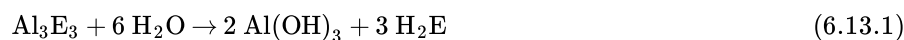# 6.13: Chalcogenides of Aluminum, Gallium, and Indium

The only stable chalcogenides of aluminum are Al_2S_3 (white), Al_2Se_3 (grey), and Al_2Te_3 (dark grey). They are each prepared by the direct reaction of the elements (100 °C) and hydrolyze rapidly in aqueous solution, (6.13.1). All the chalcogenides have a hexagonal ZnS structure in which $^2/_3$ of the metal sites are occupied.

$$Al_3E_3 + 6\,H_2O \rightarrow 2\,Al(OH)_3 + 3\,H_2E \qquad\qquad (6.13.1)$$

The chalcogenides of gallium and indium are more numerous than those of aluminum, and are listed in Table 6.13.1 and Table 6.13.2 along with selected physical properties.

Table 6.13.1: Stoichiometries, structures and selected physical properties of the crystalline chalcogenides of gallium. [a] dir = direct, ind = indirect, opt = optical.

Compound	Structural type	Crystallographic system	Cell parameters (Å, °)	Band Gap (eV)[a]
GaS		Hexagonal	$a = 3.587, c = 15.492$	3.05 (dir.), 2.593 (ind.)
GaS	ZnS or NaCl	Cubic	$a = 5.5$	4.0 (opt.)
β-GaSe	GaS	Hexagonal	$a = 3.742, c = 15.919$	2.103 (dir.), 2.127 (ind.)
γ-GaSe	GaS	Rhombohedral	$a = 3.755, c = 23.92$	
δ-GaSe	GaS	Hexagonal	$a = 3.755, c = 31.99$	
β-GaTe	GaS	Hexagonal	$a = 4.06, c = 16.96$	
GaTe	GaS	Monoclinic	$a = 17.44, b = 4.077, c = 10.456, \beta = 104.4$	1.799 (dir.)
α-Ga$_2$S$_3$	Wurtzite	Cubic	$a = 5.181$	
α-Ga$_2$S$_3$	Wurtzite	Monoclinic	$a = 12.637, b = 6.41, c = 7.03, \beta = 131.08$	3.438 (opt.)
β-Ga$_2$S$_3$	Defect wurtzite	Hexagonal	$a = 3.685, c = 6.028$	2.5 - 2.7 (opt.)
α-Ga$_2$Se$_3$	Sphalerite	Cubic	$a = 5.429$	2.1 (dir.), 2.04 (ind.)
α-Ga$_2$Te$_3$	Sphalerite	Cubic	$a = 5.886$	1.22 (opt.)

Table 6.13.2: Stoichiometries, structures and selected physical properties of the crystalline chalcogenides of indium. [a] dir = direct, ind = indirect, opt = optical. [b] High pressure phase.

Compound	Structural type	Crystallographic system	Cell parameters (Å, °)	Band gap (eV)[a]
β-InS	GaS	Orthorhombic	$a = 3.944, b = 4.447, c = 10.648$	2.58 (dir.), 2.067 (ind.)
InS[b]	Hg$_2$Cl$_2$	Tetragonal		
InSe	GaS	Rhombohedral	$a = 4.00, c = 25.32$	1.3525 (dir.), 1.32 (ind.)
β-InSe	GaS	Hexagonal	$a = 4.05, c = 16.93$	
InTe	TlSe	Tetragonal	$a = 8.437, c = 7.139$	Metallic
InTe[b]	NaCl	Cubic	$a = 6.18$	
α-In$_2$S$_3$	γ-Al$_2$O$_3$	Cubic	$a = 5.36$	
β-In$_2$S$_3$	Spinel	Tetragonal	$a = 7.618, c = 32.33$	2.03 (dir.), 1.1 (ind.)

α-In$_2$Se$_3$	Defect wurtzite	Hexagonal	$a = 16.00, c = 19.24$	
β-In$_2$Se$_3$	Defect wurtzite	Rhombohedral	$a = 4.025, c = 19.222$	1.2 - 1.5 (ind.)
α-In$_2$Te$_3$	Sphalerite	Cubic	$a = 6.158$	0.92 - 1.15 (opt.)
In$_6$S$_7$		Monoclinic	$a = 9.090, b = 3.887, c = 17.705, \beta = 108.20$	0.89 (dir.), 0.7 (ind.)
In$_6$Se$_7$	In$_6$S$_7$	Monoclinic	$a = 9.430, b = 4.063, c = 18.378, \beta = 109.34$	0.86 (dir.), 0.34 (ind.)
In$_4$Se$_3$		Orthorhombic	$a = 15.297, b = 12.308, c = 4.081$	0.64 (dir.)
In$_4$Te$_3$	In$_4$Se$_3$	Orthorhombic	$a = 15.630, b = 12.756, c = 4.441$	0.48 (dir.)

