $Hg_3Se_2I_2$ with light from a Hg-arc lamp is accompanied by a weak photocurrent (90 pA) (*310*).

The absorption and diffuse-reflection spectra of the $Hg_3Y_2X_2$ – compounds are characterized by an absorption edge in the region lying between 420 and 500 nm (*204, 376*), corresponding to band gaps of 2.1–3.2 eV (*20, 205, 242*). The forbidden-zone width is mainly determined by the halogen, and decreases with increasing atomic weight of both the halogen and the chalcogen (*20*). The electric conductivities of the sulfide halides are of the order of $10^{-10}\ \Omega^{-1}cm^{-1}$ at room temperature, and 10^{-6} at 150°C. The activation energies of 0.95–1.4 eV are smaller than the optically measured band-gaps, but exhibit the same relative orders (*378*).

The compounds $Hg_3Y_2Cl_2$ are diamagnetic, as expected (*375, 377*). The coulomb energies of their lattices have been calculated by Simon and Zeller (*358*).

IV. Group IIIB and Lanthanides

The first compound of this series, CeSI, was reported by Carter (*68*) in 1961, and later discussed by Dagron (*93*). It was obtained by the reaction of iodine with cerium sulfide at 430°C, or by direct synthesis from the elements at 500°C. This was the start of a detailed investigation of this group of compounds mainly by Dagron and co-workers. The present situation is presented in Table VII. No scandium compounds are known thus far, and the same is true for selenium and tellurium halides of these elements.

1. Preparative Methods

The best way of preparation seems to be the successive reaction of the respective elements (*94*), as described in detail for the sulfide bro-

TABLE VII

CHALCOGENIDE HALIDES OF GROUP IIIB AND LANTHANIDES: BIBLIOGRAPHY

Compound	Ref.	Compound	Ref.	Compound	Ref.
LaSI	*92,94,96,128*	LaSBr	*92,94–96,128*	LaSCl	*92,94,96,128*
α-CeSI	*68,92–94,96,115,128*	CeSBr	*92,94–96,128*	CeSCl	*92,94,96,128*
PrSI	*94*	α-PrSBr	*94–96,128*	PrSCl	*94,96,128*
		β-PrSBr	*95,128,334*		
NdSI	*94,96,128*	NdSBr	*94–96,128,334*	NdSCl	*94,96*
SmSI	*94,96,128,335*	SmSBr	*94–96,128,334*	SmSCl	*94,96*
GdSI	*94,96,128*	GdSBr	*94–96,128,334*	GdSCl	*94*
TbSI	*96,128*	TbSBr	*95,96,128,334*		
YSI	*94,96,128*	β-YSBr	*94–96*	YSCl	*94,96*
DySI	*94,96,128*	β-DySBr	*94–96,128*	DySCl	*128*
		β-HoSBr	*95,96,128*	HoSCl	*128*
ErSI	*94,96,128*	ErSBr	*94–96,128*	ErSCl	*85,94,96,128,355*
				TmSCl	*128*
YbSI	*94,96,128*	YbSBr	*94–96,128*	YbSCl	*128*
LuSI	*94,96,128*	LuSBr	*85,94–96,128*	LuSCl	*128*

mides and iodides by Dagron and Thevet (*96*). Three types of ampoule were used (see Fig. 16): (*i*) an open, quartz-glass ampoule containing very fine sheets of the metal (L); (*ii*) an ampoule (containing sulfur) that had to be sealed for the sulfide bromides and chlorides (S); and (*iii*) an ampoule containing iodine, or a sealed ampoule for bromine or chlorine (I, Br, Cl).

The ampoules are introduced into a Pyrex-glass tube which is sealed under vacuum. The first step is the reaction of the metal with the halogen. For this, iodine is heated to a temperature of 110°C, whereas, after opening of the ampoule, bromine and iodine, are kept at room temperature and −70°C, respectively,. The ampoule containing the metal is slowly heated to ~300°C, yielding grains of the metal covered with the respective halides. In the second step, the reaction product is reacted with the sulfur vapor at a temperature lying between 400 and 500°C, the other part of the ampoule being at 230°C. The sulfide halide forms, and the halogen thereby liberated attacks the unreacted metal. In this way, extremely microcrystalline, homogenous sulfide halide is slowly formed. The quartz-glass ampoule is removed from the tube, and sealed under vacuum, and the crude product is recrystallized for some weeks at 450 to 500°C.

For single crystals, the same method is applied, using an excess of metal and of halogen. After reaction, the mixture of the sulfide halide and the halide is heated to a temperature slightly above the melting point of the respective halide. Perfect, small crystals for X-ray determination are formed. The excess of the trihalide is removed by treatment with anhydrous alcohol (*92, 93, 96*). CeSI may also be prepared from the sulfides (*68, 93*); CeSCl is formed by reaction 4 (*92*).

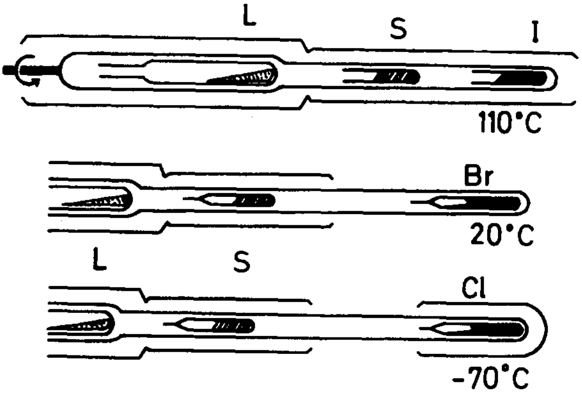

FIG. 16. Preparation of lanthanide chalcogenide halides: experimental arrangement.

$$2\ \mathrm{CeSI} + \mathrm{PbCl_2} \xrightarrow{500^\circ\mathrm{C}} 2\ \mathrm{CeSCl} + \mathrm{PbI_2} \tag{4}$$

2. *Chemical Properties*

Besides a few colorless compounds, such as YSBr, most of these compounds are slightly colored, e.g., yellow (YbSBr), green (PrSI), rose (ErSI), and orange (YbSI). They are very sensitive to humidity, and must be kept under vacuum or dry nitrogen.

3. *Crystallographic Data*

Whereas the structures of the sulfide iodides and sulfide bromides seem well established, this is not the case for the sulfide chlorides. As the sulfide and chloride ions possess the same number of electrons, they cannot be distinguished by X-ray diffraction, and neutron diffraction would have to be applied in order to obtain an unambiguous picture. Five different structure types have been observed so far (see Table VIII), based on the structure determinations shown in Table IX.

TABLE VIII

CHALCOGENIDE HALIDES OF GROUP IIIB AND LANTHANIDES

(1)[a]	LaSI		LaSBr	LaSCl
	α-CeSI		CeSBr	CeSCl
	β-CeSI			
	PrSI		α-PrSBr	PrSCl[b]
(2)				
			β-PrSBr	
	NdSI		NdSBr	NdSCl
	SmSI	(4)	SmSBr	SmSCl
	GdSI		GdSBr	GdSCl
	TbSI		TbSBr	
	YSI		β-YSBr	YSCl
(3)	DySI		β-DySBr	DySCl[b,c]
		(5)	β-HoSBr	HoSCl[b,c]
	ErSI		ErSBr	ErSCl
				TmSCl[b,c]
	YbSI		YbSBr	YbSCl[b,c]
	LuSI		LuSBr	LuSCl[b,c]

[a] Structure types (1) α-CeSI; (2) SmSI; (3) hexagonal, structure unknown; (4) NdSBr; (5) FeOCl. [b] Structure type doubtful. [c] Existence doubtful.

TABLE IX

CHALCOGENIDE HALIDES OF LANTHANIDES: STRUCTURE DETERMINATIONS

Structure type[a]	Compound	Ref.	*a* (Å)	*b* (Å)	*c* (Å)	Degrees	Crystallographic system
(1)	α-CeSI	*115*	7.33	14.35	7.05		Orthorhombic
(2)	SmSI	*335*	11.21			23.37 (α)	Rhombohedral
(3)[b]	GdSI	—	10.73	4.24			Hexagonal
(4)	NdSBr	*334*	6.94	6.91	7.05	99.28 (β)	Monoclinic
(5)	LuSBr	*85*	5.274	3.995	8.085		Orthorhombic
	ErSCl	*355*	5.31	3.96	7.45		

[a] See footnote *a*, Table VIII. [b] Structure unsolved.

For the still-unsolved, hexagonal structure type of GdSI, only the cell dimensions are presented. The structures were described in detail by Dagron and Thevet (*96*). Their common building-principle is a layer structure formed by planar layers $[LS]_n$ (L = metal), separated by a double layer of bromine or iodine.[3] The plane layers $[LS]_n$ are formed by the juxtaposition of metal tetrahedra enclosing sulfur, $[L_4S]$. These layers exhibit two different symmetries.

(*i*) This is tetragonal. Fig. 17 shows schematically the sequence of the tetrahedra, which is such that each of the four apexes of a tetrahedron belongs simultaneously to four neighbors, and two edges of the tetrahedra are common to two neighbors. This arrangement can support deformations leading to the orthorhombic symmetry of the CeSI and FeOCl type, respectively, and to the monoclinic NdSBr type.

(*ii*) This is hexagonal. Here, in the SmSI type, the apexes of the tetrahedra $[L_4S]$ are common to four neighbors as well (see Fig. 18). Three tetrahedra are arranged at an angle of 120° around a common apex, so that one of the faces lies in the plane of the base. The fourth tetrahedron has an inverse arrangement with respect to the other three, and has three of its edges in common with the others. This arrangement leads to octrahedral holes, forming channels that cross the layers of tetrahedra, and these holes contain the iodide ions.

In the CeSI (*115*) and NdSBr (*334*) type of structure, bromine and iodine are coordinated to five metal ions (four of the same layer, and one of the opposite layer) and four halogen ions of the double layer. In the SmSI type (*335*), iodine is coordinated to three metal ions of a $[LS]_n$ layer and three other iodine ions of the double layer. In the FeOCl type of compound, such as ErSCl (*355*) and LuSBr (*85*), the halogen is surrounded by a polyhedron formed by six sulfur and four halogenide ions.

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[3] In the case of the sulfide chlorides, S and Cl are indistinguishable.

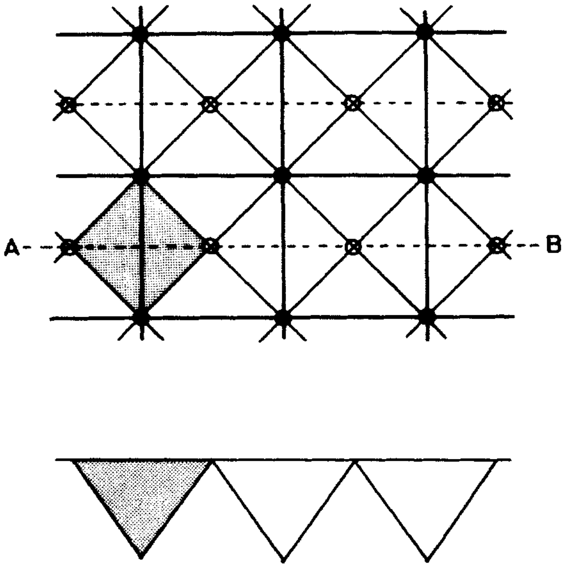


FIG. 17. Tetragonal symmetry: projective view (above) and cut A–B (below) of a $[LS]_n$-layer formed by a sequence of $[L_4S]$ tetrahedrons (ideally: PbFCl-type; distorted: CeSI-, FeOCl-, and NdSBr-types). (Redrawn from C. Dagron and F. Thevet, *Ann. Chim.* **6**, 67 (1971), Fig. 6, p. 77.)

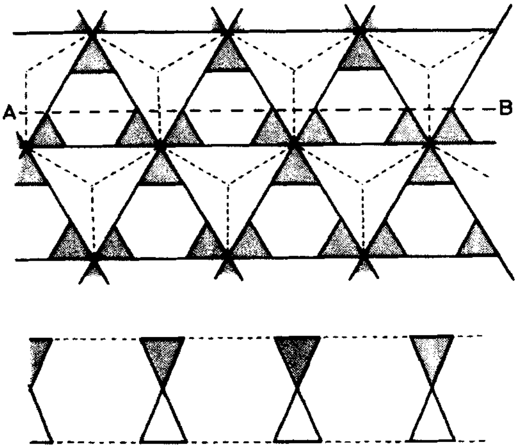


FIG. 18. Hexagonal symmetry: projective view (above) and cut A–B (below) of a $[LS]_n$-layer formed by a sequence of $[L_4S]$ tetrahedrons (SmSI-type). (Redrawn from C. Dagron and F. Thevet, *Ann. Chim.* **6**, 67 (1971), Fig. 7, p. 77.)

4. *The Lanthanide Contraction*

In the sequence of structures from the large to the small rare-earth elements, the lanthanide contraction is manifested as shown in Figs. 19a and 19b. Within a structure, the cell volume diminishes linearly with the atomic number. If a certain, limiting value is reached, there is

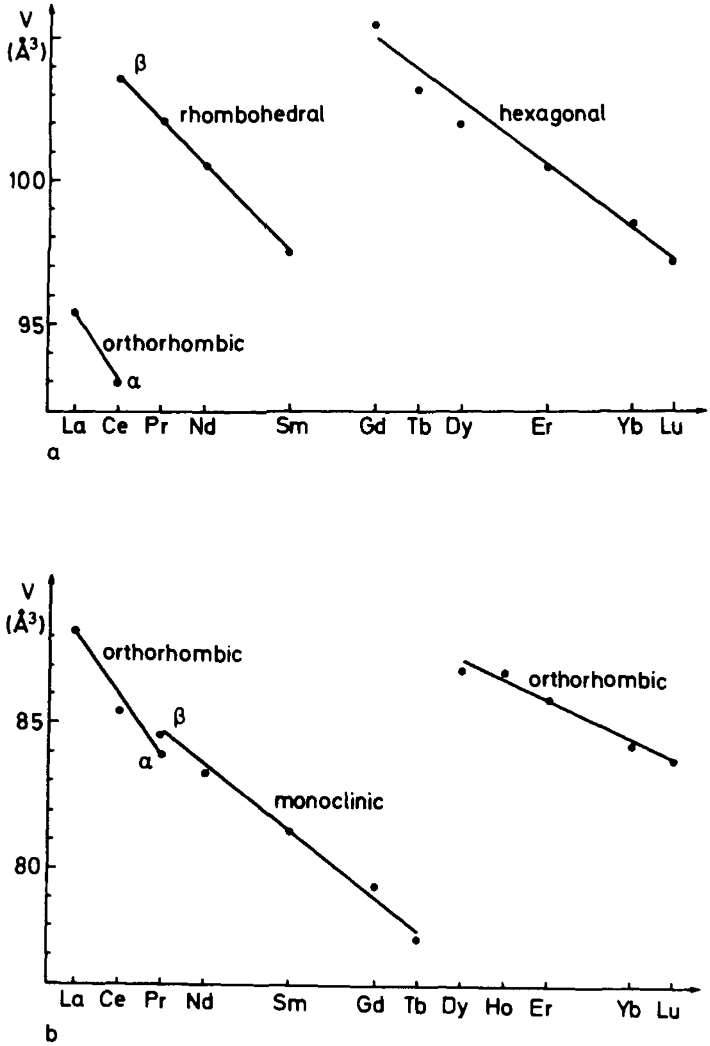


FIG. 19. Molecular-volume variation in relation to the atomic number: a, sulfide iodides; b, sulfide bromides. (From C. Dagron and F. Thevet, *Ann. Chim.* **6**, 67 (1971), Figs. 2 and 3, p. 72.)

a jump to another structure more adapted to the respective ionic radii. This change in structure may be accompanied by a large jump in the cell volume.

V. Group IVB

Very little is known about chalcogenide halides of Group IVB elements. Although the existence of sulfide chlorides (*45, 274, 329, 365*) and of a selenide chloride (*329*) of titanium was claimed in early publications, their true composition, and even their existence, remains doubtful. They have usually been obtained by the reaction of titanium chlorides with sulfur and selenium, respectively, or with hydrogen sulfide. The synthesis of a pure compound, $TiSCl_2$, was published in 1959 (*113*). It is an intermediate of the reaction of $TiCl_4$ with H_2S.

$$TiCl_4 + H_2S \xrightarrow{<0^\circ} TiCl_4{\cdot}H_2S \xrightarrow{>0^\circ} TiSCl_2 \xrightarrow{>136^\circ} TiS_2 \qquad (5)$$

An optimal reaction-temperature of 65°C was claimed. The blackish brown $TiSCl_2$ is very sensitive to oxygen and humidity. As no X-ray measurements have been made, additional work is needed. Titanium sulfide halides have also been claimed as catalysts for the polymerization of propylene (*363*).

Nothing has thus far been reported concerning chalcogenide halides of other elements of Group IVB.

VI. Group VB

Although not yet published in a journal, according to thesis work, the vanadium compounds VSCl (*11*), VSBr, and VSI (*208*) seem to exist. Numerous niobium chalcogenide halides have been reported, and among these are the best characterized examples of Group VB (see Table X). Only two tantalum compounds, TaS_2Cl_2 (*361*) and $TaSCl_3$ (*13*) have thus far been described in the literature.

1. *Preparative Methods*

Compounds of the type NbY_2X_2 (Y = S, Se; X = Cl, Br, I) were prepared by the chemical-transport technique (*336*, see Section VI,5), using a slight excess of the halogen and a stoichiometric metal: chalcogen ratio. The starting materials, elements and, in some cases, S_2Cl_2 or $NbCl_5$, are heated in sealed glass or quartz-glass tubes in a temperature gradient in the temperature region between 300 and 500°C. Ex-

TABLE X

CHALCOGENIDE HALIDES OF NIOBIUM: BIBLIOGRAPHY

Compound	Preparation	Crystallographic data	Optical properties	Magnetic data	Other physical data
NbS_2Cl_2	*271,322,339*	*322,339,347*	*271,322*	*322,339*	*322*
NbS_2Br_2	*271,322,339*	*322,339*	*271*	*322,339*	
NbS_2I_2	*271,322,339*	*322,339*	*271*	*322,339*	
$NbSe_2Cl_2$	*322,339*	*322,339*		*322,339*	
$NbSe_2Br_2$	*322,339*	*322,339*		*322,339*	
$NbSe_2I_2$	*322,339,406*	*322,339*		*322,339,406*	*322,406*
$Nb_{1.1}Se_2I_2$	*322*	*322*			
NbS_2Cl	*322,361*	*322*			
NbS_2I	*322*	*322*			
$Nb_5Se_8Cl_{10}$	*322*	*322*			
$NbSe_2Br$	*322*				
$NbSe_3Cl$	*322*	*322*			
$NbSe_4I_{0.33}$	*223*	*223*			
$NbSCl_3$	*13,131*		*13,131*		
$NbSBr_3$	*131*		*131*		
$NbSeCl_3$	*131*		*131*		
$NbSeBr_3$	*131*		*131*		

perimental details were given (*322, 339*), and additional information has been published about $NbSe_2I_2$ (*406*). Besides NbY_2X_2 and niobium chalcogenides, other chalcogenide halides are also formed by these reactions: NbS_2Cl, NbS_2I, $NbSe_2Br$, $NbSe_3Cl$, $Nb_5Se_8Cl_{10}$, and $Nb_{1.10}Se_2I_{1.96}$ (*322*). Single crystals of $NbSe_4I_{0.33}$ (together with NbS_2) have been obtained in this way by transport of $NbSe_3$ in iodine vapor (*223*). This compound may also be obtained by direct reaction of a mixture of Nb + 4 Se + I in a sealed tube at 700°C. The excess of iodine is removed by extraction with CCl_4 (*223*). $NbSCl_3$ and $TaSCl_3$ were prepared by the reaction of stoichiometric amounts of the respective pentachlorides and B_2S_3 in a sealed tube at 90°C (Nb) or 80°C (Ta) (*13*).

$$6\ NbCl_5 + 2\ B_2S_3 \rightarrow 6\ NbSCl_3 + 4\ BCl_3 \tag{6}$$

The reaction starts at room temperature. The BCl_3 formed is condensed in a side arm cooled by liquid nitrogen.

In a similar way, the compounds $NbSCl_3$, $NbSeCl_3$, and $NbSeBr_3$, as well as $TaSCl_3$, $TaSBr_3$, and $TaSeBr_3$, are obtained by reacting the respective pentahalide with Sb_2S_3 and Sb_2Se_3, respectively, in the presence of CS_2 as the solvent at room temperature for 1 to 3 days. In the case of $TaSeBr_3$, the reaction mixture is heated to 50°C. VSCl has been prepared by the direct reaction of VCl_5 and Sb_2S_3 in a sealed tube (*11*).

By mixing solutions of sulfur and the pentachlorides of niobium and tantalum in benzene in a dry, inert atmosphere at room temperature, fine crystalline powders are formed having the compositions NbS_2Cl and TaS_2Cl_2, respectively (*361*). By the direct interaction of sulfur with the pentachlorides in a sealed tube at 240–300°C, a reaction product sublimes; it has the composition $M(S_2)_mCl_n$, where M is Nb or Ta, and $m = 1$–3, $n = 1$–4, depending on the initial ratio of MCl_5 to S.

2. *Chemical Properties*

The platelike crystals of the compounds NbY_2X_2 are stable in air, and dissolve in hot HNO_3 with precipitation of Nb_2O_5, and in 20% $KOH–H_2O_2$, affording a clear solution. At 10^{-4} torr, they completely decompose as follows.

$$3\ NbS_2Cl_2 \rightarrow NbS_2 + S_2,g + 2\ NbSCl_3,g \qquad (7)$$

(also, for NbS_2Br_2, $NbSe_2Cl_2$, and $NbSe_2Br_2$).

$$NbS_2I_2 \rightarrow NbS_2 + I_2,g \qquad (8)$$

(also for $NbSe_2I_2$) (*339*).

At atmospheric pressure, $NbSe_2I_2$ is thermally stable up to 380°C (*406*).

The compounds $NbSCl_3$ and $TaSCl_3$ (*13*), as well as NbS_2Cl and TaS_2Cl (*361*), are reported to be sensitive to humidity. They are insoluble in organic solvents, but $NbSCl_3$ and $TaSCl_3$ dissolve in acetonitrile, forming $MSCl_3 \cdot 2\ CH_3CN$ (*13*).

3. *Crystallographic Data*

The compounds NbY_2X_2 were investigated by X-ray powder diffraction, and by the single-crystal, Weissenberg technique. They crystallize in two different structures, monoclinic and triclinic. Some of them occur in both crystallographic forms (see Table XI). Both the monoclinic and the triclinic NbY_2X_2 compounds have layer structures. The layers are parallel to the *a,b* plane for the monoclinic form, and parallel to the *a,c* plane for the triclinic form (*322*). For NbS_2Cl_2, a complete structure-determination has been performed (*347*). A layer structure comparable to that of $MoCl_3$ or $AlCl_3$ if one Cl is replaced by an S_2 group was found. Besides the S_2 groups, it is the occurrence of metal–metal bonds that is most characteristic for this compound, and that is typical for a great number of transition-metal compounds in lower oxidation states (*340*) (see also, Section VII,B). Here, NbS_2Cl_2 exhibits the specific properties of almost all Nb(IV) compounds: the connection of

TABLE XI

CRYSTALLOGRAPHIC DATA FOR NIOBIUM CHALCOGENIDE HALIDES

	Unit-cell parameters						
Compound	*a* (Å)	*b* (Å)	*c* (Å)	α (°)	β (°)	γ (°)	Symmetry
NbS_2Cl_2	6.27	11.09	6.68		111.07		
NbS_2Br_2	6.54	11.32	6.91		110.54		
$NbSe_2Cl_2$	6.65	11.44	6.96		109.02		Monoclinic
$NbSe_2Br_2$	6.76	11.53	7.20		113.90		C2/m
$NbSe_2I_2$	6.89	12.34–12.46	7.51		112.26		
NbS_2Br_2	6.589	7.254	6.528	112.63	120.05	67.72	
NbS_2I_2	6.80	7.23	6.77	102.3	117.4	73.8	
$NbSe_2Cl_2$	6.538	7.261	6.350	11.35	119.01	66.93	Triclinic
$NbSe_2I_2$	7.207	7.757	7.060	113.20	121.10	67.59	
NbS_2Cl	8.615	24.754	6.719	98.77	106.58	128.88	
NbS_2I	7.032	24.892	6.818	94.66	118.75	104.07	
$NbSe_3Cl$	11.790	18.847	7.196		95.41		Monoclinic
$Nb_5Se_8Cl_{10}$	9.365	12.673	7.579		124.78		$P2_1$ or $P2_1/m$
$NbSe_4I_{0.33}$	9.489		19.13				Tetragonal P4/mnc
$Nb_{1.1}Se_2I_2$	12.874	25.829	7.815		99.98		Monoclinic $P2_1/c$

two niobium by a metal–metal bond. The coordination is shown in Fig. 20, and the situation is best described by the formula $^2_\infty[Nb_2(S_2)Cl_{8/2}]$. Every Nb_2 group is coordinated to two S_2 groups, and two such $Nb_2(S_2)_2$ units are linked by 4 Cl.

$NbSe_4I_{0.33}$ is tetragonal, and has the space group P4/mnc. The structure is built up of chains of rectangular, $NbSe_8$ antiprisms. Iodine atoms are situated between these chains. With respect to the crystallographic data, a great similarity to the β-phase of "$NbSe_4$" exists. The structure is better expressed by the formula $Nb_{12}Se_{48}I_4$, instead of $NbSe_4I_{0.33}$ (*223*). Crystallographic data for these and other niobium compounds are summarized in Table XI.

X-Ray powder diffraction photographs suggest that $NbSCl_3$ and $TaSCl_3$ are isostructural (*13*).

4. *Physical Properties*

IR and Raman spectra of the NbS_2X_2 compounds have been measured, and assigned to the different modes (*271*). Especially in the absence of X-ray data, such measurements serve to prove the presence of S–S and Nb–S modes (see Table X). Magnetic data are available for

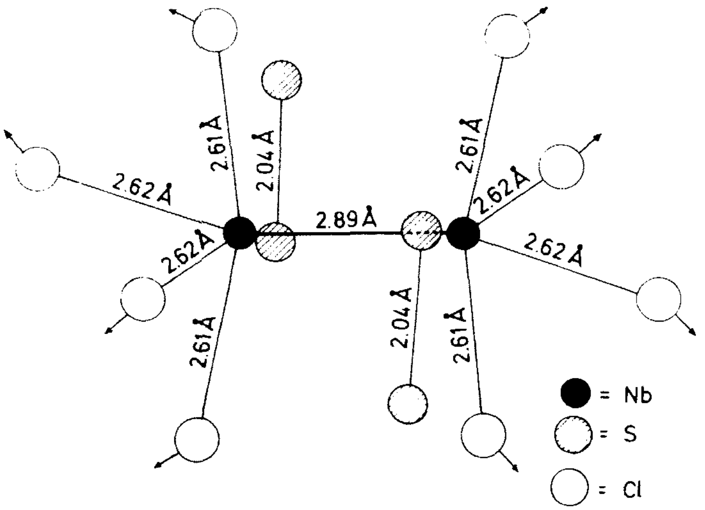


FIG. 20. Coordination polyhedron of NbS_2Cl_2. (Redrawn from H. G. v. Schnering and W. Beckmann, *Z. Anorg. Allg. Chem.* **347**, 231 (1966), Fig. 3, p. 238.)

the NbY_2X_2 compounds (*322, 339*). They exhibit a temperature- and field-strength-independent diamagnetism; this proves the absence of isolated, Nb^{4+} ions, in accordance with the result of the structure determination (*339*). Conductivity and photoelectric effects have been measured on $NbSe_2I_2$ single crystals. An activation energy of 0.26 eV was found for the high-temperature branch of the conductivity curve (*406*). The absorption spectrum of NbS_2Cl_2 single crystals is caused by indirect band-to-band transitions, the indirect band-gap observed being 1.89 eV at ambient temperature (*322*). NbY_2X_2 compounds are diamagnetic semiconductors having high electrical resistivities.

5. *Chemical-Transport Reactions*

A "chemical transport reaction" may be defined as the transference of a condensed phase through a gaseous phase by means of a chemical reaction in which gases $B_{(g)}$, $C_{(g)}$, $D_{(g)}$ · · · are involved.

$$A_{(s)} + B_{(g)} \rightleftharpoons C_{(g)} \cdots ; \Delta H^0_{\text{react.}} \tag{9}$$

This definition of the process shows that it differs essentially from sublimation and distillation. A chemical-transport reaction is necessarily reversible; a concentration gradient is induced, e.g., by means of a temperature gradient that reverses the reaction and causes substance A to precipitate out of the gas phase. The direction of transport of a solid in a temperature gradient ($T_1 < T_2$) is given by the sign of $\Delta H^0_{\text{react.}}$.

$$\text{Endothermic reaction: } T_2 \rightarrow T_1$$

$$\text{Exothermic reaction: } T_1 \rightarrow T_2$$

In preparative work, it may be advantageous to superimpose a transport reaction on the synthesis. In this way, the reaction product is prevented from covering the surface of the starting material, a process that would slow, or completely stop, the reaction. As the vapor pressure of the condensed phases may be negligibly small in the range of temperature within which transport takes place, lower temperatures than would otherwise be feasible may be employed. The desired substance is transported in a temperature gradient, and separated from the starting material, and is, in this way, at the same time also purified (see Fig. 21). In the case of niobium sulfide halides, the chemical transport can be described by the following equations.

$$NbS_2Cl_{2,(s)} + NbCl_{4,(g)} \rightarrow 2\ NbSCl_{3,(g)}\text{; endothermic (analogous } NbS_2Br_2,\ NbSe_2Cl_2,\ NbSe_2Br_2) \quad (10)$$

$$NbS_2I_{2,(s)} + I_{2,(g)} \rightarrow NbI_{4,(g)} + S_{2,(g)}\text{; endothermic (analogous } NbSe_2I_2) \quad (11)$$

Generally, it is not important in which form the components are introduced into the transport tube, because the transport reaction transfers the whole system into a reversible state. In the preparation of NbS_2Cl_2, for example, Nb and S_2Cl_2, as well as Nb, S, and $NbCl_5$, have been used as starting materials (*339*). The principles of chemical transport reactions are treated in refs. (*241, 336, 337, 338*).

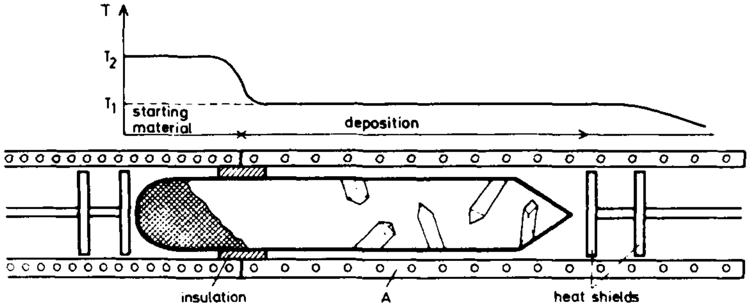


FIG. 21. Reaction scheme of crystal growth by chemical transport: A, transport furnace having two consecutive heating coils.

VII. Group VIB

A. CHROMIUM

The work on chromium compounds is based on two publications only (*17*, *181*). By the reaction between Cr_2S_3 and $CrBr_3$ or CrY (Y = S, Se, Te) and I_2 in sealed, quartz or glass tubes, the compounds shown in Table XII have been obtained.

Preliminary X-ray work on CrSBr crystals, probably formed via a chemical-transport reaction, shows rhombic symmetry (*181*). Powder patterns of the iodides can be indexed with respect to a hexagonal lattice, and are similar to those of CrI_3 (*17*, *181*).

The ideal composition CrYI does not seem to be attained in all cases (see Table XII). Whether this is due to the existence of extended phases (e.g., $CrSI_{1-x}$) or represents an individual phase is not known. The compounds are described as black, and sensitive to air. Additional work should be done for the chromium system.

B. MOLYBDENUM

Just as, in Group VB, niobium, so, in this Group, molybdenum provides most of the examples of the chalcogenide halides. The occurrence and preparation of such compounds are described in numerous publications. In most cases, they have been obtained as powders, with the composition based on chemical analyses only. The presence of defined, homogeneous phases is, therefore, in many cases doubtful. In addition, some published results are contradictory. A decision is possible where a complete structure analysis has been made. As will be shown later, the formation of metal–metal bonds (so-called clusters), as in the case of niobium, is the most characteristic building-principle. Such clusters

TABLE XII
CHALCOGENIDE HALIDES OF CHROMIUM

Phase	Reaction temperature (°C)	Density (g/cm³)	Ref.
CrSBr	870	3.99	*181*
$CrSI_{0.83}$	420	4.51	*181*
CrSeI	400	5.41	*181*
$CrTe_{0.73}I$	315	5.77	*181*
CrTeI	190	5.50	*17*

may or may not be maintained in a chemical reaction, and they therefore account for some divergent observations.

1. Preparative Methods

In this section, a review is given of preparative work on chalcogenide halides. Table XIII summarizes the proposed compositions thus far described in the literature.