The hexagonal β-form of Ga$_2$S$_3$ is isostructural with the aluminum analogue; however, while the α-phase was proposed to be hexagonal it was later shown to be monoclinic. A cubic α-phase has been reported. Cubic Sphalerite structures are found for Ga$_2$Se$_3$, Ga$_2$Te$_3$, and In$_2$Te$_3$, in which the structure is based on a cubic close packing of the chalcogenides and the metal atoms occupying $^1/_3$ of the tetrahedral sites. These structures are all formed with rapid crystallization; slow crystallization and/or thermal annealing leads to ordering and the formation of more complex structures. The indium sulfides, and selenides derivatives are spinel (γ-Al$_2$O$_3$), and defect Würtzite, respectively.

Unlike the chalcogenides of aluminum, those of gallium and indium also form subvalent compounds, i.e., those in which the metal is formally of an oxidation state less than +3. Of these subvalent chalcogenides the (formally) divalent materials are of the most interest. The thermodynamically stable phase of GaS has a hexagonal layer structure (Figure 6.13.1) with Ga-Ga bonds (2.48 Å). The compound can, therefore, be considered as an example of Ga(II). Each Ga is coordinated by three sulfur atoms and one gallium, and the sequence of layers along the z-axis is $\cdots$S-Ga-Ga-S$\cdots$S-Ga-Ga-S$\cdots$.
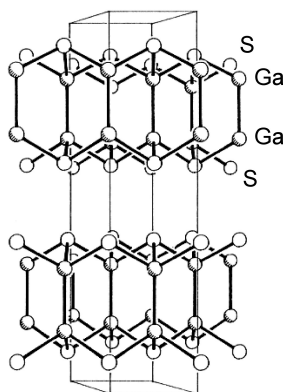

Figure 6.13.1: The $\cdots$S-Ga-Ga-S$\cdots$S-Ga-Ga-S$\cdots$ structure of hexagonal GaS. Gallium atoms are shown shaded.

The structures of β-GaSe, and β-InSe are similar to hexagonal GaS. The layered structure of GaTe is similar in that it consists of $\cdots$TeGaGaTe$\cdots$ layers, but is monoclinic, while InS is found in both a (high pressure) tetragonal phase (Figure 6.13.2a) as well as an orthorhombic phase (Figure 6.13.2b). By contrast to these M-M bonded layered compounds InTe (Figure 6.13.3) has a structure formalized as In(I)[In(III)Te$_2$]; each In(III) is tetrahedrally coordinated to four Te and these tetrahedra are linked *via* shared edges; the In(I) centers lying between these chains.
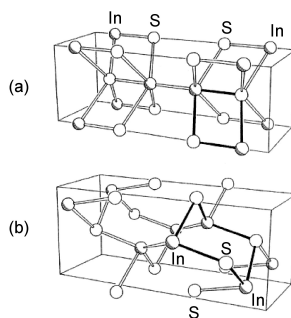
Figure 6.13.2: Unit cell of (a) tetragonal InS and (b) orthorhombic InS. Indium atoms are shown shaded, and the solid bonds represent the smallest cyclic structural fragment.
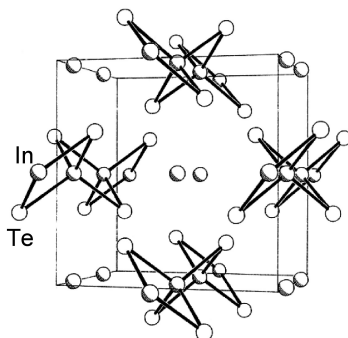

Figure 6.13.3: Unit cell of tetragonal InTe. Indium atoms are shown shaded, and the solid bonds represent the $[InTe_2]_\infty$ chains.

Further sub-chalcogenides are known for indium, e.g.; In_4Se_3, which contains $[In(III)_3Se_2]^{5+}$ groups (Figure 6.13.4). While the formally In(I) molecule In_2S has been detected in the gas phase, it is actually a mixture of In and InS in the solid state.
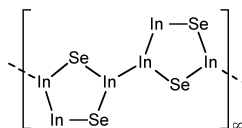

Figure 6.13.4: Structure of $[In(III)_3Se_2]^{5+}$ groups in In_4Se_3.

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