The first report dates from 1894: Mo and S_2Cl_2 heated to red heat should yield $Mo_5S_8Cl_9$ (*362*). No further work was published until the 1950s. In 1959, a compound having the composition of $Mo_5S_8Cl_9$ was considered as an intermediate step in the chlorination of MoS_2 (*138*). $MoCl_5$ reacts at 150°C with S_2Cl_2 to give MoS_2Cl_3 (*129*). A compound having this composition was also obtained, as black needles, by the reaction of S with $MoCl_3$ in S_2Cl_2 at 450°C under pressure. The composition was confirmed by structure analysis (*215, 217*). $MoTe_2$ reacts with Br at room temperature to afford $MoTe_2Br_{10}$, which loses Br_2 dur-

TABLE XIII

Chalcogenide Halides of Molybdenum: Bibliography

	Cl	Br	I
S		$Mo_6S_6Br_2$ (*354*)	$Mo_6S_6I_2$ (*354*)
		Mo_6SBr_{10} (*272*)	
	$Mo_5S_8Cl_9$ (*362*)		
	$Mo_3S_7Cl_4$[a] (*101,215,216,217,222,261*)	$Mo_3S_7Br_4$[a] (*101,215,261*)	$Mo_3S_7I_4$[a] (*101,186*)
	$Mo_2S_5Cl_3$ (*271,311*)	$Mo_2S_5Br_3$ (*311*)	
	$Mo_2S_4Cl_5$ (*311*)		
	MoS_2Cl_3[b] (*129,215,216,217*)		
	MoS_2Cl_2 (*58,311,356*)	MoS_2Br_2 (*311*)	
	$MoSCl_3$ (*12,13,57,58,131*)	$MoSBr_3$ (*131*)	
	$MoSCl_2$ (*58,138*)		
	MoSCl (*269*)	MoSBr (*269,270*)	MoSI (*269*)
Se		$Mo_6Se_5Br_3$[c] (*273,354*)	$Mo_6Se_5I_3$[c] (*273,354*)
		Mo_6SeBr_{10} (*272*)	Mo_6SeI_{10} (*272*)
	$Mo_3Se_7Cl_4$[a] (*101,222,261*)	$Mo_3Se_7Br_4$[a] (*101,265*)	$Mo_3Se_7I_4$[a] (*101,186*)
	$MoSeCl_3$ (*58,131*)	$MoSeBr_3$ (*131*)	
	$MoSeCl_2$ (*58*)		
Te		$Mo_6Te_5Br_3$[c] (*273,354*)	$Mo_6Te_5I_3$[c] (*273,354*)
		Mo_6TeBr_{10} (*272*)	Mo_6TeI_{10} (*272*)
		$MoTe_2Br_{10}$ (*260*)	
		$MoTe_2Br_8$ (*260*)	

[a] Mentioned in (*101, 186*) as $Mo_6Y_{14}X_8$. [b] Mentioned in (*129*) as $Mo_2S_4Cl_6$. [c] $Mo_6Y_5X_3$ composition with the highest X content in the solid solutions $Mo_6Y_{8-x}X_x$.

ing heating by forming $MoTe_2Br_8$, which is stable up to 300°C (*260*). Rannou and Sergent (*311*) reported in 1967 the preparation of five sulfide halides: from MoS_3 and S_2X_2 ($X = Cl$, Br), they obtained between 350 and 400°C $Mo_2S_4Cl_5$ and between 420 and 480°C $Mo_2S_5X_3$ ($X = Cl$, Br) (*311*). The reaction of elemental Mo and S_2Cl_2 and S_2Br_2 at 500°C, however, resulted in MoS_2Cl_2 and MoS_2Br_2, respectively (*311*). Formation of the compound MoS_2Cl_2 was also observed on reaction of $MoCl_4$ with H_2S in benzene (*356*) or CS_2 (*58*).

Compounds having the composition $Mo_3Y_7X_4$ were reported by Opalovskii *et al.* (*222, 261*). $Mo_3S_7Cl_4$ and $Mo_3Se_7Cl_4$ which are formed at 400 and 450°C by the reaction of $MoCl_3$ with S and Se, respectively. The same workers also prepared $Mo_3S_7Br_4$ and $Mo_3Se_7Br_4$ by replacing $MoCl_3$ with $MoBr_3$ and $MoBr_2$ in the temperature region between 250 and 300°C. These phases are, however, amorphous (*265*). Red, single crystals of $Mo_3S_7Cl_4$ and of orange $Mo_3S_7Br_4$ have been obtained by reaction of S with $MoCl_3$ and $MoBr_3$ in S_2Cl_2 and S_2Br_2 at 400 to 500°C under pressure. The compositions were confirmed independently by structure investigations (*215*). The d-values were not in agreement with those published by Opalovskii *et al.* (*261*) for $Mo_3S_7Cl_4$, but agreed with those published for $Mo_2S_5Cl_3$ (*311*). According to later data (*101, 186, 222*), all of the compounds having the composition $Mo_3Y_7X_4$ ($Y = S$, Se; $X = Cl$, Br) have now been obtained. $MoYCl_2$ compounds ($Y = S$, Se) were prepared by the introduction of Sb_2S_3 and Sb_2Se_3 into the syntheses by Britnell *et al.;* the reaction of Sb_2Y_3 with $MoCl_5$, $MoCl_4$, and $MoBr_5$ to form these compounds takes place between 100 and 300°C (*57, 58, 131*). $MoSCl_3$ may also be obtained from B_2S_3 and $MoCl_5$ (*12, 13*). Compounds of the type MoSX ($X = Cl$, Br, I) have been obtained from MoX_2, Mo, and S in stoichiometric amounts at 1000°C (*269*). The compounds are isotypic; the composition was confirmed by structure analysis of MoSBr single crystals (*270*). In a similar way, Mo_6YX_{10} compounds have been prepared, with $Y = S$, Se, or Te, and $X = Cl$ or Br, as well as Mo_6YI_{10}, with $Y = S$ or Se (*272, 273*). In this case, the structure analysis on Mo_6SeCl_{10} (*273*) also confirmed the composition proposed.

A group of compounds interesting because of their physical properties has been found by Sergent *et al.* (*272, 354*). They are derived formally and structurally, by substitution of chalcogen in Mo_6Y_8 (Mo_3Y_4) ($Y = S$, Se, Te) corresponding to $Mo_6Y_{8-x}X_x$ ($X = Cl$, Br, I). The preparation again starts from Mo, Y, and MoX_2. In the case of the selenides, solid solutions are formed, with $0 \leq x \leq 3$. The maximum halogen content corresponds to $Mo_6Y_5X_3$. Sulfur compounds exist only for Br and I. Their composition is $Mo_6S_6X_2$ (*354*), with a deficiency of halogen.

2. *Chemical Properties*

Little has been reported concerning the chemical properties of the numerous compounds mentioned in Table XIII. Also, the behavior of fine powders may differ from that of large, single crystals. Most of the compounds seem to be stable in air: MoSX (X = Cl, Br), $Mo_3Y_7Cl_4$ (Y = S, Se), $MoTe_2Br_8$, $Mo_2S_4Cl_5$, $Mo_2S_5X_3$ (X = Cl, Br), $Mo_5S_8Cl_9$, MoS_2Cl_3, and $Mo_3S_7Cl_4$. Others, such as $MoYCl_3$ (Y = S, Se) and $MoYCl_2$ (Y = S, Se), are sensitive to humidity, and decompose more or less rapidly in air. $MoTe_2Br_8$ is hydrolyzed in water, but is soluble in such polar, organic solvents as ethanol and acetone. The colorless compound can be sublimed (*260*). $MoSCl_3$ seems to form adducts with polar, organic solvents (*58*).

3. *Crystallographic Data*

The discussion will be restricted to cases for which a complete structure-determination exists. Again, as with the niobium compounds, but even more pronouncedly, the occurrence of metal–metal bonds (*340*) (see Table XIV) is most significant.

MoSBr: The cubic structure ($F\bar{4}3m$) consists of Mo_4S_4 cubes that contain Mo_4 clusters with a metal–metal distance of 2.80 Å (see Fig. 22). The clusters are connected by Br atoms in such a way that Mo is in the center of an octahedron ($MoBr_3S_3$). A molybdenum atom of a cluster is, therefore, connected to three other clusters by three Br bridges, and the compound is best described by the formula $[(Mo_4S_4)Br_{12/3}]$. The motive Mo_4S_4 is the first example in the chemistry of Mo(III) having the tetrahedral, Mo_4 cluster (*269, 270*).

MoS_2Cl_3, monoclinic ($P2_1/c$). Figure 23 shows the translational unit, with atom designations. The sulfur atoms form pairs having a distance of 1.98 Å. The molybdenum atoms also occur in pairs enclosed by two bridging S_2 groups. With two chlorine atoms in terminal and

TABLE XIV

METAL–METAL BONDS IN MOLYBDENUM CHALCOGENIDE HALIDES

Compound	Coordination	Mo–Mo distance Å	Ref.
MoS_2Cl_3	Pairs	2.83	*215*
$Mo_3S_7Cl_4$	Triangle	2.74–2.75	*215*
MoSBr	Tetrahedron	2.80	*270*
$Mo_6Cl_{10}Se$	Octahedron	2.60–2.63	*354*
Metal	Cube	2.72	

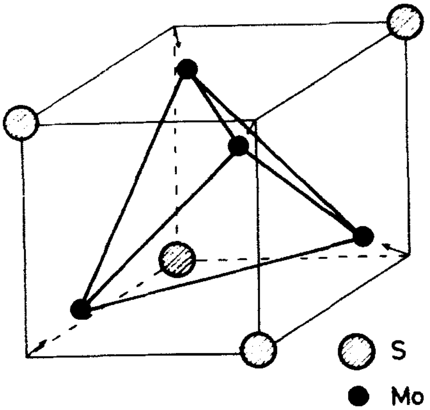


FIG. 22. Tetrahedral Mo_4-cluster in MoSBr. (Redrawn from Ch. Perrin, R. Chevrel, and M. Sergent, *C. R. Acad. Sci., Ser. C* **280,** 949 (1975), p. 951.)

two more in bridging positions, the coordination number of molybdenum is nine. The metal coordination in MoS_2Cl_3 is very similar to that in NbS_2Cl_2 (*347*), the difference in stoichiometry being adjusted by a different bridging mode of the chlorine atoms of $^1_\infty[Mo_2(S_2)_2Cl_4Cl_{4/2}]$ and $^1_\infty[Nb_2(S_2)_2Cl_{8/2}]$, respectively (*215–217*).

$Mo_3S_7X_4$ (X = Cl, Br), monoclinic ($P2_1/c$). Figure 24 shows the asymmetrical unit of the crystal structure. The three, independent molybdenum atoms form an almost equilateral triangle. Six of the seven sulfur atoms occur in three S_2 groups, each one bridging one Mo–Mo

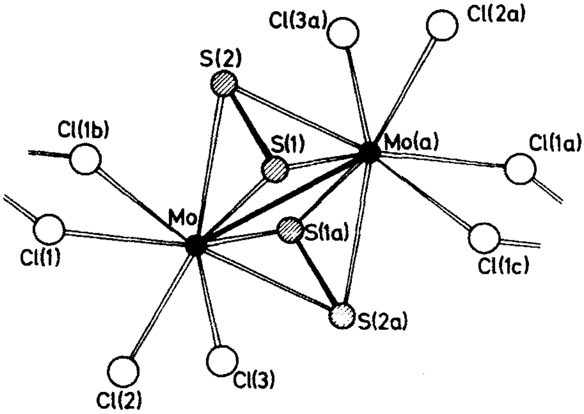


FIG. 23. Two asymmetric units forming the translational element along the *a* axis of MoS_2Cl_3. (Redrawn from J. D. Marcoll, A. Rabenau, D. Mootz, and M. Wunderlich, *Rev. Chim. Miner.* **11,** 607 (1974), Fig. 1, p. 611.)

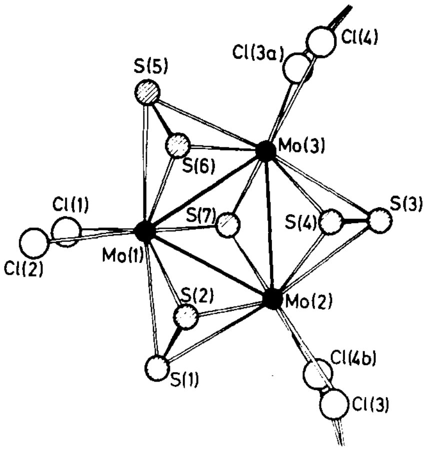


FIG. 24. Asymmetric unit of $Mo_3S_7Cl_4$, including bridging chlorine atoms. (Redrawn from J. D. Marcoll, A. Rabenau, D. Mootz, and M. Wunderlich, *Rev. Chim. Miner.* 11, 607 (1974), Fig. 4, p. 613.)

bond on the same side of the triangular plane. The seventh sulfur is bonded from the opposite side to all three molybdenum atoms. Hence, two chlorine atoms at each molybdenum atom complete the coordination at one Mo in terminal, at the other two in bridging, positions, forming an unlimited, zigzag chain $^{1}_{\infty}[Mo_3S(S_2)_3Cl_2Cl_{4/2}]$ (*215–217* Cl; *215* Br).

$Mo_6Cl_{10}Se$ has an orthorhombic structure, space group Pccn (*273*), and is isostructural with Nb_6I_{11} (*357*). Structure units $Mo_6X'_8$, where a Mo_6 cluster in the form of a strongly deformed octahedron is surrounded by a cube of 8 X′ ($X' = \frac{7}{8}$ I + $\frac{1}{8}$ Se), are linked by bridging I atoms (see Fig. 25). This results in the formula $(Mo_6Cl_7Se)Cl_{6/2}$. The chalcogenide chlorides $Mo_6Cl_{10}Y$ (Y = S, Se, Te) are isotypic (*273*).

4. *Physical Properties*

For reasons mentioned in the previous paragraph, only properties of well-defined phases will be reported.

The thiohalides MoSX are diamagnetic (*269*). In $Mo_4S_4Br_4$, molybdenum transfers 12 electrons to the anions, and 12 electrons remain for the cluster Mo_4, forming a doublet for each edge of the Mo_4 tetrahedron (*269*). The diamagnetism of the compounds of the type $Mo_6Cl_{10}Se$ can be interpreted in a similar way (*273*) from structure considerations. These compounds have been found to be dielectric (*273*).

The compounds of type $Mo_6Y_{8-x}X_x$ are conductors, and exhibit a

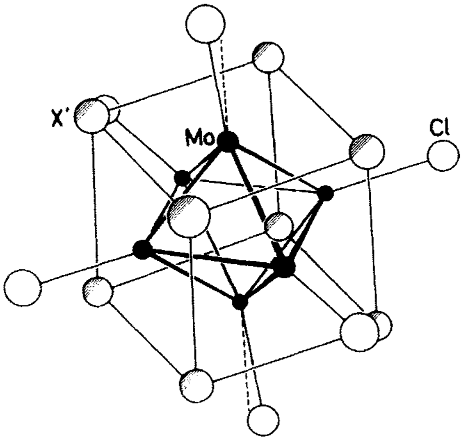


FIG. 25. The group $(Mo_6X'_8)Cl_{6/2}$ (X′ = 7/8 Cl, 1/8 Se) in Mo_6SeCl_{10}. (Redrawn from A. Simon, H. G. v. Schnering, and H. Schäfer, *Z. Anorg. Allg. Chem.* **355,** 295 (1967), Fig. 7, p. 308.)

small paramagnetism (*354*). They belong to the superconducting, Chevrel phases.

5. *Chevrel Phases*

Superconductors having extremely high critical fields have been found in ternary molybdenum chalcogenides (*127*). This class of compounds was first described by Chevrel *et al.* (*83*). The structure may be regarded as being built up by units of Mo_6Y_8, similar to the $Mo_6X'_8$ unit in $Mo_6Cl_{10}Se$ (see the preceding, and Fig. 25), but linked together directly without bridging halogens. In these high-field superconductors, metal elements M are arranged in channels formed by the Mo_6Y_8 units, the ideal formula being $M_xMo_6Y_8$, where x may lie between 0 and 2, depending on M. The superconducting properties of these compounds were discussed on the basis of the number of valence electrons (*354*). The highest critical temperatures T_c have been observed with $PbMo_6S_8$ and $SnMo_6S_8$. Of the 36 electrons of the Mo_6 cluster, 16 are transferred to the 8 S of the Mo_6S_8 unit. As Pb and Sn are supposedly divalent in MMo_6S_8, giving two p electrons to the Mo_6 4d bands, there will be 22 electrons on the Mo_6S_8 cluster in stoichiometric MMo_6S_8.

With the chacogenide halides of molybdenum of the type $Mo_6Y_{8-x}X_x$ (see the preceding), this effect of varying the number of valence electrons is achieved by replacement of the chalcogen of valency 2^- by halogen of valency 1^- of the Mo_6Y_8 unit. In $Mo_6S_6Br_2$ and $Mo_6S_6I_2$, there are, again, 22 electrons per Mo_6 cluster, exactly as in $PbMo_6S_8$. It is not surprising, therefore, that these chalcogenide halides exhibit critical temperatures T_c as high as in $PbMo_6S_8$ (*354*).

C. TUNGSTEN

Only two compounds, $W_2S_7Cl_8$ (*362*) and $W_4S_9Cl_6$ (*97*) are mentioned in the older literature, their true nature being uncertain. The existence of the other compounds in Table XV seems to be well established. All of them were reported by the same group, and, with few exceptions, it remains the only work (*57, 58, 131*). This example illustrates that the lack of information on chalcogenide halides, especially of transition elements, has its main origin in the lack of systematic investigations.

1. *Preparative Methods*

General methods of preparation are summarized in (*58*), and the specific conditions for a particular compound may be found in the references cited next. (*i*) Reaction of a metal halide with sulfur: $WSCl_4$ (*57, 58, 130*). (*ii*) Reaction of metal halides with either Sb_2S_3 or Sb_2Se_3: $WSCl_4$ (*57, 58, 130*); $WSBr_4$ (*57, 58*), $WSeCl_3$ (*58*), $WSeBr_4$ (*58*), $WSCl_3$ (*58, 130*), $WSeBr_3$ (*58*), and $WSBr_2$ (*58*). A variation is the preparation of $WSCl_4$ from WCl_6 and B_2S_3 (*13*) and of WS_2Cl_2 from $WSCl_4$ and Sb_2S_3 in CS_2 (*131*). (*iii*) Chlorination of tungsten sulfides: $WSCl_4$ (*58*). (*iv*) Reaction of metal halides with dry hydrogen sulfide in CS_2: $WSCl_4$, WS_2Cl_2 (*58*). Similarly, WS_2Cl_2 from $WOCl_4$ + H_2S in benzene (*356*). (*v*) Thermal decomposition of tungsten(V) halide sulfides and selenides: $WSCl_2$, $WSeBr_2$ (*58*).

TABLE XV

CHALCOGENIDE HALIDES OF TUNGSTEN: BIBLIOGRAPHY

Compound	Ref.	Compound	Ref.
$W_2S_3Cl_4$	*362*		
$W_4S_9Cl_6$	*97*		
$WSCl_2$	*58*	$WSBr_2$	*58*
$WSCl_3$	*57,58*		
$WSCl_4$	*13,57,58,109,130,359*	$WSBr_4$	*57,58,109*
WS_2Cl_2	*58,131,356*		
$WSeCl_2$	*58*	$WSeBr_2$	*58*
$WSeCl_3$	*58*	$WSeBr_3$	*58*
$WSeCl_4$	*56,58*	$WSeBr_4$	*58*

2. *Chemical Properties*

(*i*) Tungsten(VI) compounds. The compounds $WSCl_4$, $WSBr_4$, $WSeCl_4$, and $WSeBr_4$ are very sensitive to moisture. They can be sublimed *in vacuo,* and are soluble in benzene, carbon tetrachloride, and carbon disulfide (*58*). (*ii*) Tungsten(V) compounds. $WSCl_3$ and $WSeBr_3$ are much less reactive than the hexavalent compounds, and are hydrolyzed only slowly in moist air. They are insoluble in all nonpolar solvents. $WSeBr_3$ disproportionates readily during heating, forming $WSeBr_2$ and $WSeBr_4$. Disproportionation may, therefore, be the reason for lack of success in the preparation of $WSBr_3$ (*58*). (*iii*) Tungsten(IV) compounds. $WSCl_2$ and $WSBr_2$ are insoluble in organic solvents. They are slowly hydrolyzed by moisture (*58*).

3. *Crystallographic Data*

The structures of the tungsten(VI) sulfide halides $WSCl_4$ and $WSBr_4$ have been solved (*109*). Although the two compounds crystallize in different space groups, $P\bar{1}$ and $P2_1/c$ for $WSCl_4$ and $WSBr_4$, respectively, their molecular structures are very similar. As tungsten is in the highest valence state, no metal–metal bonds are formed. In the dimeric structure, each tungsten is 6-coordinate, being bonded to four halogen atoms in a plane with a terminal W=S at right angles to this plane (see Fig. 26). The difference between the structures lies in the arrange-

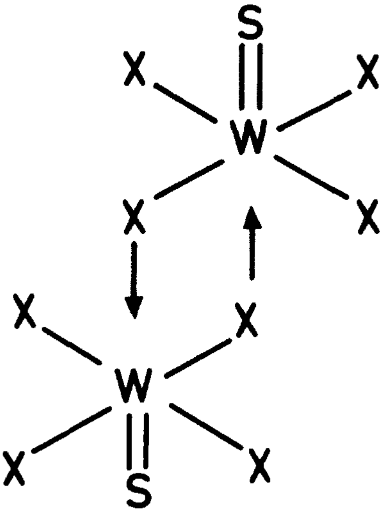


FIG. 26. Structure of WSX_4: dimeric unit of two WSX_4.

ment of the dimeric units. $WSeCl_4$ and $WSeBr_4$ are isomorphous with $WSCl_4$ and $WSBr_4$, respectively (*58, 109*).

4. *Miscellaneous*

IR spectra have been reported for $WSCl_4$ (*13, 57*), and $WSBr_4$ and $WSCl_3$ (*57*). $WSCl_4$ was also the subject of a mass-spectrometric study of the vaporization (*359*). The reaction of $WSeCl_4$ with 1,2-dimethoxyethane has been investigated (*56*).

VIII. Group VIIB

A. MANGANESE

Only two papers have been published about manganese chalcogenide halides, both by Batsanov and Gorogotskaya (*18, 19*). They reacted pink γ-MnS (wurtzite type, tetrahedral coordination) and green α-MnS (rocksalt type, octahedral coordination) with the respective halogens at moderate temperatures (*19*), and obtained two series of sulfide halogenides: γ-$MnSCl_2$, γ-MnSBr, and γ-MnSI; and α-$MnSCl_2$, α-MnSBr, and α-MnSI, respectively. The reaction products were identified as new compounds by their manganese contents and their X-ray powder patterns. The compounds are stable in air, and practically insoluble in water or the common organic solvents. Densities, refractive indices, and molecular reflections were given (*19*).

The reactions of MnSe with the halogens at room temperature or 150–170°C (for iodine) yielded the following selenide halides: MnSeCl, $MnSeBr_2$, and $MnSeI_2$ (*19*). The comparably stable $MnSeI_2$ occurs in two modifications, of which one is cubic, with $a = 6.54$ Å. MnSeCl and $MnSeBr_2$ decompose in water and organic solvents, and are thermally unstable. Heating to 70–100°C leads to formation of Mn_2Se_2Cl and Mn_2SeBr_2. The elimination of "$SeBr_2$" from $MnSeBr_2$ on heating indicates that the compounds $MnSeX_2$ (X = Br, I) are addition products of selenium halides, rather than Mn(IV) compounds. Densities, refractive indices, and X-ray powder data were reported for the more stable compounds (*19*).

B. RHENIUM

The known rhenium chalcogenides are of the composition $ReYX_2$ and $Re_3Se_2X_5$ (Y = S, Se; X = Cl, Br), including $Re_3Te_2Br_5$ (*140, 263, 264, 353, 393*). Additionally, the compounds $Re_2S_3Cl_4$ (*140*) and ReS_2Br

(*353*) are documented in the literature. Chalcogenide iodides of rhenium are not known.

1. *Preparative Methods*

There are three reasonable routes for preparing rhenium chalcogenide halides. Reactions of rhenium chalcogenides (ReS_2, $ReSe_2$, Re_2S_7, and Re_2Te_5) with halogens (Cl_2, Br_2) at elevated temperatures in sealed tubes yield the compounds $ReYCl_2$ (Y = S, Se), $Re_3Y_2Br_5$ (Y = Se, Te), and $Re_2S_3Cl_4$ (*140, 263, 264, 393*). The compounds $ReYX_2$ (Y = S, Se; X = Cl, Br) may also be obtained by the action of chalcogens on rhenium trihalides (*353*). An intermediate in the reaction of $ReBr_3$ with sulfur is ReS_2Br. Fusion of rhenium diselenide with rhenium trihalides at 700–720°C yields the compounds $Re_3Se_2X_5$ (X = Cl, Br) (*264*). The detailed conditions for all of these preparations are summarized in Table XVI.

2. *Chemical Properties*

All of the known rhenium chalcogenide halides are stable in air. With the exception of $Re_2S_3Cl_4$, they are insoluble in water, acids, and the common organic solvents. They dissolve readily in hot, 50% KOH (*263, 264*). $Re_2S_3Cl_4$ is soluble in water, and ethanol, but insoluble in nonpolar organic solvents. With acids, alkalis, or hot water, hydrolytic decomposition takes place. Alkaline solutions can be oxidized to produce perrhenate compounds.

TABLE XVI

PREPARATIVE ROUTES AND EXPERIMENTAL CONDITIONS FOR THE FORMATION OF RHENIUM CHALCOGENIDE HALIDES

Educts	Temperature range (°C)	Specific conditions	Products	Ref.
ReS_2, Cl_2	400–450		$ReSCl_2$, S_2Cl_2	*140,393*
Re_2S_7, Cl_2	100–120	Cl_2 diluted with CO_2	$Re_2S_3Cl_4$, S_2Cl_2	*140*
$ReSe_2$, Cl_2	480–500		$ReSeCl_2$	*264*
$ReSe_2$, Br_2	640–650	28–30 h	$Re_3Se_2Br_5$	*263*
Re_2Te_5, Br_2	60–70		$Re_3Te_2Br_5$, $TeBr_4$	*264*
$ReCl_3$, S			$ReSCl_2$	*353*
$ReCl_3$, Se			$ReSeCl_2$	*353*
$ReBr_3$, S			$ReSBr_2$	*353*
$ReBr_3$, Se			$ReSeBr_2$	*353*
$ReSe_2$, $ReCl_3$	700–720	Sealed ampoule, 10–15 h	$Re_3Se_2Cl_5$	*264*
$ReSe_2$, $ReBr_3$	700–720	Sealed ampoule, 10–15 h	$Re_3Se_2Br_5$	*264*

Treatment of the rhenium sulfide chlorides with an excess of chlorine at temperatures above 450°C results in formation of $ReCl_5$ (*140*). Reduction between 350 and 500°C gives binary rhenium chalcogenides (*139, 262*). Action of water vapor on rhenium sulfide chlorides at 350–500°C produces oxysulfides (*139*).

3. *Crystallographic Data*

The structures of the rhenium chalcogenide halides have not been studied. X-Ray powder data were collected, in order to prove the homogeneity of the compounds (*140, 263, 264, 353*).

IX. Group VIIIB

Only chalcogenide halides of palladium and platinum are mentioned in the literature.

Thiele and co-workers (*389*) prepared the only known palladium chalcogenide halides, PdTeI and Pd_2SeI_3, by hydrothermal synthesis in HI (see Section II,D,2) at 300°C, starting with the elements. Crystalline Pd_2SeI_3 is better obtained by reaction of PdI_2 with Se and an excess of iodine in a closed ampoule at 250°C (reaction time, 2 days).

The brass-colored PdTeI consists of Jahn–Teller distorted $PdTe_{2/2}I_{4/4}$ octahedra, which are interconnected by common edges and corners to afford a loose, spatial network. The compound is considered to be ionic, containing Pd^{3+} and Te^{2-}, although the observed diamagnetism, electronic conduction, and color suggest some metallic character.

In the black, lustrous Pd_2SeI_3, four quadratic $PdSe_{1/2}I_{3/2}$ entities are connected by a common Se_2^{2-} to a $Pd_4Se_2I_4I_{4/2}$ group (see Fig. 27). These groups combine via common iodines to form corrugated layers. The formal oxidation state of Pd is 2+.

No platinum chalcogenide halides of invariable, exact, stoichiometric compositions are known.

Batsanov *et al.* (*23*) reacted sulfur with $PtCl_2$ and $PtBr_2$ by heating mixtures of the reactants in evacuated, sealed ampoules. At 100–200°C after 12–24 h, sulfide chlorides $PtCl_xS_y$ ($1.70 \le x \le 2$; $0.6 \le y \le 3.35$) and sulfide bromides $PtBr_xS_y$ ($1.87 \le x \le 2.06$; $0.84 \le y \le 1.80$) were formed. The compositions depended on the initial PtX_2:S ratio, and the temperature. At 320–350°C, loss of chlorine led to the compounds $PtClS_y$ ($1.7 \le y \le 1.9$). According to their X-ray powder patterns, all of these products retained the main structural features of the original platinum halides. From considerations of molar volumes, the authors deduced the presence of polysulfide anions.

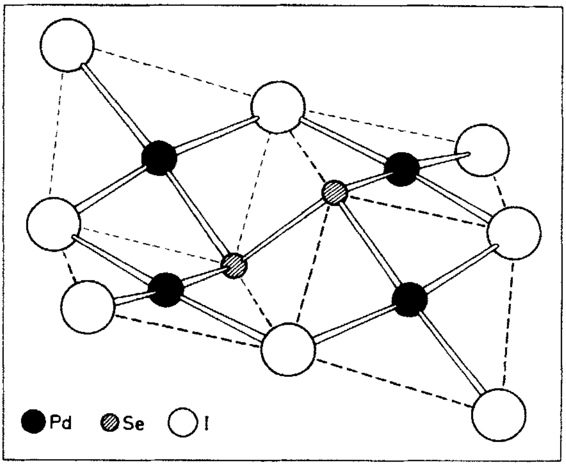


FIG. 27. $Pd_4Se_2I_4I_{4/2}$ unit of the structure of Pd_2SeI_3. (Redrawn from G. Thiele, M. Köhler-Degner, K. Wittmann, and G. Zoubek, *Angew. Chem.* **90**, 897 (1978), Fig. 2, p. 898.)

Thiele and co-workers, who tried to prepare platinum chalcogenide halides, could neither isolate nor identify any pure, homogeneous compound (*389*).

X. Group IIIA

With few exceptions, the compositions of the chalcogenide halides of the Group IIIA elements correspond to the general formula MYX (M: IIIA metal, Y: chalcogen, X: halogen). But, despite this uniformity, the structures and properties vary considerably with the metal atom, reflecting the general trends of chemical behavior within this group. The semimetal boron forms covalent, organiclike BYX (Y = S, Se; X = Cl, Br, I) and $B_2S_3X_2$ (X = Cl, Br, I) compounds, which are liquids or volatile solids having molecular structures. With decreasing electronegativity of the metal atom, the ionic character of the compounds increases, along with a gain in thermal and chemical stability, which reach a maximum for indium. The low stability of the TlYX compounds (Y = S, Se; X = Cl, Br, I) may be ascribed to the inert, electron-pair effect, which favors the oxidation state +1 for thallium. Therefore, thallium also forms chalcogenide halides of Tl(I). TlTeX compounds are not known.

A. BORON

As already mentioned, the boron chalcogenide halides are covalent, organiclike compounds. The sulfide halides $B_3S_3X_3$ (X = Cl, Br, I) (*345, 409–411*) and $B_2S_3X_2$ (X = Cl, Br, I) (*343–345*), as well as $B_2Se_3I_2$ (*346*), form five- or six-membered rings. They are liquids or low-melting solids that readily dissolve in many organic solvents. The boron selenide halides BSeX (X = Cl, Br, I) (*91, 152*) are solids that do not dissolve in organic solvents, and decompose without melting. Their degree of polymerization therefore seems to exceed the value of three. Because of their organiclike nature, the boron chalcogenide halides will not be considered in detail.

B. ALUMINUM

Aluminum forms a complete series of AlYX compounds (Y = S, Se, Te; X = Cl, Br, I). Furthermore, a number of compounds with Se(IV) and Te(IV) are known, such as $TeCl_3^+$ $AlCl_4^-$ (*197*) and $SeCl_3^+$ $AlCl_4^-$ (*364*), which are not considered here. A borderline case consists in the reduced phases found in the systems ($TeCl_4 + 4AlCl_3$)–Te and ($SeCl_4$ + $4AlCl_3$)–Se (*88*), e.g., Te_4^{2+} $(AlCl_4^-)_2$ (*89*), Te_6^{2+} $(Al_2Cl_7^-)_2$ (*89*), Te_6^{2+} $(AlCl_4^-)_2$ (*88*), Se_4^{2+} $(AlCl_4^-)_2$ (*88*), and Se_8^{2+} $(AlCl_4^-)_2$ (*87*), which contain cyclic polytellurium and polyselenium cations. For a detailed review of homopolyatomic ions of the posttransition elements, see (*86*).

1. *Preparative Methods*

The compounds AlYX are best prepared by direct reaction between the respective aluminum halide and chalcogenide in a sealed ampoule at 350°C. The reaction is complete after 2 weeks. In the case of the iodides, a mixture of Al and I_2 (molar ratio 3:10) is used instead of AlI_3. Other preparative methods, such as the reaction of an aluminum halide with Zn or Cd chalcogenide, or with the chalcogen itself, are applicable to the bromide and chloride only, and give poor yields (15–20%) (*158, 159, 266, 327, 328*).

Growth of single crystals. Crystals of the aluminum selenide halides (needles, maximum length 15 mm) were grown by vapor transport in sealed ampoules between two temperatures (380 and 320°C for AlSeCl, and 350 and 300°C for AlSeBr and AlSeI) over a period of two months. A large excess of the halogenide was used (*266*).

2. *Chemical Properties*

The colorless, hygroscopic compounds AlYX are insoluble in common organic solvents. They decompose into the corresponding halide and chalcogenide at temperatures between 280 (AlYI) and 400°C (AlYCl). With water vapor, hydrolysis to $Al(OH)_3$ occurs. In the case of the sulfide halides, the intermediate oxide halide can be isolated. With oxygen γ-Al_2O_3 is formed at temperatures between 25 (AlTeI) and 200°C (AlSCl). Again, the sulfide halides, which are more inert against oxygen than the other compounds, react via an intermediate oxide halide. Reaction with chlorine leads to the formation of $AlCl_3$. With NH_3, chalcogenide amides of the general formula $AlY(NH_2)\cdot NH_3$ are obtained (*158, 159, 266, 327, 328*).

3. *Crystallographic Data*

AlSCl has an orthorhombic structure, with the lattice constants $a = 8.09$, $b = 10.52$, $c = 3.86$ Å, and $Z = 4$. It is probably isotypic with SbSCl and BiSCl, crystallizing in a layer type of lattice (*157*) (see Section XII,C,5). The selenide halides are monoclinic, with the probable space-group $P2_1/m$. The lattice constants are given in Table XVII. The constancy of the b parameters for all three compounds suggests the general presence of an Al–Se chain extending in that direction (*266*).

Structural data, except powder patterns, for the other compounds are not known.

C. GALLIUM

Like aluminum, gallium forms a series of GaYX compounds (Y = S,Se,Te; X = Cl,Br,I) (*160*). Hardy and Cottreau (*165*) noticed that at least GaSCl and GaSBr do not correspond exactly to this stoichiometry. These phases are halogen-rich, according to the formula $Ga_9S_8X_{11}$ (X = Cl,Br).

TABLE XVII

CRYSTALLOGRAPHIC DATA FOR ALUMINUM CHALCOGENIDE HALIDES

Compound	Symmetry	a (Å)	b (Å)	c (Å)	β (degrees)	Z	d_{ex} (g/cm^3)	Ref.
AlSCl	Orthorhombic	8.09	10.52	3.86		4	1.87	*157*
AlSeCl	Monoclinic	16.33	12.87	18.172	94.0	4	2.43	*266*
AlSeBr	Monoclinic	16.97	12.87	18.731	94.0	4	2.98	*266*
AlSeI	Monoclinic	18.11	12.87	19.973	94.0	4	3.30	*266*

1. *Preparative Methods*

The chalcogenide bromides and chlorides may be prepared by the reaction of the halide with the respective chalcogenide in a sealed ampoule. A mixture of gallium metal and chalcogen may be used, instead of the chalcogenide. The chalcogenide iodides are synthesized directly from the elements. The exact preparative conditions are listed in Table XVIII (*160, 165*).

Growth of single crystals. $Ga_9S_8Cl_{11}$ and $Ga_9S_8Br_{11}$ have been obtained as needle-shaped, single crystals, 40–50 mm long. They were prepared by the reaction of Ga, S, and an excess of the halogenide at 400 ($Ga_9S_8Cl_{11}$) or 450°C ($Ga_9S_8Br_{11}$) (*165*).

2. *Chemical Properties*

The gallium chalcogenide halides are hygroscopic compounds that decompose (without melting) at temperatures between 240 and 380°C to a mixture of chalcogenide and halide (see Table XVIII). The telluride halides are yellow, and the other compounds are colorless (*160, 165*).

TABLE XVIII

PREPARATION AND PROPERTIES OF GALLIUM CHALCOGENIDE HALIDES

Compound	Preparation[a]	Temperature (°C)	Time (days)	Temperature of decomposition (°C)	d_{ex} (g/cm^3)	Ref.
GaSCl	A,B	260	14	250–260	2.96	*160*
$Ga_9S_8Cl_{11}$	A	250	0.1	400	2.52	*165*
	B		14–21			
GaSBr	A,B	305–345	14	360–370	3.37	*160*
$Ga_9S_8Br_{11}$	A	330	0.1	450	3.20	*165*
	B		14–21			
GaSI	C	300	10–15	370–380	3.74	*160*
GaSeCl	A,B	260	8–12	240–250	3.54	*160*
GaSeBr	A,B	300–340	12–15	280–290	3.96	*160*
GaSeI	C	300	14–21	320–330	4.23	*134,160*
GaTeCl	A,B	260–270	10–15	230–240	4.17	*160*
GaTeBr	A,B	260–270	10–15	250–260	4.83	*160*
GaTeI	C	260–280	5–10	240–250	4.75	*160*
				800		*200*

[a] A: $GaX_3 + Ga_2Y_3$; B: $GaX_3 + 2\ Ga + 3Y$; C: from the elements.

3. *Crystallographic Data*

$Ga_9S_8Cl_{11}$ and $Ga_9S_8Br_{11}$ are monoclinic; probable space-group P2/m, $Z = 20$. The lattice constants are $a = 17.74$ and 18.15, $b = 58.9$ and 59.65, $c = 18.92$ and 19.88 Å, and $\beta = 122.2$ and 121.5° for the chloride and bromide, respectively (*165*).

D. INDIUM

Again, the complete series of InYX compounds (Y = S,Se,Te; X = Cl,Br,I) exists. Of the Group IIIA chalcogenide halides, the indium compounds have been the most extensively studied.

1. *Preparative Methods*

Indium chalcogenide chlorides and bromides are obtained by heating mixtures of the chalcogenide and the halide in sealed ampoules to temperatures between 200 and 420°C (see Table XIX). For the preparation of the chalcogenide iodides, In and I_2 are used instead of InI_3. InTeI may be synthesized directly from the elements (*161*).

The preparation conditions are listed in Table XIX. InTeCl and InTeI may also be obtained by fusing stoichiometric mixtures of Te and InCl, or InI (*80, 331*).

Growth of single crystals. Single crystals of the selenide and telluride halides can be grown by recrystallization at 360–390°C, or sublimation at 420 (InSeCl) and 370°C (InTeI), respectively (*162*).

TABLE XIX

PREPARATION AND PROPERTIES OF INDIUM CHALCOGENIDE HALIDES

Compound	Preparation[a]	Temperature (°C)	Time (days)	Color	d_{rx} (g/cm³)	Ref.
InSCl	A	200–225	35	Light grey	3.68	*161,162*
InSBr	A	200–225	35	Light grey	4.32	*161,162*
InSI	B	170–190	14	Yellow	4.11	*161,162*
InSeCl	A	400–420	14	Dark yellow	4.52	*161,162*
InSeBr	A	380–440	14–20	Dark brown	5.11	*161,162*
InSeI	B	380–400	7–14	Light yellow	4.69	*161,162*
InTeCl	A	400–410	14	Brown	4.52	*81,161,162*
InTeBr	A	380–420	14–20	Yellow-brown	4.40	*161,162*
InTeI	C	350–400	8–14	Red-brown	5.07	*80,161,162*

[a] A: $InX_3 + In_2Y_3$; B: $In_2Y_3 + In + 3/2\ I_2$; C: from the elements.

2. *Chemical Properties*

The indium chalcogenide halides are more stable than their aluminum and gallium analogs. Thus, only the sulfide halides are moisture-sensitive, and must be kept and handled under an inert-gas atmosphere. Generally, the chemical stability increases in the orders $S < Se < Te$ and $I < Br < Cl$. The indium chalcogenide halides are only slowly, if at all, attacked by water. With strong acids, decomposition, usually accompanied by evolution of H_2Y gas, takes place. The attack of hot bases leads to the formation of $In(OH)_3$. Only the sulfide halides decompose before melting. The thermal behavior is described in (*80, 81, 161*). At elevated temperatures, all of the compounds become air-sensitive. InTeCl, the most stable one, is oxidized in air at 360°C, but is stable up to 680°C under argon (*81*).

3. *Phase Diagrams*

Safonov *et al.* (*331*) determined the liquidus surface of the ternary In–Te–Cl system by DTA, X-ray diffraction, and crystal optical methods. Only one ternary compound, InTeCl, exists. The crystallization field of InTeCl occupies 6% of the diagram, which demonstrates the considerable thermodynamic stability of this compound. InTeCl melts congruently at 453°C. It forms part of the two pseudobinary systems In_2Te_3–$InCl_3$ and InCl–Te (*81*). Whereas the first consists of the two eutectic parts In_2Te_3–InTeCl and InTeCl–$InCl_3$, the latter is more complicated. It is composed of the monotectic system InTeCl–InCl and the eutectic system Te–InTeCl, where tellurium forms a solid solution with InTeCl containing from 100 to 82 atom% of Te at the eutectic temperature (*81*).

Safonov *et al.* (*330*) also investigated the In–Te–I system by DTA and X-ray diffraction. The system contains three, congruently melting, ternary compounds: InTeI, $InI_3 \cdot 2TeI_4$ and $InI_3 \cdot 3TeI_4$, of which the latter two are out of the scope of this review. InTeI melts congruently at 475°C. It forms part of the quasibinary cuts In_2Te_3–InI_3 and InI–Te, where the sections InTeI–In_2Te_3, InTeI–InI_3, InTeI–InI, and InTeI–Te are all of the eutectic type (*80*).

4. *Crystallographic Data*

InSCl, InSBr, InSeCl, and InSeBr are isotypic, and crystallize in the hexagonal $CdCl_2$ lattice type. The halide and chalcogenide ions are statistically distributed among the Cl sites. As in $CdCl_2$, the bonding within the $InY_{3/3}X_{3/3}$ octahedra should be predominantly ionic (*162*).

The symmetry of the isotypic compounds InSI and InSeI is tetragonal (*162*).

The telluride halides crystallize in monoclinic lattices, but only InTeBr and InTeI are isotypic (*162*). InTeCl forms a layer type of structure, as do InSCl and its analogs, but, owing to the size of the Te atom and the enhanced covalency of the In–Te bond, only a coordination number of 4 for indium is realized. The structure is built up of strongly distorted, $InTe_{3/3}Cl_{1/1}$ tetrahedra that share the corners and edges occupied by Te atoms. The Cl atoms are coordinated to one tetrahedron each, and do not take part in the layer formation (*324, 325*).

The crystallographic data are summarized in Table XX.

E. Thallium

Three groups of thallium chalcogenide halides have been reported, corresponding to the formulas TlYX (Y = S,Se;X = Cl,Br,I) (*22*), Tl_4YCl_4 (Y = S,Se) (*321*), and Tl_2YX_4 (Y = S,Se;X = Br,I) (*21*). Thallium telluride halides are not known.

1. *Preparative Methods*

The sulfide halides TlSX are prepared by heating a stoichiometric mixture of the thallium halogenide and sulfur in a sealed ampoule at 180°C for 30 h. The mixture is then slowly cooled to room temperature. The compounds TlSeX are obtained by reaction between thallium metal and selenide halide at 280°C during 40 h (*22*). On heating TlYCl to 500°C *in vacuo*, the compounds Tl_4YCl_4 result (*321*). Dissolution of

TABLE XX

Crystallographic Data for Indium Chalcogenide Halides

Compound	Symmetry	*a* (Å)	*b* (Å)	*c* (Å)	*β* (degrees)	*Z*	Ref.
InSCl	Hexagonal	3.728		17.78		3	*162*
InSBr	Hexagonal	3.820		18.59		3	*162*
InSI	Tetragonal	18.28		9.96		32	*162*
InSeCl	Hexagonal	3.860		18.58		3	*162*
InSeBr	Hexagonal	3.935		19.13		3	*162*
InSeI	Tetragonal	18.70		10.15		32	*162*
InTeCl	Monoclinic	7.42	14.07	7.13	92.1	8	*162*
		7.42	14.06	7.07	92.1	8	*324,325*
InTeBr	Monoclinic	7.350	7.577	8.343	117.61	4	*434*
InTeI	Monoclinic	8.42	7.73	7.44	94.3	4	*162*

Tl_2S in an alcoholic Br_2 solution, and evaporation of the solvent, yields Tl_2SBr_4. The same procedure with iodine gives Tl_2SI_4. Tl_2SeBr_4 is prepared by the action of Br_2 on powdered Tl_2Se, whereas I_2 and Tl_2Se, heated together in a sealed tube at 140°C for 40 h, form Tl_2SeI_4 (*21*).

2. *Miscellaneous*

The compounds TlYX are insoluble in water and organic solvents. Decomposition with oxidizing acids and bases leads to segregation of the chalcogen. On heating, disintegration into Tl(I) halide and chalcogen takes place between 96 and 132°C (*22*). The decomposition is incomplete for the chlorides, which form Tl_4YCl_4 (*321*). The electric conductivity of Tl_2S–TlCl melts has been measured (*404*).

Tl_4SCl_4 and Tl_4SeCl_4 melt at 440 and 442°C, respectively. They can be distilled between 650 and 700°C without decomposition. They are insoluble in H_2O and organic solvents, but soluble in aqueous alkaline solutions. With conc. acids, decomposition takes place. The electric conductivity has been determined to be $1.4 \cdot 10^{-7}$ and $2.1 \cdot 10^{-7}\ \Omega^{-1}\ cm^{-1}$ for Tl_4SCl_4 and Tl_4SeCl_4, respectively. The probable structural formula is $Tl_3(TlCl_4Y)$. The compounds thus, presumably, consist of $Tl_{1/4}Cl_{4/4}Y_{2/8}$ octahedra that are interconnected by the chalcogen atoms to linear chains (*321*).

The Tl_2YX_4 compounds are all hygroscopic. The greenish-yellow Tl_2SBr_4 reacts with water, or HCl, to give $TlBr_2$. The black-violet iodine derivatives are insoluble in these solvents. Organic solvents tend to wash the halogen away (*21*).

XI. Group IVA

A. CARBON, SILICON, AND GERMANIUM

For these three elements, for the first time in this Chapter, combinations of a nonmetal with chalcogens and halogens have to be discussed. As regards their structure and properties, most of these do not belong to the field of this review as described in the introductory Chapter. For those interested in the ternary carbon compounds that have the composition CSX_2 (X = Cl, Br, I), information may be found in an issue of "Gmelin" (*142*).

Only sulfide chlorides of silicon have thus far been described (e.g., *143*). Among these, a nonvolatile compound, $Si_2S_3Cl_2$, was mentioned (*351*), but no details were given. Areas of vitrification have been found in the systems Si–S–Br (*185*), Si–S–I (*185*), Si–Se–Br (*185*), and Si–

Se–I (*100, 185*). These chalcogenide halide glasses belong to the so-called "semiconducting glasses" that have attracted much attention in solid-state physics, because of their physical properties (see Section XII,B); they are, however, not treated in this review.

The tendency to glass formation is even more pronounced in the systems containing germanium, such as Ge–S–Br (*185*), Ge–S–I (*77, 99, 185*), Ge–Se–Br (*185*), Ge–Se–I (*100, 185*), and Ge–Te–I (*118*). In these systems, such phases as $GeSI_2$ (*99, 185, 278*), $GeSeI_2$ (*100, 185*), $Ge_2Se_3I_2$ (*100*), and Ge_2SeI_6 (*100*) have been investigated, and some of them can be recrystallized, to yield individual compounds. A germanium sulfide bromide, $Ge_4S_6Br_4$, and, probably, the homologous iodide were discovered by Pohl (*275*). The almost colorless bromide, which decomposes at 305°C, has a molecular structure. According to their phase diagrams (*213, 254*), GeS and GeI_2 do not form ternary compounds.

B. TIN

The first chalcogenide halides of tin were reported in 1963 (*24*). Although numerous publications since then have been devoted to this subject, the existence and true composition of some the compounds described here still seem questionable. It is, therefore, advisable to start with a discussion of the systems $SnY–SnX_2$ ($Y = S, Se, Te$; $X = Cl, Br, I$).

1. *Phase Diagrams*

a. SnS–SnX₂. The systems $SnS–SnX_2$ are presented in Fig. 28 (*48, 144*); however, the discussion that follows should be noted. SnS and $SnCl_2$ form a simple eutectic system without any ternary phase (*48, 231*). In the eutectic system $SnS–SnBr_2$, an incongruently melting compound having the approximate composition $Sn_9S_2Br_{14}$ was reported by Blachnik and Kasper (*48*). For this compound, however, Thevet *et al.* (*386*), gave the composition Sn_2SBr_2 and a hexagonal structure (*385*). The composition $Sn_7S_2Br_{10}$ has since been claimed, from a single-crystal measurement for the ternary compound, and it was claimed to be isostructural with $Pb_7S_2Br_{10}$ (*104*). The situation as regards the eutectic system SnS–SnI is even more complicated. Novoselova *et al.* (*253*) claimed the formation of the compounds Sn_3SI_4 and $Sn_7S_3I_8$, melting incongruently at 330 and 410°C, respectively, the first of which exhibited an additional, thermal effect at 266°C. Their phase diagram is included in Fig. 28 (*48*). By contrast, the phase diagram published by Thevet *et al.* (*386, 388*) differed with respect to the composition, not only of the eutectic but also of the ternary phase. The latter compound,

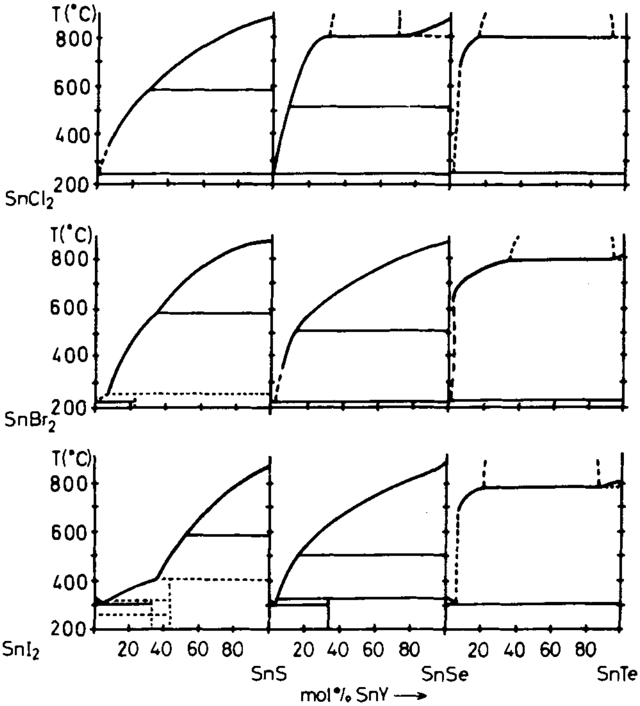


FIG. 28. Systems SnY–SnX_2 (Y = S, Se, or Te; X = Cl, Br, or I). (Redrawn from R. Blachnik and F. W. Kasper, *Z. Naturforsch.* **29B**, 159 (1974), Fig. 2, p. 160; and R. Blachnik and G. Kudermann, *Z. Naturforsch.* **28B**, 1 (1973), Fig. 1, p. 2.)

Sn_2SI_2, was said (*385*) to exist in an α and a β form. The crystal structures of both forms have been elucidated (*119, 239, 240, 388*). Apart from questions that still remain concerning the true relationship of α- and β-Sn_2SI_2, a publication by Fenner (*121*) on the synthesis and structure of a new ternary phase, Sn_4SI_6, contradicts both of the phase diagrams already mentioned.

b. SnSe–SnX₂. All systems belong to the eutectic class, the system SnSe–$SnCl_2$ being of the monotectic type (see Fig. 28). The compound Sn_4SeBr_6 is mentioned in the literature (*104*), and Blachnik and Kasper (*48*) reported the peritectic compound Sn_3SeI_4, the composition of which has been confirmed by Thevet *et al.* (*387*), correcting an earlier (wrong) composition of Sn_2SeI_2 (*385*).

c. SnTe–SnX₂. All three systems are of the monotectic type (see Fig. 28) and show no ternary. A ternary compound of the composition Sn_4TeBr_6 has, however, been reported (*104*).

d. Sn(IV) Compounds. In the literature the, following compounds with the oxidation state +4 for tin were reported, and identified as single phases by X-ray patterns (*24*):$Sn_2Cl_2S_3$ (*16, 24*), $Sn_3Se_5Cl_2$, and $Sn_4Te_7Cl_2$ (*16, 24*). No compounds have been found in the systems SnS_2 $-SnI_4$ (*383*).

2. *Preparative Methods*

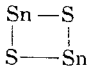
All tin(IV) compounds may be obtained by annealing stoichiometric mixtures of the binary tin compounds in closed ampoules. α-Sn_2SI_2 can only be obtained free from the β-phase by applying an excess of SnI_2 at a temperature below 350°C (*388*). An excess of SnI_2 cannot be removed from α-Sn_2SI_2 by sublimation without transforming the α into the β form (*388*).

Tin(IV) chalcogenide chlorides are obtained by oxidation of $SnCl_2$ with the respective chalcogen (*24*). For $Sn_2Cl_2S_3$, the chloride and sulfur, in the ratio of 1:1, or 1:2, are heated in sealed tubes at 140–150°C for 8 hours. The volatile by-products $SnCl_4$ and SCl_2 are removed in a vacuum desiccator. In a similar way, $Sn_2Cl_2Se_5$ and $Sn_4Cl_2Te_7$ are obtained by fusing 1:1 mixtures of $SnCl_2$ and Se, or Te, at 240 and 480°C, respectively.

3. *Crystallographic Data*

Table XXI shows the crystallographic data as far as they are known. The structures of the three sulfide iodides have been determined by single-crystal studies. Powder patterns of the Sn(IV) compounds not given here have been reported elsewhere (*24*).

a. SnS_2I_2. The structures of the α and β modification are similar, and contain common, structure elements. A detailed description is therefore restricted to β-SnS_2I_2. This orthorhombic structure (see Table XXI), published independently by two groups (*119, 240, 388*), is built up of $(Sn_4S_2I_4)_\infty$ ribbons extending in the direction of the shortest axis (the b-axis). The main part of such an arrangement is a folded ribbon formed of



groups with outward-pointing SnI_2 (see Fig. 29). Tin forms five, sulfur two, and iodine two or four, bonds, respectively. The coordination of tin may be considered to be a deformed octahedron, the sixth coordinate

TABLE XXI

CRYSTALLOGRAPHIC DATA FOR TIN(II) CHALCOGENIDE HALIDES

Compound	Symmetry	Space group	a (Å)	b (Å)	c (Å)	β (degrees)	Z	Ref.
α-Sn_2SI_2	Monoclinic	B2/m	14.305	17.281	4.435	110.47	6	*239,388*
β-Sn_2SI_2	Orthorhombic	Pnma	17.475	4.412	25.390		12	*119,240,388*
Sn_4SI_6	Monoclinic	C2/m	14.129	4.425	25.15	93.42	4	*121*
Sn_2SBr_2	Hexagonal		12.239		4.390		4	*385*
Sn_3SeI_4	Tetragonal	$P4_2/nmc$	8.455		15.87		4	*387*
$Sn_7S_2Br_{10}$	Hexagonal	$P6_3/m$ or $P6_3$	11.35		4.40		1	*104*
Sn_4SeBr_6	Orthorhombic	Pnma or $Pn2_1a$	8.74	4.15	10.50			*104*
Sn_4TeBr_6	Orthorhombic	Pnma or $Pn2_1a$	8.95	4.22	10.65			*104*

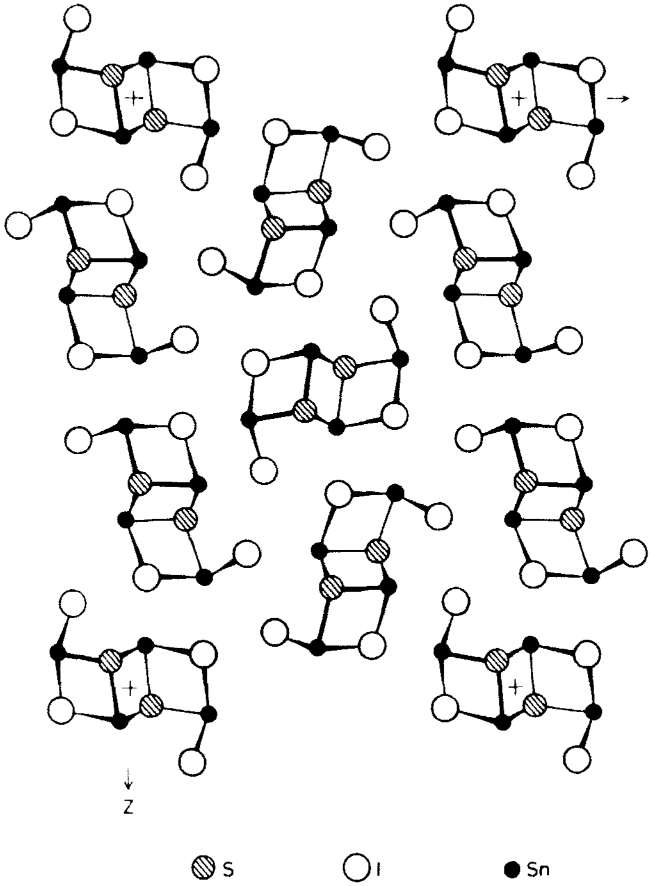


FIG. 29. Structure of β-Sn_2SI_2. (Redrawn from J. Fenner, *Naturwissenschaften* **63**, 244 (1976), Fig. 1, p. 244.)

being represented by a relatively distant iodine. If the longest Sn–I distance of this octahedron that exceeds the common bonding-length is neglected, a truncated quadratic pyramid is obtained that has tin below the basal plane (see Fig. 30). Two types of such pryamids exist, those in which (*A*) the base consists of four I atoms and the apex of an S atom, and (*B*) the base consists of two I atoms and two S atoms, the apex being a third S atom. The pyramids of type *A* are connected with those of type *B* in two ways: by a face consisting of S and I atoms, and by a vertical edge of S atoms. Whereas the pyramids of type *B* are interconnected by a face consisting of S atoms, the pyramids of type *A* do not share common atoms. In the structure of β-Sn_2SI_2, hexagonal

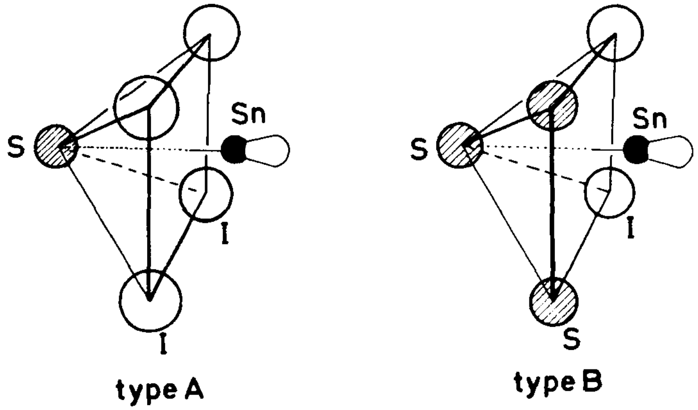


FIG. 30. Pyramids of type A and B, including the lone-electron pair. (Redrawn from Nguyen-Huy-Dung and F. Thevet, *Acta Cryst.* **B32,** 1112 (1976), Fig. 3, p. 1114.)

channels of iodine exist that contain tin and sulfur in an ordered arrangement. The structure elements just described are also found in the monoclinic α-Sn_2SI_2 (*239, 388*). The main difference consists in the occupation of the vast, hexagonal, iodine channels which, in the α modification, should contain tin and sulfur statistically distributed on the same crystallographic sites. Although the authors used this argument for explaining the possibility of a deviation from stoichiometry (*239*), this unusual result requires further discussion. With the exception of the tin atoms in the hexagonal channels, each tin has the same pyramidal environment as in SnS and SnI_2, the binary constituents of the phase diagram.

b. Sn_4SI_6. In addition to structure elements of β-Sn_2SI_2, the third ternary compound, Sn_4SI_6, contains domains of pure SnI_2 (Sn_6I_{12}), as shown in Fig. 31 (*121*). The structure may be considered to be a variety of the SnI_2 structure, with layers perpendicular to the *c* axis. Sulfur is built into these layers in such a way that structure elements of β-Sn_2SI_2 are formed (*121*).

4. *Physical Properties*

The ^{119}Sn Mössbauer data for $Sn_7S_2Br_{10}$, Sn_4SeBr_6, and Sn_4TeBr_6 have been measured, and compared with those of the parent halides and chalcogenides. The data are consistent with a random distribution of halide and chalcogenide anions (*104*). Thus far, the reflection spectra of a few tin(IV) compounds assumed to be semiconductors have

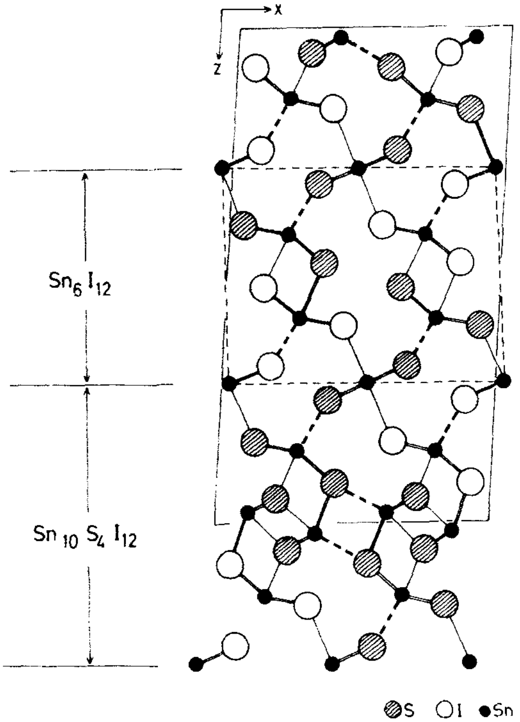


FIG. 31. Structure of Sn_4SI_6. (Redrawn from J. Fenner, *Z. Naturforsch.* **33B**, 479 (1978), Fig. 1, p. 480.)

been measured. The following, optical band-gaps, ΔE, have been reported: $Sn_2S_3Cl_2$, 2.7 eV; $Sn_3Se_5Cl_2$, 1.5 eV; and $Sn_4Te_7Cl_2$, 1.1 eV (*16*).

C. LEAD

Although the phase diagrams of all of the systems $PbY-PbX_2$ ($Y = S, Se, Te$; $X = Cl, Br, I$) have been published (see Fig. 32), contradictory data are to be found in the literature with respect to the existence and composition of ternary phases. Only four of them could be identified by structure determinations. They are summarized in Table XXII.

1. Phase Diagrams (Fig. 32)

a. Lead Sulfide Halides. The phase diagrams $PbS-PbBr_2$ (*247, 249, 302*) and $PbS-PbI_2$ (*247, 248, 302*) are of the peritectic type, with

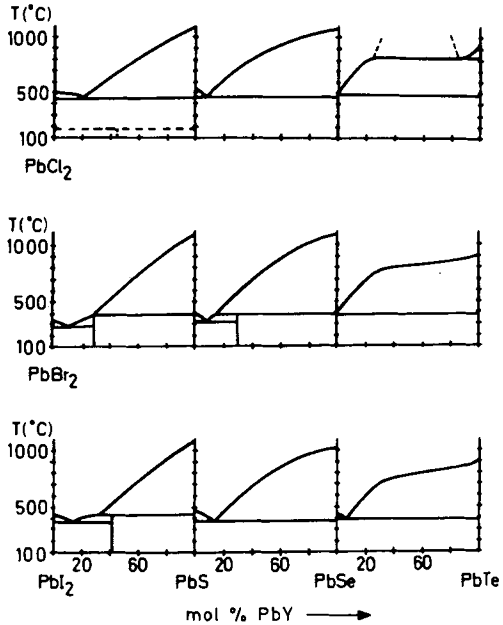


FIG. 32. Phase diagrams of the systems PbY–PbX_2 (Y = S, Se, or Te; X = Cl, Br, or I). (Redrawn from A. V. Novoselova, I. N. Odin, and B. A. Popovkin, *Russ. J. Inorg. Chem.* 14, 1402 (1969), Fig. 1, p. 1403.)

$Pb_7S_2Br_{10}$ and $Pb_5S_2I_6$ as the only thermodynamically stable lead sulfide halides. They decompose peritectically at 381°C ($Pb_7S_2Br_{10}$) and 418°C ($Pb_5S_2I_6$), and their composition has been confirmed by structure analyses. No compound exists in the eutectic system PbS–$PbCl_2$ (*26, 302, 394, 401, 412*). A phase having the composition Pb_4SCl_6, which is isotypic with Pb_4SeBr_6 (*196, 302*), can, however, be obtained by quenching a melt of this composition, and it may be stable at tempera-

TABLE XXII

CRYSTALLOGRAPHIC DATA FOR LEAD CHALCOGENIDE HALIDES

Compound	Symmetry	*a* (Å)	*b* (Å)	*c* (Å)	*β* (degrees)	*Z*	Space group	Ref.
Pb_4SCl_6[a]	Orthorhombic	4.23	14.96	9.22		2	Imm2	*196,302*
$Pb_7S_2Br_{10}$	Hexagonal	12.273		4.319		1	$P6_3/m$	*196*
$Pb_5S_2I_6$	Monoclinic	14.338	4.437	14.552	98.04	2	C2/m	*196*
Pb_4SeBr_6	Orthorhombic	4.361	15.780	9.720		2	Imm	*196*

[a] Structure not determined; isotypic with Pb_4SeBr_6.

tures below 180°C (*247, 250, 302*). All other lead sulfide halides mentioned in the literature seem to be metastable with respect to the binary phases. Typically, they are found as precipitates obtained from lead salts in solution. Thus far, only some of them have been identified as single phases by their X-ray patterns, as, for instance, $Pb_3S_2Br_2$ [$2PbS{\cdot}PbBr_2$, (*302*)], Pb_2SI_2, and Pb_2SBr_2 (*164*). Such "precipitation reactions" were discussed in (*203*) and (*302*). The numerous reports that appeared before 1964 are cited in (*145*).

b. Lead Selenide Halides. No ternary compound exists in the eutectic systems $PbSe-PbCl_2$ (*247, 250*) and $PbSe-PbI_2$ (*246, 247*). The only stable lead selenide halide has been found in the peritectic system $PbSe-PbBr_2$ (*247, 249*), but, in contrast to the data in these studies, the true composition of the ternary is Pb_4SeBr_6, as has been shown by the synthesis of single crystals (*302*) and a structure determination (*196*).

c. Lead Telluride Halides. No ternary compounds have been observed in the systems that PbTe forms with $PbCl_2$ [monotectic (*247, 252*)], $PbBr_2$ [eutectic (*247, 249*)], and PbI_2 [eutectic (*43, 247, 251*)]. The same holds for the systems PbI_2-TeI_4 [eutectic (*212, 332*)], PbI_2-Te (*256*), and PbTe–I [not quasibinary (*211*)]. In the eutectic system $PbTe-TeI_4$, an incongruently melting compound having the composition $Pb_3Te_5I_8$ has been observed, and confirmed as a single phase by X-ray diffraction (*42*).

2. *Preparative Methods*

The stable compounds $Pb_7S_2Br_{10}$, $Pb_5S_2I_6$, Pb_4SeBr_6, and $Pb_3Te_5I_8$ can be obtained in a polycrystalline form by annealing stoichiometric amounts of the binary phases just below the peritectic temperatures of 381, 418, 383, and 385°C, respectively. Pure, and well-recrystallized, Pb_4SCl_6 is formed by quenching a melt of the composition $PbS{\cdot}3PbCl_2$ after annealing at 600°C (*302*). Single crystals of the sulfide and selenide halides can be prepared by hydrothermal syntheses in the respective hydrohalic acids (*300, 302;* see also, Section II,D,2). The crystallization conditions of $Pb_5S_2I_6$ in the system $Pb-S-I-R-H_2O$, R being a solvent, have been investigated (*226, 429*). So far, few of the metastable sulfide halides have been prepared in pure form by precipitation from solution. A phase of the composition $2PbS{\cdot}PbBr_2$ has been isolated by dilution of a solution prepared from PbS and hydrobromic acid (*302*). Another example is the phase Pb_2SI_2, formed by the reaction of H_2S with a solution of $KPbI_3$ in acetone (*164*).

3. *Crystallographic Data*

The crystal structures of Pb_4SeBr_6, $Pb_5S_2I_6$, and $Pb_7S_2Br_{10}$ have been determined from single-crystal, X-ray analyses (*196*). The unit-cell data are given in Table XXII. The compounds have common structural features with respect to the pure halides of lead. In Pb_4SeBr_6, all of the Pb atoms are coordinated by a trigonal prism of Br (Se) atoms. Additional neighbors above the prism faces complete the coordination number to 7, 8, or 9. In $Pb_5S_2I_6$, some of the Pb atoms are surrounded by 6 I + 1 S, or 5 I + 3 S, in the same, extended, trigonal, prismatic arrangement, and others occupy the centers of PbI_6 octahedra. In $Pb_7S_2Br_{10}$, which is isostructural with Th_7S_{13} (*417*), the Pb atoms are coordinated by 8, or 9, nonmetal atoms in a trigonal-prismatic 6 + 2, or 6 + 3, coordination. Part of the metal and part of the nonmetal positions show a statistical occupancy. The types of coordination in the

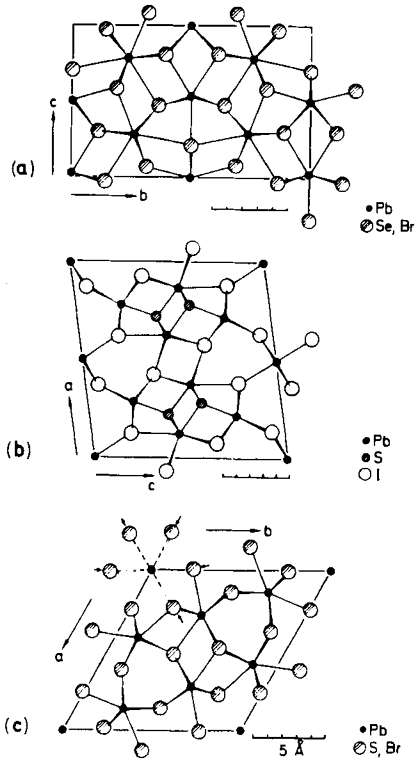


FIG. 33. Structure relationships and coordinations of lead chalcogenide halides: a, Pb_4SeBr_6; b, $Pb_5S_2I_6$; c, $Pb_7S_2Br_{10}$. (Redrawn from B. Krebs, *Z. Anorg. Allg. Chem.* **396**, 137 (1973), Figs. 1; 2, and 3, pp. 141, 147, and 148.)

three structures are given in Fig. 33, a–c. The compound Pb_4SCl_6 is isotypic with Pb_4SeBr_6. In the case of the bromides $Pb_7S_2Br_{10}$ and Pb_4SeBr_6, unusually high temperature-factors for the lead atoms have been observed (*196*) that indicate an incomplete occupancy of the metal atoms. For both compounds, a homogeneity range has been reported in the literature (*247, 249*).

4. *Physical Properties*

Reflection spectra of some sulfide and selenide halides have been measured (*302, 303*). The compounds are assumed to be semiconductors. Their optical band-gaps are found to be Pb_4SeBr_6, 1.6 eV; $Pb_5S_2I_6$, ~2 eV; $Pb_7S_2Br_{10}$, ~2 eV; and Pb_4SCl_6, 2.5 eV. The reflection spectra of Pb_2SI_2 and Pb_2SBr_2 were reported to correspond to those of $Pb_5S_2I_6$ and $Pb_7S_2Br_{10}$ (*164*).

XII. Group VA

A. NITROGEN AND PHOSPHORUS

As in the case of Group IVA, combinations with these typical nonmetals will not be treated in detail insofar as nitrogen compounds are concerned. Of interest with respect to this review are the highly conducting compounds that are obtained by the room-temperature reaction of tetrasulfur tetranitride with halogens, e.g., $(SNBr_{0.4})_x$ (*1, 366, 423*).

Phosphorus thiohalides are reviewed in (*146*), and, with more relevance to this review, in (*407*). Four structural types exist. These are as follows. (*i*) PSX_3 [X = Cl (*203*), Br]: tetrahedral molecules $S{=}PX_3$; (*ii*) $P_2S_2I_4$ (*90*) and $P_2Se_2I_4$ (*25*), probably $I_2YP{-}PYI_2$; (*iii*) $P_2S_5Br_4$ and $P_2S_4Br_2$. The structure of the latter, formed by the action of Br_2 on P_4S_6, is known. It consists of a P_2S_4 ring in a skew conformation, each P being attached to two atoms, either Br or S (*114*). (*iv*) $P_4S_3I_2$ and $P_4Se_3I_2$. The former exists in two forms. α-$P_4S_3I_2$, prepared in CS_2 solution from the elements, consists of one six- and two five-membered rings in different relative arrangements of the P and S atoms as compared with P_4S_3 (*413*). β-$P_4S_3I_2$, which forms by the reaction of P_4S_3 with I_2, has a structure closely related to that of P_4S_3 (*268*), and is isostructural with $P_4Se_3I_2$ (*267*).

B. ARSENIC

Although arsenic is a nonmetal, the chalcogenide halides of this element bear a strong relationship to the antimony and bismuth systems, and will therefore be treated separately.

Numerous compounds are mentioned in the literature, but only in a few cases, however, was their existence based on X-ray powder patterns or the preparation of single crystals: AsSI and AsSeI (*74, 76, 79, 98*); $As_4Te_5I_2$ (*75, 77, 79, 98*) and $As_8Te_7I_5$ (*77*). The preparation of these compounds from the elements or binary arsenides requires a special annealing treatment in order to overcome the glassy state. Single crystals of AsSI, AsSeI, and $As_4Te_5I_2$ have been obtained by sublimation of the polycrystalline material at temperatures below 200°C in a vertical-gradient furnace (*79*); AsSI has also been obtained by hydrothermal synthesis (*282*). With the exception of $As_4Te_5I_2$, which is said to be cubic (*77*), no crystallographic data are available for the arsenic chalcogenide halides. Phase diagrams of these systems, as far as they have been published, are included in Tables XXV–XXIX. In contrast to the antimony and bismuth compounds, the crystalline material has not attracted any attention with regard to its physical properties.

Vitreous Semiconductors

The main interest in these systems has focused on the glass-forming regions, because of the search for vitreous semiconductors. This category of glasses is sometimes referred to as "chalcogenide glasses" (*232*), distinguished from the oxide type of glasses by their high electronic conductivity and absence of ionic conductivity. They constitute an extensive group of materials whose optical, electrical, and other properties may vary with composition within a fairly wide range. Many of them are typical semiconductors whose distinctive features are the absence of long-range order, their homogeneity, the independence of their properties on small amounts of impurities, and small mobility of charge carriers. For further study of this subject, a chapter on glasses in a book by Krebs (*195*), and, especially, a review article by Kolomiets (*190*), should be of interest.

Most of the contributions on arsenide systems have been made by Russian scientists, and their publications are not available in English. An X-ray diffraction study (*277*), viscosity and structure investigation (*78*) of the system As_2Y_3–AsI_3 (Y = S,Se), and optical and magneto-optical properties of the systems As–S–I and As–S–Br (*60*) appeared in the translation "Inorganic Materials." A good insight into the situation is provided by the extensive work on As–Te–I glasses by Quinn and Johnson (*295*), where many references may be found.

C. ANTIMONY AND BISMUTH

Chalcogenide halides of antimony and bismuth have been known since the end of the last century, mainly through contributions by Ouvrard and Schneider. With the exception of BiSeCl, only thiohalides were reported. The early work is summarized in (*147*) (Sb, before 1948) and (*148*) (Bi, before 1927), and it will only occasionally be dealt with. Beyond that, these materials had not found much interest.

However, the situation changed dramatically with the discovery of the photoconductivity of SbSI in 1960 (*243*) and its ferroelectric properties (*117*). Innumerable publications on the chalcogenide halides of antimony and bismuth then appeared, and are still appearing, with the result that these compounds, and, especially, SbSI, now belong to the most well known chalcogenide halides. As it is impossible to cover the whole field of these investigations in this review, especially where the physical properties, glassy systems, and films are concerned, these topics will only be mentioned. The bismuth and antimony compounds will be treated together, as they possess much similarity. Tables XXIII and XXIV list the chalcogenide halides of antimony and bismuth, the existence of which has been established.

In the early 1950s, in a systematic study, Dönges (*106–108*) discovered most of the chalcogenide halides of antimony and bismuth that are known today, and then solved their structures.

1. *Preparative Methods*

The chalcogenide halides in Tables XXIII and XXIV having a reference in the column "solid-state reactions" can be obtained in a polycrystalline form by annealing an intimate mixture of the respective chalcogenides M_2Y_3 and halides MX_3 in stoichiometric ratios in closed ampoules. Other ways of preparation that partially date back to the early work of Ouvrard and Schneider (especially for the thiochalcogenides), and that may still be of interest in special cases, are summarized in (*147*) (Sb) and (*148*) (Bi). Preparative work has since been devoted, however, to the preparation of single crystals for X-ray structure determinations and physical measurements. Small crystals, sufficiently large for X-ray work, can be obtained by the aforementioned method, provided that prolonged annealing-times are applied. The methods mentioned in Tables XXIII and XXIV are of greater importance.

TABLE XXIII

CHALCOGENIDE HALIDES OF ANTIMONY: PREPARATION, BIBLIOGRAPHY

		References			
Compound	Color	Melt growth	Vapor growth	Hydrothermal synthesis	Solid-state reactions
$Sb_4S_5Cl_2$	Red–brown				*106*
SbSCl				*279,282,283*	
SbSBr	Orange	*117,244*	*187*	*279,282,283,285,312*	*106*
SbSI	Red	*38,117,163, 220,235,391,421*	*112,163,166,183, 236,255,281,418,425*	*279,280,282,283,285,312*	*106*
SbSeCl				*282*	
SbSeBr	Dark red	*117,244*	*171,187*	*279,282,283,285*	*106*
SbSeI	Black	*117,244*	*166,237,238*	*279,282–285*	*106,238*
SbTeBr				*285*	
SbTeI	Black	*117*	*166,403*	*283,285,286*	*108*

TABLE XXIV

CHALCOGENIDE HALIDES OF BISMUTH: PREPARATION, BIBLIOGRAPHY

		References			
Compound	Color	Melt growth	Vapor growth	Hydrothermal synthesis	Solid-state reactions
BiSCl	Red	*117,244*		*279,282,283*	*106*
$Bi_{19}S_{27}Cl_3$					*193*
$Bi_4S_5Cl_2$	Dark grey				*194*
BiSBr	Dark red	*117,244*	*191*	*279,282,283,285*	*106*
$Bi_{19}S_{27}Br_3$	Black		*192*	*219*	*192*
BiSI	Black	*117,244*		*279,282,283,285*	*106*
$Bi_{19}S_{27}I_3$			*67,225*		
BiSeCl	Dark red	*117*		*279,283*	*107*
BiSeBr	Black	*117,244*	*171*	*279,283,285*	*107*
BiSeI	Black	*117,244,398*	*172*	*279,283,285*	*107*
BiTeBr	Black		*259,395*	*283,285*	*108,259*
BiTeI	Black	*170,428*	*71,170,259*	*283,285*	*71,108,170,259*

a. Melt growth. The method was applied by Nitsche *et al.* (*243, 244*). Single crystals in the form of needles up to 2 cm long have been obtained by slow cooling of the molten compounds at a rate of 5°C/h. The crystals are washed with dilute hydrochloric aicd to remove surplus trihalide, rinsed with alcohol, and dried (*243*). In the Bridgman–Stockbarger technique (*55*), the melt is homogenized in a pointed-growth ampoule and then lowered in a temperature gradient in a two-zone furnace (1 mm/h). The cylindrical ingot consists of densely packed, single-crystal needles whose axes, corresponding to the crystallographic *c* axis, are parallel to the ingot axis (*38, 170, 244, 391, 398*). The equipment used for BiTeI (*170*) is shown in Fig. 34. The growth of SbSI under pressure has been reported (*220*). The melt need not necessarily have the stoichiometric composition. In some cases, an excess of the halogenide proved to be useful [flux technique (*55*), e.g., (*170, 235, 391, 398, 421*)].

b. Vapor growth. The common feature of this method is simple sublimation in a closed tube. The tubes are placed, vertically or horizontally, in a two-zone furnace, with the starting material at the higher temperature. The method, first reported by Kern for SbSI (*183*), has been applied for a number of substances mainly by Horak and coworkers (*71, 166, 170–172, 187, 191, 237, 238, 395;* see also, Tables XXIII and XXIV, where experimental details may be found). The arrangement is similar to that depicted in Fig. 21 (Section VI,B,5).

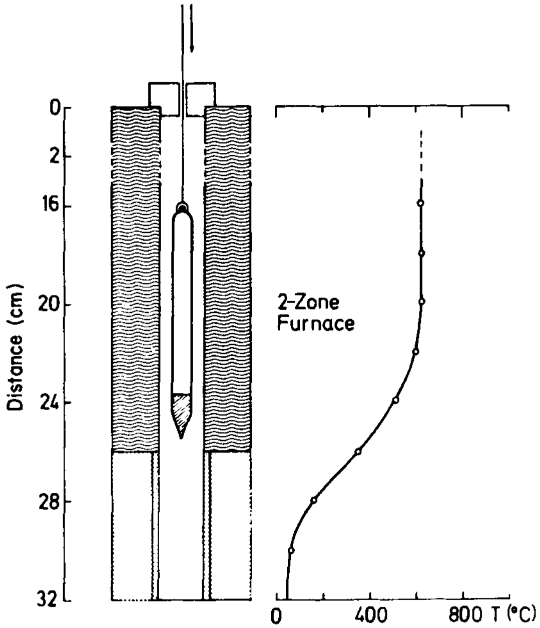


FIG. 34. Bridgman–Stockbarger technique for BiTeI. (Redrawn from J. Horak and H. Rodot, *C. R. Acad. Sci., Ser. B.* **267**, 363 (1968), Fig. 2, p. 364.)

BiTeI has been grown by chemical transport from Bi_2Te_3 and BiI_3, using Br_2 as the transport agent (*218*).

c. Hydrothermal growth. The applicability of hydrothermal synthesis in acid solution (see Section II,D,2) to the growth of Group VA chalcogenide halides was first observed by Rau and Rabenau for SbSI and SbSBr (*312*). In succeeding years, the method was extensively studied by Popolitov and co-workers for a great number of compounds (see Tables XXIII and XXIV, and *279–287*). They used standard autoclaves lined with Teflon for low temperatures (≤300°C) and quartz glass, titanium, and platinum for higher temperatures (*282, 283*). In order to evaluate optimal growth-conditions, they constructed Eh–pH diagrams for different A^{V}–B^{VI}–C^{VII}–H_2O systems (*282, 285*), and determined crystallization regions in such systems (*284–286*). Although, for practical purposes, the experimental parameters lie in the range of 200–400°C and pressures of 200–530 atm (*283*), the influence of high pressure has been investigated for the systems Sb–Se–I–R–H_2O (*284*), Sb–Te–I–R–H_2O (*286*), and Bi–Se–I–R–H_2O (*287*), R being a solvent such as HCl, HI, or C_2H_5OH, at pressures up to 2000 atm.

It was found that the region of formation of the chalcogenide halides depends on the pH, the solvent concentration, and the ratios of the initial components in the charge. Temperature and pressure have practically no influence on the phase formation in these systems (*285*). The use of bromine (*283*) and $SeBr_2$ as the solvent leads to a different mechanism, having different kinetics of formation and different growth-forms of the crystals (*285*).

The main problem in the crystal growth of antimony and bismuth chalcogenide halides is the growth of large, isometric crystals. In most of the experiments, a needle morphology predominated, with the growth rate estimated to be more than 50 times larger parallel the *c* direction than perpendicular to it (*227*). This growth-rate anisotropy seems to be an inherent characteristic of the material (*235*). For the growth of SbSI from the vapor phase, the relationship between the morphology of the crystals and the condition of the crystallization process was investigated (*112*). It has been found (*418*) that isometric crystals up to $5 \times 7 \times 10$ mm^3 may be grown from the vapor on a seed by applying crystallization by temperature-gradient reversal in a Scholz ampoule (*348–350*) geometry. Principally, the Scholz apparatus is an axially symmetrical, vertical ampoule, the crystallization taking place in a zone along its axis, whereas the source material is placed on the periphery, concentric to this zone. The needle morphology of large SbSI crystals has also been successfully controlled by a modified, flux technique using an excess of SbI_3 as the solvent. By preventing additional, disturbing nucleation during growth, the crystals are forced to grow in thickness,· yielding crystals up to 1 cm in diameter. The method seems also to be applicable to other chalcogenide halides (*235*).

2. *Chemical Properties*

The chalcogenide halides of antimony and bismuth are stable in air, and do not dissolve in H_2O or diluted acids. Their colors, mainly referring to single-crystal needles, are given in Tables XXIII and XXIV.

3. *Phase Diagrams*

Knowledge of phase diagrams is not only a prerequisite for efficient crystal-growth, but also provides information on the formation of solid solutions, in which, for example, physical properties may change continuously. The numerous publications concerning Group VA systems are summarized in Tables XXV–XXVII, together with the respective references and the most important information. Abbreviations used

TABLE XXV

SYSTEM INVESTIGATIONS: CUTS Me_2Y_3–MeX_3

System	Ref.	Remarks
As_2S_3–AsI_3	*76*	T − x; AsSI
As_2Se_3–$AsBr_3$	*73*	T − x; no compound
As_2Se_3–AsI_3	*76*	T − x; AsSeI
As_2Te_3–AsI_3	*75*	T − x; $As_4Te_3I_2$
Sb_2S_3–SbI_3	*38,255,391*	T − x; SbSI
Sb_2S_3–SbSI	*2*	SbSI − $(Sb_2S_3)_x, x = 0.03$–0.12, p-T
Sb_2Se_3–SbI_3	*37, 103*	T − x; SbSeI
Sb_2Te_3–SbI_3	*3,27,75,397,403*	p − T; SbTeI (*3,27*); T − x, SbTeI (*397,403*)
Bi_2S_3–$BiBr_3$	*202*	BiSBr, thermodynamics
Bi_2S_3–BiI_3	*202*	BiSI, thermodynamics
Bi_2Se_3–$BiBr_3$	*201*	Vapor pressure
Bi_2Se_3–BiI_3	*36,398,399*	BiSeI; reaction (*399*), T − x; BiSeI, $9Bi_2Se_3 \cdot BiI_3$
Bi_2Te_3–$BiBr_3$	*201*	Vapor pressure
Bi_2Te_3–BiI_3	*27,170,390,402*	T − x; $Bi_{1.00}Te_{0.98}I_{1.02}$ (*390*). BiTeI, T − x; p − T; BiTeI (*402*), T − x; BiTeI (*170*)

are T − x = temperature–concentration diagram; p − T = pressure–temperature diagram; s.s. = solid solution.

The composition and pressure of the gas phase over SbSI and Sb_3S_3 (*392*) and SbSeI and BiSeI (*102*) have been measured, leading to the thermodynamic values: $-\Delta H_f^0 = 25.4 \pm 2.4, 22.3 \pm 2.7$, and 27.2 ± 2.4 kcal/mol, and $\Delta S^\circ = 26.9 \pm 1.3$, 31.1 ± 1.7, and 33.4 ± 2.5 cal/(mol·deg) for SbSI, SbSeI, and BiSeI, respectively.

TABLE XXVI

SYSTEM INVESTIGATIONS: MeYX − Me′Y′X′

System	Ref.	Remarks
AsSI–AsSeI	*74*	T − x; s.s.
AsSI–SbSI	*74,333*	T − x; eutectic (*74*), peritectic finite s.s. (*333*)
SbSBr–SbSI	*61,136,151,396*	s.s. (*396*), T − p − x (*61*)
SbSI–SbSeI	*31,32,294*	T − x; s.s. (*32*)
SbSeI–SbTeI	*33,245*	T − x; s.s. (*33*)
SbSI–BiSI	*30,137,245*	T − x; s.s. (*30*)
SbTeI–BiTeI	*31,34*	T − x; finite s.s. (*34*)
SbSeI–BiSeI	*29,35,214*	T − x; s.s. (*35*)

TABLE XXVII

SYSTEM INVESTIGATIONS: MISCELLANEOUS

System	Ref.	Remarks
SbI_3–Se	*82*	T – x, eutectic
SbSeI–Se	*82*	T – x, eutectic
Sb_2Se_3–I	*82*	T – x
Bi_2Te_3–I	*28*	$Bi_2Te_3 \cdot I_2$, $Bi_2Te_3 \cdot 3I_2$(?)
As–Se–I	*199*	Vapor pressures
$As_4Te_5I_2$–As	*77*	T – x
Sb_2S_3–I	*38*	T – x,$Sb_2S_3 \cdot I_2$,$Sb_2S_3 \cdot 3I_2$
BiTeI–Te	*116*	T – x, eutectic
BiI_3–Te	*116*	T – x, eutectic

4. *Crystallographic Data*

The crystallographic data are summarized in Table XXVIII. The best known structure is that of the compounds belonging to the so-called SbSI type (see Table XXVIII), which was proposed by Dönges (*106, 107*), and confirmed for SbSBr (*84*), SbSI (*153, 174, 184, 258*), and BiSI (*153*).

Characteristic of this SbSI type is the formation of infinite, $(Sb_2S_2I_2)_\infty$ double-chains parallel to the *b* axis, as shown in Fig. 35 (notation: International Tables for X-ray Crystallography), which explains the needle-like shape of these crystals. The relationship to the needle-like sulfides Sb_2S_3 and Bi_2S_3, which crystallize in the same space-group, has been pointed out (*106, 153*): one S of the sulfide is replaced by two halogens in such a way that the $(Me_4S_6)_\infty$ chains of the sulfides split into two $(Me_2S_2X_2)_\infty$ chains. The relationship to the sesquisulfide is even stronger for the $Bi_{19}S_{27}X_3$ [X = Cl (*193*), Br (*192, 219*), I (*225*)] compounds, which consist of $(Bi_4S_6)_\infty$ chains connected by the halogens and one extra Bi atom, leading to the formulation $Bi(Bi_2S_3)_9X_3$.

The phase transiton from a paraelectric to a ferroelectric state, most characteristic for the SbSI type compounds, has been extensively studied for SbSI, because of its importance with respect to the physical properties of this compound (e.g., *153, 173–177, 184, 257*). The first-order transition is accompanied by a small shift of the atomic parameters and loss of the center of symmetry, and is most probably of a displacement nature. The true structure of $Sb_4S_5Cl_2$ (*106*), $Bi_4S_5Cl_2$ (*194*), and SbTeI (*108, 403*) is still unknown. In contrast to the sulfides and selenides of bismuth, BiTeBr (*108*) and BiTeI (*108, 390*) exhibit a layer structure similar to that of the CdI_2 structure, if the difference between Te, Br, and I (see Fig. 36) is ignored.

TABLE XXVIII

CRYSTALLOGRAPHIC DATA FOR ANTIMONY AND BISMUTH COMPOUNDS

Compound	Symmetry	a (Å)	b (Å)	c (Å)	β (degrees)	Z	Space group	Ref.
$Sb_4S_5Cl_2$	Orthorhombic	10.53	9.38	11.08		4	Pnma (?)	*367*
SbSBr	Orthorhombic	8.20	3.95	9.70		4	Pnma	*367*
SbSI		8.49	4.16	10.10				
SbSeBr		8.30	3.95	10.20				
SbSeI		8.65	4.12	10.38				
BiSCl		7.70	4.00	9.87				
BiSBr		8.02	4.01	9.70				
BiSI		8.46	4.14	10.15				
BiSeBr		8.18	4.11	10.47				
BiSeI		8.71	4.19	10.45				
BiSeCl	Orthorhombic	12.37	18.10	4.08		12	Pmmm	*367*
SbTeI	Orthorhombic	9.18	10.8	4.23		4	Pmmm, Pnmm, Pmmn	*108*
SbTeI	Monoclinic	14.55	4.23	13.72	81.12	8	C2/c, Cc	*403*
BiTeBr	Hexagonal	4.23		6.47		1	$P\bar{3}m1$	*108*
BiTeI		4.31		6.83				
$Bi_{19}S_{27}Cl_3$	Hexagonal	15.40		4.02		2/3	$P6_3$	*193*
$Bi_{19}S_{27}Br_3$		15.55		4.02				*219*
$Bi_{19}S_{27}I_3$		15.63		4.02				*225*
$Bi_4S_5Cl_2$	Rhombohedral	19.80		12.4		15	R32, R3m, $R\bar{3}m$	*194*

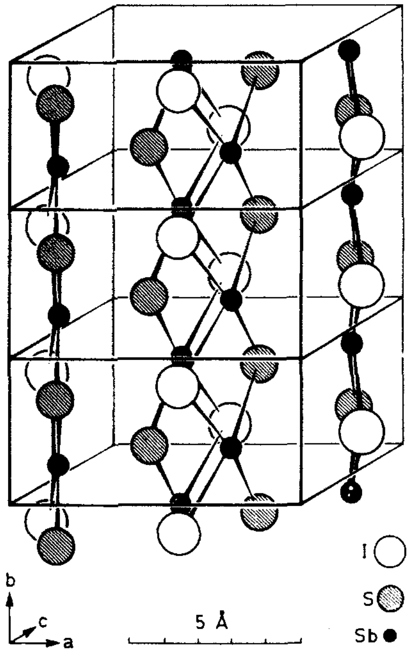


FIG. 35. $[Sb_2S_2I_2]_\infty$ double chain in the structure of SbSI. (Redrawn from E. Dönges, *Z. Anorg. Allg. Chem.* **263**, 112 (1950), Fig. 11, p. 129.)

5. *Physical Properties*

The semiconducting properties of the compounds of the SbSI type (see Table XXVIII) were predicted by Mooser and Pearson in 1958 (*228*). They were first confirmed for SbSI, for which photoconductivity was found in 1960 (*243*). The breakthrough was the observation of ferroelectricity in this material (*117*) and other SbSI type compounds (*244*; see Table XXIX), in addition to phase transitions (*184*), nonlinear optical behavior (*156*), piezoelectric behavior (*44*), and electromechanical (*183*) and other properties. These photoconductors exhibit abnormally large temperature-coefficients for their band gaps; they are strongly piezoelectric. Some are ferroelectric (see Table XXIX). They have anomalous electrooptic and optomechanical properties, namely, elongation or contraction under illumination. As already mentioned, these fields cannot be treated in any detail in this review; for those interested in ferroelectricity, review articles (*224, 352*) are mentioned. The heat capacity of SbSI has been measured from − 180 to + 40°C and, from these data, the excess entropy of the ferro-paraelectric transition

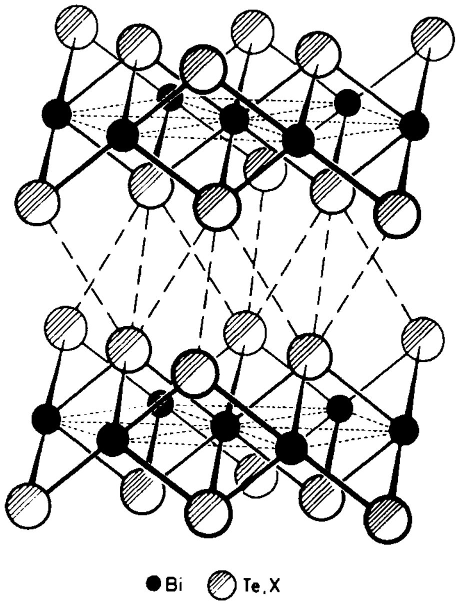


FIG. 36. Structure of BiTeBr and BiTeI.

has been calculated to be ΔS = 53 mcal/(mol·deg), plausible for a displacement transition (*384;* see also, *Crystallographic Data*).

^{121}Sb Mössbauer spectra of SbSBr, SbSI, SbSeBr, SbSeI, and SbTeI have been obtained at 4.2 K. The quadrupole coupling-constant of the iodides decreases in the order SbSI > SbSeI > SbTeI, becoming nega-

TABLE XXIX

SOME PHYSICAL PROPERTIES OF ANTIMONY AND BISMUTH CHALCOGENIDE HALIDES

Compound	Band gap (eV)	Ref.	Magnetic susceptibility ref.	Curie point (°C)	Ref.
SbSBr	2.22	*6*	*221*	−180	*244*
SbSI	2.12	*6*	*41,221*	22	*117*
SbSeBr	1.84	*169*			
SbSeI	1.61	*6*	*221*		
BiSCl	1.89	*39*	*221*		
BiSBr	1.88	*169*		−170	*244*
BiSI			*221*	−160	*244*
BiSeBr			*221*		
BiSeI	1.32	*40*	*41,221*		
BiTeBr	0.54	*293*			
BiTeI	0.38	*293*	*41,420*		

tive for the last (*105*). A selection of band gaps of MXY compounds is included in Table XXIX. Although somewhat differing values are reported for some of the compounds, and the uncertainty is ~0.2 eV, the sequence of decreasing band gaps shows that it is mainly the decrease in electronegativity differences that influences the band gap (*149;* see also, Section II,A,5).

With respect to the physical properties mentioned, band-structure calculations have attracted considerable interest, e.g., for SbSBr, SbSI, and SbSeI (*234*). For the compounds having reference *221* in column 4 of Table XXIX, a temperature-independent diamagnetism has been found, with values of about 10^{-7} $cm^{-3}g^{-1}$ between 77 and 340 K. A small temperature-dependence is exhibited by BiTeI, a narrow-gap semiconductor (*41*). The anisotropy of the magnetic susceptibility has been studied for SbSI, BiSeI, and BiTeI (*41, 420*).

Appendix

After submitting the manuscript some interesting new results were published, the most important of which are presented here. Less relevant contributions are not specifically mentioned. They are all listed in the Appendix References (*420–433*) and referred to by number herein.

II. Copper: The first two structures of copper selenide halides have now been solved. $CuSe_2Cl$ turned out to be a true isotype of $CuTe_2Cl$, containing infinite, pseudofourfold, selenium helices (*433*). The crystals are systematically twinned, which is the reason for the wrong lattice constants given earlier (*307*). $CuSe_3Br$ is unique by the occurrence of chair-type Se_6-rings (*424*). As in $CuSe_2Cl$, the copper atoms are coordinated by two selenium and two halogen atoms in a distorted tetrahedral arrangement.

II. Silver: According to DTA data and conductivity data, Ag_3SBr and Ag_3SI undergo phase transitions at 120 and 163 K, respectively. In Ag_3SI the transition to the low-temperature phase is accompanied by the appearance of additional x-ray reflections (*427*).

VI. Niobium: Two new niobium selenide halides, $Nb_3Se_5Cl_7$ and $Nb_3Se_5Br_7$, were prepared by Rijnsdorp and Jellinek (*431*). $Nb_3Se_5Cl_7$ was obtained by annealing $NbSe_2Cl_2$ and $NbCl_4$ in a 2:1 ratio at 530°C for 2–3 weeks. The isotypic bromine compound was formed by thermal decomposition of $NbSe_2Br_2$ in the presence of $NbSeBr_3$. The compounds are monoclinic with $a = 7.599$, $b = 12.675$, $c = 8.051$ Å, $\beta = 106.27°$ (space group $P2_1/m$) and $a = 7.621$, $b = 12.833$, $c = 8.069$ Å, $\beta =$

106.21°, respectively. The crystal structure and XPS spectra show $Nb_3Se_5Cl_7$ to be a mixed valence compound which can be formulated as $[Nb_2^{4+}Nb^{5+}(Se_2)_2^{2-}Se^{2-}Cl_7^-]$. $[Nb_2Se_4]$-cages with Nb–Nb pairs (Nb–Nb = 2.94 Å), as in $NbSe_2Cl_2$ (*347*, see Fig. 20), are interconnected by faces of three bridging chlorines to form linear chains of $[Nb_2^{4+}(Se_2)_2^{2-}Cl_5^-]$, to which side chains $[Nb^{5+}Se^{2-}Cl_2^-]$ are attached. In accordance with these results, the compound is a diamagnetic semiconductor with a band gap (1.49 eV at 300 K) very close to that of $NbSe_2Cl_2$.

Bullett has calculated band structures and densities of states for $NbSe_2Cl_2$, $NbSe_2Cl_2$, $Nb_3Se_5Cl_7$, and $NbSe_4I_{0.33}$ on the basis of the geometries of the Nb_2Y_4-clusters. Metal–metal bonding results in very narrow bands largely composed of niobium *d*-orbitals at the band edges (*422*).

VII. Molybdenum: A recent review of molybdenum chalcogenide halides is contained in a paper of Tsigdinos (*432*).

XII. Antimony: Of various new papers on the crystal growth of SbSI, the one by Ishikawa *et al.* (*425*) is worth mentioning, since it describes a new device especially designed to avoid formation of hollows in vapor-grown crystals.

XII. Bismuth: As shown by a recent single-crystal structure determination by Krämer (*426*), $Bi_4S_5Cl_2$ crystallizes in the rhombohedral space group $R\bar{3}$. The Cl^- and S^{2-} ions display a light-packed framework of statistically distributed anions. Unusually high coordination numbers of eight and nine for bismuth are attained by extended planar–pyramidal and trigonal–prismatic coordinations, i.e., three additional ions are located either below the basal planes of the pyramids or above the rectangular faces of the prisms with cation–anion distances ranging from 2.62 to 3.66 Å.

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